



## Extraction of Rare Earth Elements using Magnetite@MOF Composites

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# Extraction of Rare Earth Elements using Magnetite@MOF Composites

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**Abstract:** Magnetic core-shell microspheres were developed to extract rare earth elements (REEs) from aqueous and brine solutions with up to 99.99% removal efficiency. The shell, composed of a thermally and chemically stable functionalized metal-organic framework (MOF), is grown over a synthesized  $\text{Fe}_3\text{O}_4$  magnetic core (magnetite@MOF). The composite particles can be removed from the mixture under an applied magnetic field, offering a practical, and efficient REE-removal process.

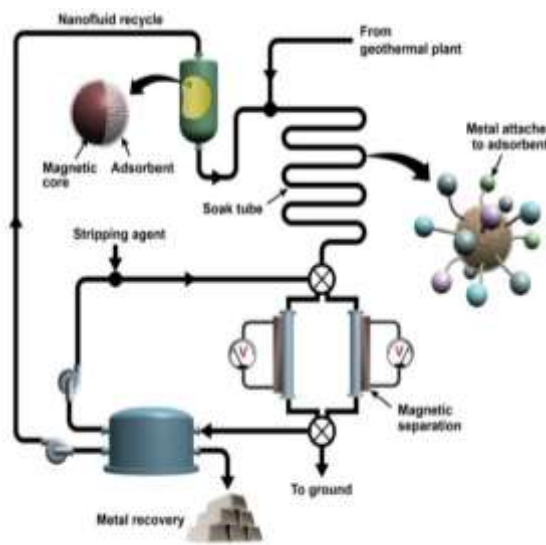
Rare earth elements (REEs) play a critical role in our modern technology-oriented world.<sup>1-3</sup> With applications related to high-tech consumer products, catalysis, luminescence, and high-performance magnets, the demand for REEs is predicted to increase exponentially.<sup>4</sup> Although such elements are not considered rare in the Earth's crust by overall amount, a low concentration in mineable ores makes conventional extraction of REEs expensive and feasible at only a few locations worldwide.<sup>5</sup> Thus, there is significant interest in new methods to extract REEs from unconventional sources, such as coal fly ash, produced water from hydraulic fracturing, and geothermal wells.<sup>6</sup> Sourcing REEs from geothermal wells is of particular interest because there is an attractive concentration of dissolved metal ions in the saline fluid (known as geothermal brine), ranging from parts per million (ppm) to parts per billion (ppb).<sup>7</sup> While this idea has been recognized as an attractive opportunity for additional revenue streams, as well as the geographic diversification of REE production, there is a lack of economically attractive methods for the recovery of REEs from geothermal wells.<sup>8-10</sup>

To this end, we present a *proof-of-concept* study for efficient extraction of selected REEs from brine solutions using magnetic metal-organic framework (MOF) composites. The introduction of a MOF 'shell' over a magnetite ( $\text{Fe}_3\text{O}_4$ ) 'core' offers a promising approach to the extraction of REEs, as the magnetic core-shell composites (herein, magnetite@MOF) can be easily isolated and recovered by the application of an external magnetic field.<sup>11-13</sup> This approach affords a facile strategy for a high level recyclability of MOFs by prohibiting significant material loss (process envisioned in Figure 1).<sup>14</sup> Indeed, magnetic particles functionalized with chelating groups have demonstrated promising performance for the adsorption of REEs from aqueous solutions.<sup>15, 16</sup> The inherent synthetic and chemical tunability of a MOF<sup>17-19</sup> shell significantly expands the scope and complexity of a magnetic extraction process.

