

FUNCTIONALISED MIL-101(Cr) AS NOVEL EUROPIUM ADSORBENT

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Abstract

In this contribution we report the synthesis of a novel MOF-based adsorbent for europium. MIL-101(Cr) is functionalised in a stepwise manner to create a material bearing carbamoylmethylphosphine oxide (CMPO) ligands, which are selective towards lanthanide complexation. Analysis showed that the adsorbent contains ~0.7 mmol of CMPO ligands per gram. Preliminary adsorption capacity tests have been performed resulting in a capacity of ~17 mg Eu/g adsorbent.

Introduction

The rare earth elements (REEs), a group of valuable metals, are gaining an ever-increasing importance to our modern society. Mainly consisting of the fifteen lanthanides, these rare earth metals are found in a variety of high-tech applications. Especially in the field of clean energy, many of the lanthanides (*e.g.*, neodymium, dysprosium, europium,...) play a critical role in the design and operation of appliances and machinery such as wind turbines, hybrid and electrical vehicles and lighting technology¹. With China currently controlling about 97% of the rare earth production, only a fraction of the mined metals reaches the international market as export product². Opposite to this limited supply stands a rapidly increasing demand that is unlikely to decelerate. Maintaining the rare earth supply will be crucial to a technologically sustainable future. One important way to achieve this goal is to anticipate on rare earth recycling. In this contribution we allude to one specific part in the complex chain of recycling processes, namely the recovery of rare earth metals from dilute aqueous streams.

Many metal recycling processes (and also primary mining processes, for that matter) end up with acidic solutions in which various metals are present in their dissolved ionic form. The current state-of-the-art (rare earth) recovery techniques consist of sequential liquid-liquid extractions or precipitation processes to selectively separate the valuable metals from any unwanted species³. While these techniques have proven their worth in terms of selectivity, their recuperation yield is not 100 %. Typically, these techniques generate aqueous waste streams containing several hundreds of milligrams of rare earth metals per litre. In the past decade it was not necessary, nor was it economically feasible to recover these small amounts of rare earths. But with

their increasing scarceness, the incentive has become far greater to expand industrial recovery to these streams as well.

An efficient and cost-effective way to remove and/or recover specific species from dilute solutions is adsorption. Being a heterogeneous process, adsorption has the advantage of easy separation and reuse. An adsorbent for rare earth metals, however, must meet several requirements. First of all, the adsorbent needs to interact selectively with the rare earth cations. This implies the embedding of specific functionalities into the adsorbent support, which neglect unwanted cations (transition metals, alkali metals,...) as much as possible, if not completely. Another important property is adsorbent stability. Not only does the support material have to perfectly survive the acidic aqueous conditions during the adsorption and regeneration, also the linkage between support and the immobilised functionality requires the proper stability to prevent leaching and to promote reuse of the adsorbent.

In this study, metal-organic-frameworks (MOFs) are introduced as a novel support in the field of liquid adsorption. More specifically the chromium based MIL-101 was functionalised and applied as selective adsorbent for europium. MIL-101(Cr) is a type of mesoporous cage-MOF, introduced in 2005 by Ferey *et al.*⁴. Its three-dimensional framework is made up of inorganic chromium-oxide clusters connected via terephthalate linkers, forming cages of super tetrahedra (Figure 1). The presence of the aromatic linkers makes post-functionalization of the MOF particularly easy. The MIL-101(Cr) is amongst the most stable mesoporous MOFs to date, possessing excellent resistance to acidic aqueous media^{5,6}. Furthermore, it is a highly porous MOF, where the mesoporous cages permit the incorporation of spacious molecules.

