Harnessing biomethanation for sustainable lithium depletion from sea water brine and energy generation: an integrated waste management strategy

Arianna Vizzarro[1,2], Chiara Magrini[1,2], Nicolò Santi Vasile[1, 2], Ilaria Bassani[1], Ruggero Bellini[1], Filippo Drago[3], Luisa Baudino[1,4], Barbara Menin[1,5], Candido Fabrizio Pirri[1,4], Francesca Verga[2], Annalisa Abdel Azim[1,4*]

[1] Centre for Sustainable Future Technologies, Fondazione Istituto Italiano di Tecnologia, Via Livorno 60, 10144 Turin, Italy, [2] Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24,10129 Turin, Italy, [3] Italian Institute of Technology, Genova Morego, [4]Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24,10129 Turin, Italy, [5]Istituto di Biologia e Biotecnologia Agraria, Consiglio Nazionale delle Ricerche, Via Alfonso Corti 12,20133 Milan, Italy;

*Presenting author email: annalisa.abdelazim@polito.it

Keywords: biomethanation, seawater brine, digestate, lithium depletion

Introduction

Lithium (Li), a critical element in renewable energy storage and battery technology, faces soaring global demand due to its extensive use in rechargeable batteries for electric vehicles, mobile devices, and renewable energy systems. However, traditional extraction methods, such as solar evaporation and chemical precipitation, are environmentally intensive, water-demanding, and geographically constrained to specific regions, such as South America's lithium triangle. Simultaneously, seawater desalination produces vast amounts of brine waste, which is not only rich in lithium and other valuable dissolved metals but also poses significant environmental challenges and disposal costs. The direct discharge of brine into marine ecosystems disrupts the local environment due to its high salinity and chemical content. Besides, methanogenic archaea, widely recognized for their role in methane production, demonstrate remarkable resilience in extreme environments, including high salinity [1], making them promising candidates for applications in brine management. These microorganisms have been documented to interact with various metal ions, participating in bioreduction and chelation processes. While direct studies linking methanogens to lithium recovery remain limited [2], they have already demonstrated the ability to recover metals such as vanadium, chromium, and cobalt [3–6] possibly suggesting potential applicability in lithium recovery processes. This work proposes a biomethanation-based approach exploring the synergistic use of anaerobic digestate and seawater brine to couple lithium recovery with renewable biomethane generation, offering a sustainable and integrated waste management strategy. This approach offers a novel circular economy solution by turning waste streams into critical resources while minimizing environmental impact.

Methodology

Herein, anaerobic digestate from organic municipal solid waste is proposed as an inoculum and nutrient source. A synthetic solution with a salinity of 77 g/L and a pH ranging from 6 to 7 is used to simulate a sea water brine. Lithium recovery and methane production are optimized under controlled H_2/CO_2 atmospheres at temperatures of 55°C and 65°C and at 1:1 and 2.33:1 brine-to-digestate ratio, with a final salinity of 38.5 g/L and 54 g/L respectively (**Figure 1**). Gas and liquid samples were analyzed via gas chromatography, HPLC, ICP-OES analysis. The metagenomic analysis was assessed through sequencing of V3-V4 regions of 16S rRNA bacterial and archaeal genes.

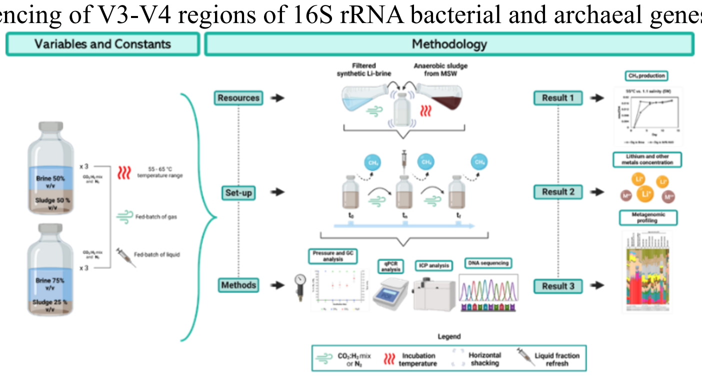

Figure 1 Overview of the experimental setup including key parameters and analysis.

Results and Discussion

Metagenomic analyses identified a dominance of hydrogenotrophic methanogens, including the *Methanothermobacter* and *Methanosarcina* genera. These taxa were enriched under H_2/CO_2 optimal condition, with *Methanothermobacter* doubling in relative abundance at 55°C. Moreover, methane production was most significant in the 1:1 brine-to-digestate ratio condition (**Figure 2**), achieving the maximum methane evolution rate (MER) after 15 days of incubation (data not shown). The 2.33:1 brine-to-digestate ratio experiment exhibited negligible methane production, probably due to osmotic stress caused by higher salt concentrations.