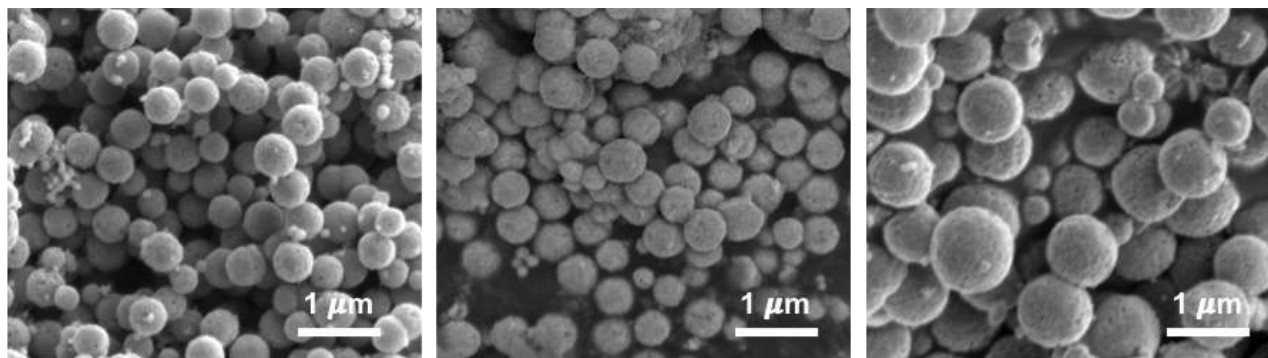
Specifically, we report two functionalized magnetite@MOF composites, magnetite@MIL-101- $\text{SO}_3$  (MIL: Materials of Institute Lavoisier) and magnetite@In-MOF (In-MOF also known as *sod*-ZMOF, ZMOF: zeolite like MOF, *sod*: sodalite topology)<sup>20, 21</sup> for the extraction of REEs. Five REEs, considered to be very critical for clean energy applications with high supply risk, were chosen: cerium (Ce), neodymium (Nd), dysprosium (Dy), europium (Eu) and yttrium (Y).<sup>22</sup> MIL-101- $\text{SO}_3$ , known to be air and water stable,

possess high density of negatively charged sulfonic acid ( $\text{SO}_3^-$ ) groups uniformly distributed on the pore surface which are readily exchangeable with the REE cations in aqueous and brine solutions.<sup>23</sup> Whereas, In-MOF, also known to be stable, has an anionic framework that can be treated with diethylene triamine (DETA) which functions as a chelating agent for REEs through pendant amine groups (DETA-In-MOF).<sup>24,25</sup> We demonstrate that the composites are air and water stable after activation and have very fast (<5 min) REE uptake kinetics—factors that are important to reduce cost and improve recyclability of the material for commercial operations.

Recovery of REEs is well established using conventional extraction methods, with a variety of sorbents materials, ranging from commercial ion-exchange resins to nanocomposites, demonstrating promising affinity and uptake kinetics of REEs.<sup>25-39</sup> However, these methods are not designed for the economic extraction of REEs from a geothermal power plant with throughputs of geothermal brine exceeding 400 L/s.<sup>40</sup> Herein we describe a simple and highly cost-effective nanofluid-based method. By introducing the magnetic composites at low concentration ( $\approx 0.05$  wt%), the brine is exposed to a very high concentration of sorption sites without a need to pass through a large and costly traditional packed bed or membrane system. Instead, after a short residence time in the brine, the particles are effectively separated out with an electromagnet and standard extraction methods follow to strip the rare earth metals from the magnetic particles. With this in mind, we designed a series of experiments to approximate the conditions of a geothermal plant.