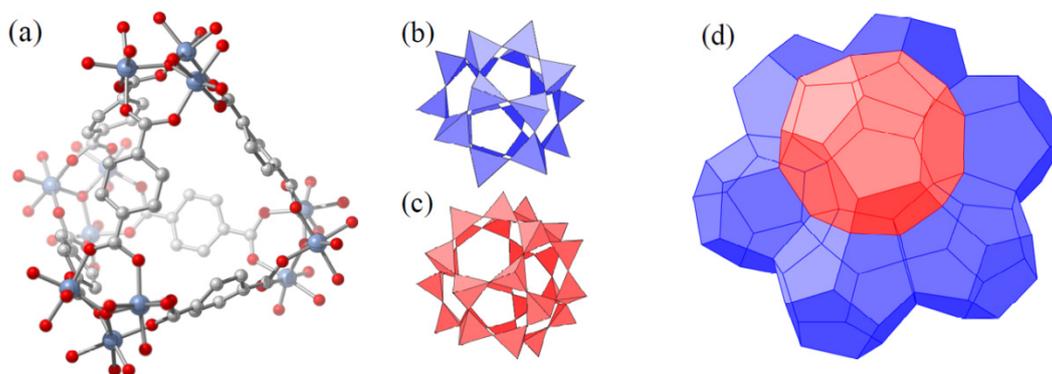


Figure 1: (a) MIL-101(Cr) super tetrahedron. (b) Small super cage. (c) Large super cage. (d) MIL-101 MTN zeotype structure.

All of the lanthanides form trivalent cations and as a general rule, these cations tend to be fairly hard Lewis acids as a result of their high oxidation states. Therefore, when designing a ligand field to selectively bind the lanthanide cations, it is advisable to incorporate hard Lewis bases into the ligand structure (*cfr.* the *HSAB* concept). In addition, an interesting phenomenon arises with these cations, in which the binding of one class of ligands to the cation enhances the affinity of another class of ligands. This results in a very selective complexing behaviour⁷⁻⁹. For the rare earth cations, the

most important types of synergistic ligands are the amide carbonyl group and phosphine oxide based ligands¹⁰. A very efficient system based on the aforementioned ligand combination is the so-called CMPO ligand (carbamoylmethylphosphine oxide, Figure 2). These ligands are known to be very selective towards lanthanide complexation, while having little to no affinity for ordinary transition- or alkali metals¹¹.

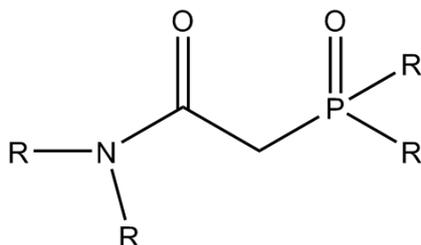


Figure 2: Carbamoylmethylphosphine oxide (CMPO) ligand structure.

By heterogenising these kinds of ligands, one can create a selective adsorbent for rare earth elements. In this on-going research, we aim to develop a selective adsorbent based on the MIL-101 as solid support. This is performed by a step-wise build-up of the ligand onto the MOF support. The materials are tested in the adsorption of europium from aqueous solutions. In these preliminary tests, we investigate the europium retention capacity of these developed adsorbents.

Experimental

Chemicals

Europium(III) oxide (99.9 %) was purchased from Alfa Aesar. Europium standard solution (1,000 mg/l Eu^{3+} in dil. nitric acid) was purchased from VWR Chemicals. All other chemicals were purchased from Sigma Aldrich.

Synthesis of MIL-101(Cr)

MIL-101(Cr) was synthesized based on an adapted recipe from Jiang *et al.*¹². In a typical experiment, terephthalic acid (0.665 g, 4 mmol) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.608 g, 4 mmol) were added to deionised water (20 ml). The resulting suspension was added to a Teflon-lined autoclave and subjected to 210 °C during 8 hours under autogenous pressure (2 hours warm-up). After cooling down to room temperature, the mixture was filtered and the solid green product was collected and washed thoroughly with dimethylformamide (DMF) and water in order to purify the material by removing any unreacted reagents. Samples were vacuum dried at 120 °C for 24 hours.

