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Synthesis of manganese oxide adsorbent as a tool for selective Lithium extraction from geothermal brines

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Lithium (Li) is one of the crucial elements for the realization of electric mobility, energy transition and digitization, with rising demand and prices over the last decades. However, with an import rate of 86% (2010 –2014) and a contribution to global Li-production of less than 1% (2017), Europe depends almost entirely on Li-import. To reduce the dependency, Li deposits and new and unconventional sources are searched for within in the EU. One possible source are the geothermal brines of the Upper Rhine Graben with Li concentrations of up to 200 mg/L.

However, extraction of Li through evaporation cannot be applied in the Upper Rhine Graben because of an unsuitable climate and the need for huge evaporation ponds or a large amount of energy. Instead, one way for economic Li extraction is the application of synthesized manganese oxide adsorbents, which is based on the selective adsorption of the dissolved Li. The high selectivity towards Li is a result of a tunnel structure of the manganese oxide with diameters slightly larger than the ionic radius of Li, thus hindering competing ions to adsorb onto the inner surface of the adsorbent and simultaneously creating a high specific surface area. Lithium is desorbed from the Mn oxides through exchange with H+-ions, which is achieved by applying an acidic solution. From the resulting solution, Li can be precipitated as Li2CO3 or LiCl and the Li-free adsorbent can be reused. The adsorption and desorption capacity are influenced by brine-related parameters like pH, temperature, salinity and further depend on the chemical composition and mineralogical structure of the adsorbent. In our study, a manganese oxide adsorbent (Li1.6Mn1.6O4) was synthesised to prove the suitability of the approach for the geothermal brines of the Upper Rhine Graben.

XRD and SEM analyses of the synthesised adsorbent shows a comparatively high amount of amorphous phases (~12 ¬ 18% semi-quantitatively) covering and coagulating the adsorbent particles (diameter of <1 –2 µm) to aggregates with diameters >10 µm. The XRD analyses of the synthesised Li1.6Mn1.6O4 shows a mixture of a Li-Mn-oxide phase and a Mn2O3 phase, which is an intermediate product of the synthesis, indicating that the transformation of the synthesis educts is incomplete.

Experiments with LiOH solutions show that Li is readily adsorbed and desorbed but the Li adsorption capacity is lower than expected. Additionally, more Li is desorbed than adsorbed indicating that Li originating from the synthesis educts is still present. Reaction kinetics are fast with an adsorption and desorption of more than 50% in several minutes proving the suitability of the method for the application in geothermal power plants. However, since the presence of intermediate products and amorphous phases significantly lower the Li adsorption capacity, a revised hydrothermal synthesis for the manganese oxide adsorbents is developed. Thereby, the synthesis parameters calcination duration and temperature, Mn-Li-ratio and duration of crystallization period are optimized to reach a transformation rate of synthesis educts of >90% and an amorphous percentage <5% to produce an adsorbent with which Li can be produced economical from the geothermal brines.

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