**Figure 1.** Conceptual drawing of magnetic REE extraction from geothermal brine.

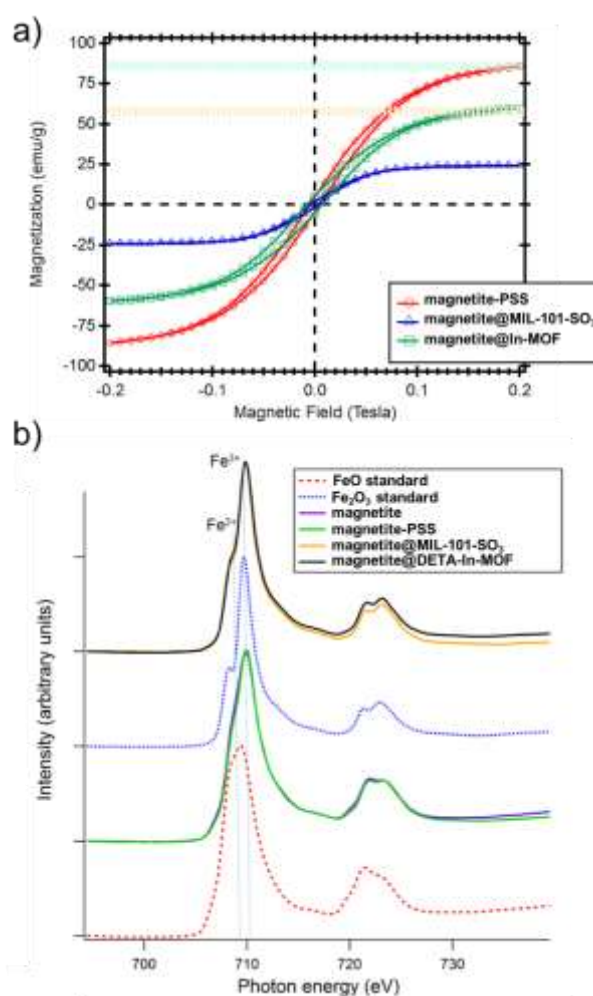


**Figure 2.** SEM of the magnetic core-shell microspheres: SEM images of magnetite, magnetite-PSS, and magnetite@DETA-In-MOF (left to right).

Recently, we have reported on the synthesis of magnetite@MIL-101-SO<sub>3</sub>, as well as the impact the MOF growth had on the magnetic properties of the iron oxide core.<sup>41</sup> Hence, here we will focus on the synthesis of the magnetite@DETA-In-MOF. The magnetite microspheres were synthesized according to a known procedure<sup>42</sup> and functionalized with a binding agent, polystyrene sulfonate (PSS) for a better adherence of the MOFs with the surface of the magnetite core.<sup>43</sup> *In-situ* solvothermal synthesis techniques were used to coat In-MOF on magnetite-PSS microspheres (see method and supplementary section). The In-MOF coated magnetite (now magnetite@DETA-In-MOF) was then exposed to a solution of DETA for 24 h. Work by Chen et al. suggests that amine species can be covalently grafted to In-MOF via a condensation reaction with the uncoordinated carboxylic acid groups in the framework.<sup>44</sup> Ongoing studies are examining whether DETA is covalently grafted or impregnated in the framework: a decrease in the Brunauer–Emmett–Teller (BET) surface area after DETA exposure and subsequent washing, adsorption studies, and FT-IR spectra showing N-H stretches (see supplemental Figure S4) support that the In-MOF can indeed be loaded with DETA. Further uncoordinated DETA in the pore space of In-MOF can be removed by activating the MOF at high temperature. The core-shell particles were isolated by magnetic separation, and the phase purity and porosity of the as-synthesized magnetite@MOF materials were carried out by powder X-ray diffraction (XRD) and BET surface area analysis (see supplemental Figures S1-S10). Furthermore, particle size of the magnetic core and the thickness of the MOF 'shells' on its surface were measured and characterized using SEM (Figure 2). Electron microscopic imaging suggests the pristine magnetite microspheres were found to be spherical with an approximate diameter of 300-500 nm. The diameter of the collected magnetite@DETA-In-MOF microspheres goes up to ~800-900 nm after MOF coating, without any change in shape and morphology.

The magnetite@In-MOF cores were further characterized by magnetic saturation experiments to understand their intrinsic magnetic properties. Saturation magnetization (Ms) of pristine magnetite and PSS- loaded magnetite was found to be 91 emu/g, consistent with literature values.<sup>45</sup> The coercive field (Hc) value was found to be consistent with magnetic particles of >75 nm diameter. Saturation magnetization, Ms and coercive field of magnetite@DETA-In-MOF was reduced by ~30% (65 emu/g) as compared to starting pristine Fe<sub>3</sub>O<sub>4</sub> microspheres (Figure 3a). The reduction in Ms can be attributed to partial oxidation of the Fe<sup>2+</sup> of

the Fe<sub>3</sub>O<sub>4</sub> core to Fe<sup>3+</sup> during *in-situ* MOF coating. This was clearly demonstrated by us recently using the combination of spectroscopic techniques.<sup>41</sup> To verify this possibility, synchrotron



**Figure 3.** Magnetic Saturation, Mossbauer and X-ray absorption Spectra. (a) Magnetic saturation of magnetite-PSS (red), magnetite@MIL-101-SO<sub>3</sub> (blue) and magnetite@DETA-In-MOF (green) at room temperature (notice bulk magnetite and maghemite saturation magnetization in light green and orange). (b) X-ray absorption spectroscopy (XAS) data of FeO standard (red), Fe<sub>2</sub>O<sub>3</sub> standard (blue), magnetite (violet), magnetite-PSS (green), magnetite@MIL-101-SO<sub>3</sub> (yellow) and magnetite@DETA-In-MOF (black).