Characterization

Nitrogen gas sorption experiments were conducted at 77 K with a Micromeritics Tristar 3000. Samples were vacuum dried at 120°C prior to analysis. The specific surface area was calculated using the Langmuir method. DRIFTS-spectra were measured on a Nicolet 6700 FTIR spectrometer (Thermo-Scientific) with an MCT detector. Analyses were performed at 120 °C under vacuum. X-ray fluorescence (XRF) spectroscopy

measurements were performed on an energy-dispersive Rigaku NexCG spectrometer. Elemental analysis (CHNS) was performed on a Flash 2000 (Thermo-Scientific). Powder X-ray diffraction analyses were performed on an ARL X'tra diffractometer (Thermo-Scientific). Flame Atomic Emission spectroscopy (AES) was performed on a Varian SpectrAA 220FS, using 4 bar acetylene and 0,7 bar nitrous oxide. Adsorption tests were performed using a thermostatic shaking device (Infors HT Multitron standard, Analis, 25 °C, 220 rpm, 24 hours). In a typical adsorption test, 50 mg of adsorbent was added to 50 ml of aqueous 100 ppm Eu^{3+} -solution (pH 4 with HCl) in glass vials (w/ plastic lids). The tests were performed in triplicate. The europium concentration before and after the tests was analysed by means of Flame-AES.

Results and Discussion

Build-up of the CMPO-ligand onto the MIL-101

Figure 3 gives an overview of the functionalization process of the MIL-101(Cr). In the first step, the material was chloromethylated to provide a proper anchoring point for further functionalization. In this procedure¹³ the sample (1 g) was suspended in 70 mL of nitromethane. Subsequently 1.9 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.4 g of methoxyacetyl chloride were added. The mixture was then stirred for 5 hours at 100 °C, after which the solid material was filtered off and washed thoroughly with nitromethane, water and acetone. The sample was then vacuum dried at 120 °C for 24 hours. The material was analysed for its chlorine content prior and post chloromethylation with XRF and was found to contain ~5 mmol chloromethyl-groups per gram material.

The chloromethylated MOF (1 g) was then reacted with 1,4-diaminobutane (2.2 g) in 70 mL of DMF under inert atmosphere, by letting the mixture stir for 24 hours at 80 °C (Step 2). The material was filtered off, thoroughly washed with DMF and acetone, and vacuum dried at 120°C prior to elemental analysis. The sample contained approx. 5.5 wt.% additional nitrogen after this functionalization step, corresponding to 2 mmol diaminobutane per gram. Current research is focussing on increasing this loading.

The third step involves the coupling of the carboxylic end-groups of diethylphosphonoacetic acid with the primary amines of the functionalised MOF, forming the amide part of the CMPO-ligand. A total of 500 mg of amine-functionalised MOF is suspended in 25 mL of anhydrous DMF. In a separate round-bottom flask, 0.6 g of diethylphosphonoacetic acid (3 mmol) is dissolved in anhydrous DMF at room temperature (inert atmosphere), after which an equimolar amount of carbonyldiimidazole (CDI, 0.48 g) is added and the mixture is moderately stirred¹⁰.