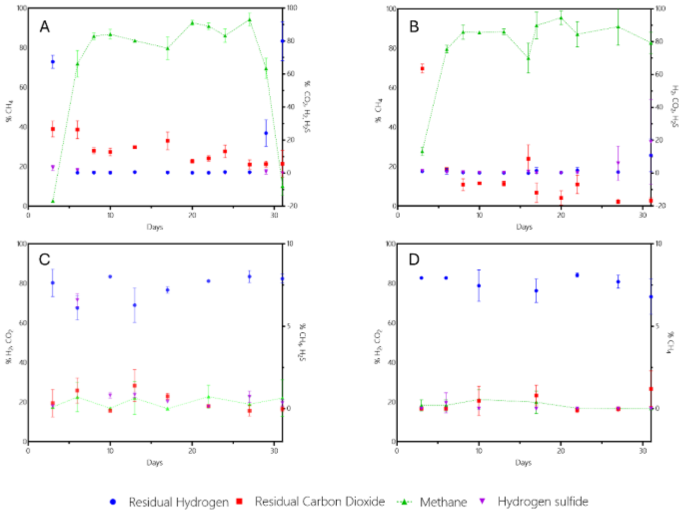

Figure 2 Bottle headspace gas composition under different experimental conditions applied: (A) 1:1 brine-to-digestate ratio at 55°C, (B) 1:1 brine-to-digestate ratio at 65°C, (C) 2.33:1 brine-to-digestate ratio at 55°C and (D) 2.33:1 brine-to-digestate ratio at 65°C.

Predictive functional analyses revealed the presence of key genes for lithium transport and tolerance mechanisms, potentially enabling microbial activity in high-salinity environments. Lithium depletion varied with brine concentration and temperature. Lithium was mostly recovered at the lowest brine concentration due to the additional microbial activity attributed to the methanogenic population that is favored at lower salinity. In fact, at 1:1 brine-to-digestate ratio lithium depletion achieved the highest values, reaching 72% and 55% at 55°C and 65°C, respectively. The lower occurrence and activity of the methanogenic community in 2.33:1 brine-to-digestate ratio tests also reflects on lithium depletion, which reach lower levels.

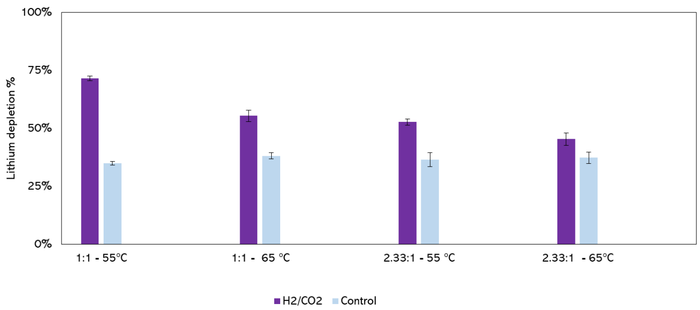

Figure 3 Percentage of depleted lithium compared to the initial concentration at the different experimental conditions. Control condition does not contain active microorganisms; hence in this case the lithium depletion is due to a passive sorption mechanism.

Moreover, control experiments conducted with sterile digestate, hence excluding the active play of microorganisms, showed that an average of 36% lithium is passively recovered at any experimental condition (**Figure 3**). Thus, lithium could be indiscriminately absorbed by dead biomass, metabolites and other sorbents naturally part of digestate.

Conclusion

This study demonstrates the feasibility of a biomethanation-based approach for an alternative and circular lithium recovery from simulated seawater brine. The integration of anaerobic digestate as a nutrient and microbial inoculum source offers a dual-function solution for brine valorization and a pathway to circular resource management, turning waste streams into valuable resources while mitigating environmental impacts. Compared to direct lithium extraction technologies, the biomethanation process is less resource-intensive and provides the additional benefit of renewable methane production. However, challenges such as scalability, selectivity for lithium, and microbial adaptation to high salinity remain critical for further optimization. Future work should focus on pilot-scale validation and enhancing microbial tolerance to salinity.

References

1. McGenity, T.J.; Sorokin, D.Y. Methanogens and Methanogenesis in Hypersaline Environments. In Biogenesis of Hydrocarbons; Dr. Alfons J. M. Stams, Dr. Diana Z. Sousa, Eds.; Springer International Publishing: Cham, 2019; pp. 283–309.

2. Abdel Azim, A.; Vizzarro, A.; Bellini, R.; Bassani, I.; Baudino, L.; Pirri, C.F.; Verga, F.; Lamberti, A.; Menin, B. Perspective on the Use of Methanogens in Lithium Recovery from Brines. Front Microbiol 2023, 14, doi:10.3389/fmicb.2023.1233221.

3. Krzmarzick, M.J.; Taylor, D.K.; Fu, X.; McCutchan, A.L. Diversity and Niche of Archaea in Bioremediation. Archaea 2018, 2018, doi:10.1155/2018/3194108.

4. Holmes, D.E.; Orelana, R.; Giloteaux, L.; Wang, L.Y.; Shrestha, P.; Williams, K.; Lovley, D.R.; Rotaru, A.E. Potential for Methanosarcina to Contribute to Uranium Reduction during Acetate-Promoted Groundwater Bioremediation. Microb Ecol 2018, 76, 660–667, doi:10.1007/s00248-018-1165-5.

5. Zhang, B.; Hao, L.; Tian, C.; Yuan, S.; Feng, C.; Ni, J.; Borthwick, A.G.L. Microbial Reduction and Precipitation of Vanadium (V) in Groundwater by Immobilized Mixed Anaerobic Culture. Bioresour Technol 2015, 192, 410–417, doi:10.1016/j.biortech.2015.05.102.

6. Zhang, J.; Dong, H.; Zhao, L.; McCarrick, R.; Agrawal, A. Microbial Reduction and Precipitation of Vanadium by Mesophilic and Thermophilic Methanogens. Chem Geol 2014, 370, 29–39, doi:10.1016/j.chemgeo.2014.01.014.