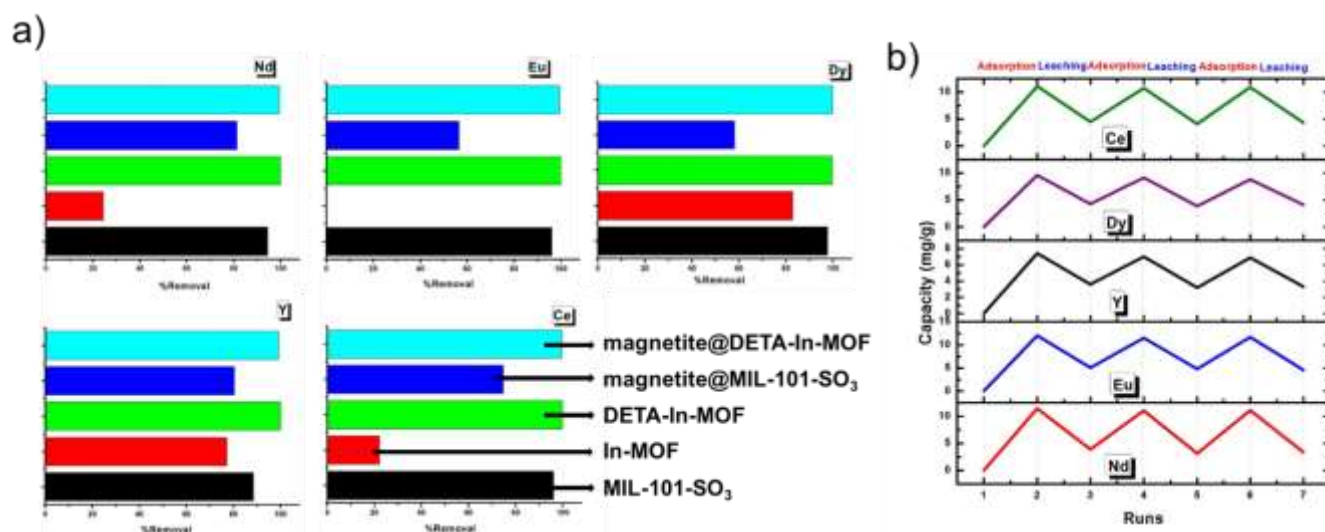
based X-ray absorption near edge spectroscopy (XANES) reveals that the magnetite and magnetite-PSS microspheres have significant contribution of  $\text{Fe}^{2+}$  oxidation state, wherein magnetite@In-MOF, the Fe oxidation state is dominated by  $\text{Fe}^{3+}$  oxidation state (Figure 3).<sup>46</sup> This finding is consistent with the results reported for magnetite@MIL-101- $\text{SO}_3$ .<sup>41</sup>

After synthesis of the magnetite@MOF composites we evaluated the REEs removal efficiency of pristine MIL-101- $\text{SO}_3$  and DETA-In-MOF in aqueous conditions. Indeed, both were found to be very selective towards extracting all the REEs, with DETA-In-MOF reaching a ~99% removal efficiency for all five REE cations within first 5 minutes at relatively low concentration (~0.0005 M), MIL-101- $\text{SO}_3$  also showed similar level of removal efficiency. Next, the REEs removal efficiency of magnetite@MIL-101- $\text{SO}_3$  and magnetite@DETA-In-MOF were evaluated under similar experimental conditions as pristine MOFs (see supplemental for more details). The magnetic adsorbent materials were facilely collected with the help of a permanent magnet, followed by powder XRD analysis to confirm the retention of core-shell structure after the cation exchange (see supplemental Figures S1-S4). Figure 4 depicts the %removal of all five REE cations. The results show that magnetite@DETA-In-MOF retains essentially all its removal efficiency as compared with the pristine MOF. The capacity of the magnetite@MIL-101- $\text{SO}_3$  microspheres was not retained quite as well with an overall reduction of about 20% as compared with pristine MIL-101- $\text{SO}_3$ . The reduction in capacity was attributed to the difference in surface area between pristine MIL-101- $\text{SO}_3$  and magnetite@MIL-101- $\text{SO}_3$ : 1368  $\text{m}^2/\text{g}$  and 376  $\text{m}^2/\text{g}$ , respectively (Figure S6 and S7).

