## World Academy of Science, Engineering and Technology International Journal of Geological and Environmental Engineering Vol:19, No:02, 2025

## Selective Extraction of Lithium from Native Geothermal Brines Using Lithium-ion Sieves

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Abstract: Lithium is recognized as the critical energy metal of the 21st century, comparable in importance to coal in the 19th century and oil in the 20th century, often termed 'white gold'. Current global demand for lithium, estimated at 0.95-0.98 million metric tons (Mt) of lithium carbonate equivalent (LCE) annually in 2024, is projected to rise to 1.87 Mt by 2027 and 3.06 Mt by 2030. Despite anticipated short-term stability in supply and demand, meeting the forecasted 2030 demand will require the lithium industry to develop an additional capacity of 1.42 Mt of LCE annually, exceeding current planned and ongoing efforts. Brine resources constitute nearly 65% of global lithium reserves, underscoring the importance of exploring lithium recovery from underutilized sources, especially geothermal brines. However, conventional lithium extraction from brine deposits faces challenges due to its time-intensive process, low efficiency (30-50% lithium recovery), unsuitability for low lithium concentrations (<300 mg/l), and notable environmental impacts. Addressing these challenges, direct lithium extraction (DLE) methods have emerged as promising technologies capable of economically extracting lithium even from low-concentration brines (>50 mg/l) with high recovery rates (75-98%). However, most studies (70%) have predominantly focused on synthetic brines instead of native (natural/real), with limited application of these approaches in real-world case studies or industrial settings. This study aims to bridge this gap by investigating a geothermal brine sample collected from a real case study site in the UK. A Mn-based lithium-ion sieve (LIS) adsorbent was synthesized and employed to selectively extract lithium from the sample brine. Adsorbents with a Li:Mn molar ratio of 1:1 demonstrated superior lithium selectivity and adsorption capacity. Furthermore, the pristine Mn-based adsorbent was modified through transition metals doping, resulting in enhanced lithium selectivity and adsorption capacity. The modified adsorbent exhibited a higher separation factor for lithium over major coexisting cations such as Ca, Mg, Na, and K, with separation factors exceeding 200. The adsorption behaviour was welldescribed by the Langmuir model, indicating monolayer adsorption, and the kinetics followed a pseudo-second-order mechanism, suggesting chemisorption at the solid surface. Thermodynamically, negative  $\Delta G^{\circ}$  values and positive  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ values were observed, indicating the spontaneity and endothermic nature of the adsorption process.

Keywords: adsorption, critical minerals, DLE, geothermal brines, geochemistry, lithium, lithium-ion sieves

Conference Title: ICGE 2025: International Conference on Geological Engineering

**Conference Location :** Lisbon, Portugal **Conference Dates :** February 08-09, 2025