To further understand the kinetics of magnetite@MOFs, the  $\text{Eu}^{3+}$  extraction using magnetite@MIL-101- $\text{SO}_3$  was studied as a function of contact time. The  $\text{Eu}^{3+}$  with magnetite@MIL-101- $\text{SO}_3$  combination was chosen due to a low uptake efficiency in a 5 minute window. It is evident that the  $\text{Eu}^{3+}$  removal efficiency reaches ~97% after 4 hours (see supplementary Figure S14). Furthermore, we conducted initial studies into the recyclability and

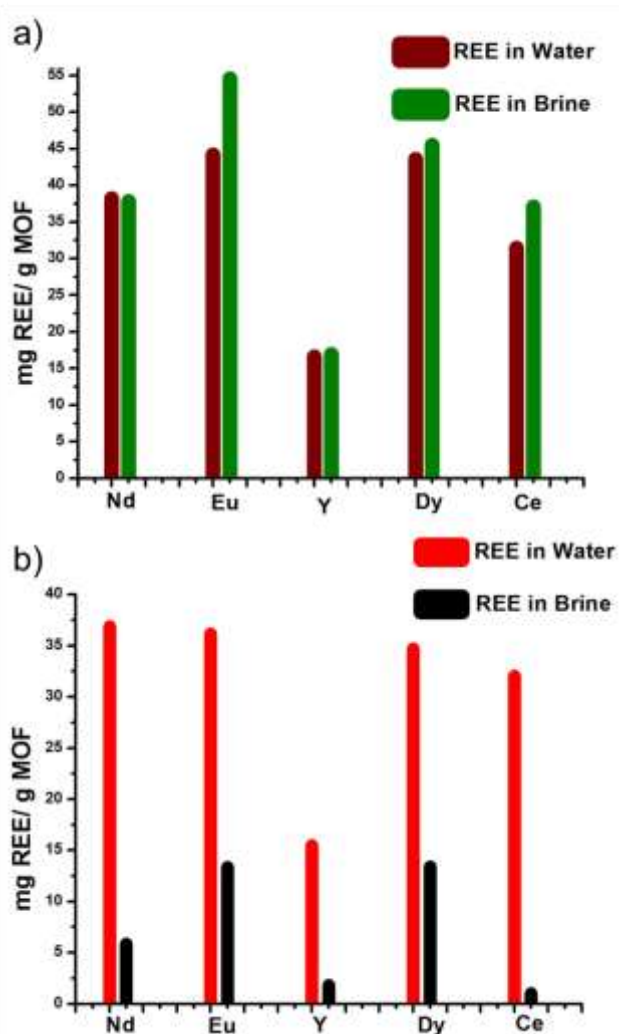
the efficiency of REEs removal under dynamic conditions (Figure 4b). To a packed bed of magnetite@MIL-101- $\text{SO}_3$ , alternating solutions of 0.0005 M REE and 2 M  $\text{HNO}_3$  solutions were eluted and the REE concentration was determined. Although the chosen washing conditions did not completely remove adsorbed REE, leading to a decrease in the working capacity for subsequent runs, the particles did maintain loading capacity throughout the small number of cycles. Changes to the MOF/magnetite ratio, however, were observed in the XRD before and after REE extraction. Differences in the relative intensity of the peaks corresponding to MIL-101- $\text{SO}_3$ , compared that those of magnetite, suggest a reduction in the MOF shell (see supplemental Figure S3). Initial adsorption results, however, indicate a high-level of recyclability of magnetite@MIL-101- $\text{SO}_3$ .

In order to study the efficiency of magnetite@MOFs toward extraction of REE from brine solution, REE extraction experiments were performed on both magnetic core materials (Figure 5). Known amount of magnetite@DETA-In-MOF and magnetite@MIL-101- $\text{SO}_3$  were placed in a brine and water solution containing REE's (0.0005 M). The extraction of REE's from brine solution was unaffected by magnetite@DETA-In-MOF whereas extraction ability of magnetite@MIL- $\text{SO}_3$  was dropped by more than 50%.<sup>47</sup> Based on hard and soft acid and base theory, hard acids (metal ions with high oxidation states, low polarizability) preferentially bind with hard bases (high electronegativity, highest occupied molecular orbitals), while soft acids preferentially react with soft bases. REE's are trivalent ions have the behavior of hard acids, and have higher affinity for hard bases (electron donors such as amino, hydroxide, alkoxide, or hydrazine). Hence, DETA is a hard Lewis base therefore it shows stronger affinity toward hard Lewis acids such as REEs and weaker interaction toward the soft Lewis acid such as the interfering metal ions from brine solution. The same principle was used to explain the extraction of Uranyl ions ( $\text{UO}_2$ ) selectively from sea water using DETA functionalized MOFs and chelation.<sup>47-50</sup> While in case of magnetite@MIL-101- $\text{SO}_3$ , the drop in the



**Figure 4.** a) Percent of REEs (Nd, Eu, Y, Dy and Ce) removal from aqueous solution by MIL-101- $\text{SO}_3$ , In-MOF, DETA-In-MOF, magnetite@MIL-101- $\text{SO}_3$ , and magnetite@DETA-In-MOF after 5 min. b) Cycle experiments with REEs solution by magnetite@MIL-101- $\text{SO}_3$ . 2M  $\text{HNO}_3$  solution was used to remove REEs from the packed bed.

extraction capacity presumably because  $\text{SO}_3^-$  has lower selectivity and weaker interaction toward REE in the presence of other interfering metal ions from the brine solution. Apart from REE complexation towards DETA groups, pH plays a critical role in extraction and binding of REEs. At higher pH ( $>7$ ) REEs form hydroxide complexes and precipitate out from the solution. Similarly, at lower pH say below ( $<4$ ) the DETA groups protonate and form quaternary ammonium salts as a result inefficient to chelate REE's therefore, based on own experiments and literature data on uranyl sorption experiments, pH 5 to 6 is ideal for extraction of REE using magnetite@DETA-In-MOF.<sup>47, 48</sup>



**Figure 5.** The REE removal efficiency of (a) magnetite@DETA-In-MOF and (b) magnetite@MIL-101-SO<sub>3</sub> from water and brine solution.

In order to understand the binding affinity of these magnetic cores towards REEs, the distribution coefficient ( $K_d$ ) was calculated, which is usually used to reflect the binding affinity of metal ion and a sorbent. A higher  $K_d$  value more than  $>5000$  means stronger affinity thus higher performance. As suspected from the REE extraction performance in brine, the two MOF materials had greatly different  $K_d$  ranges:  $7.72 \times 10^3$  to  $3.62 \times 10^4$  for the MIL-101-

SO<sub>3</sub> and  $1.4 \times 10^5$  to  $5.75 \times 10^6$  for DETA-In-MOF. However, both MOFs had higher  $K_d$  values than commercial available sorbents DOWEX ( $\sim 800 - 10,000$ , see supplemental Table S4), indicating a higher binding affinity for the selected REEs and a promising step forward in the design of a magnetic extraction process.

In summary, the design and synthesis of magnetic core-shell composite materials provides a promising approach to the extraction of REEs—even from brines. As a result of the added complexity afforded by the introduction of MOFs, two core-shell composites materials, magnetite@DETA-In-MOF and magnetite@MIL-101-SO<sub>3</sub>, were found to be highly effective for REE removal. Among these two adsorbent materials, DETA-In-MOF is ideal compared to MIL-101-SO<sub>3</sub> because of possible chromium leaching into the brine solution during the acid stripping, which has environmental concerns. Therefore care must be taken in selecting MOFs for extraction of REE from brine solution. Initial recyclability studies, combined with ease of isolation, suggest that further elaboration on this *proof-of-concept* report is warranted for the envisioned magnetic extraction process.

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