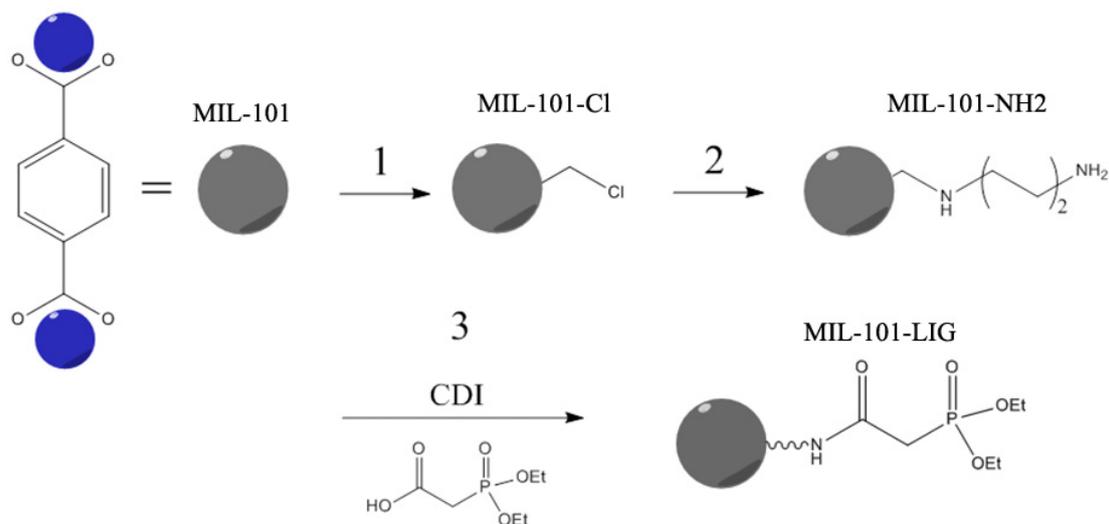


Figure 3: Stepwise build-up of the CMPO-ligand on MIL-101(Cr). Initial MOF: MIL-101, chloromethylated: -Cl, aminated: -NH₂, full ligand on MOF: MIL-101-LIG.

CDI is a known coupling agent for peptide synthesis, requiring water-free conditions¹⁴. The reaction of CDI with the carboxylic end-group can be visually monitored because the mechanism leads to formation of CO₂. The mixture is stirred until the evolution of CO₂ ceases (about 15 minutes). Afterwards both mixtures are combined and stirred for another 12 hours at room temperature. After filtration and washing with DMF, water, and acetone the sample is vacuum dried at 120 °C.

The following characterization analyses were performed on each stage of the (un)functionalised material: (1)nitrogen sorption measurements to determine the specific surface area of the material, which indicates the anchoring of species (weight-based result) and indirectly confirms the (in)stability of the material in the respective reaction conditions (shape of the isotherm); (2)DRIFTS-analyses to confirm whether the proper groups are anchored onto the material; (3)XRF-measurements to estimate the loading of the final ligand (via phosphorous analysis); (4) XRD measurements to further confirm the stability of the material in each step. The results are depicted in figures 4 to 6.

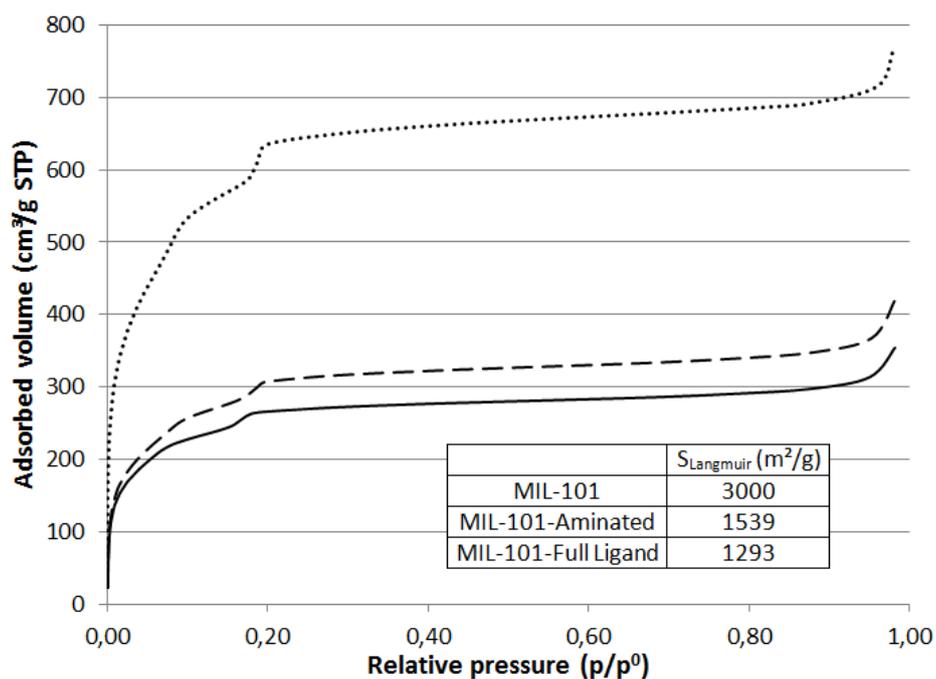


Figure 4: Nitrogen adsorption isotherm of the unfunctionalised MIL-101 (•), aminated MIL-101 (--) and finalised ligand MIL-101 (—).

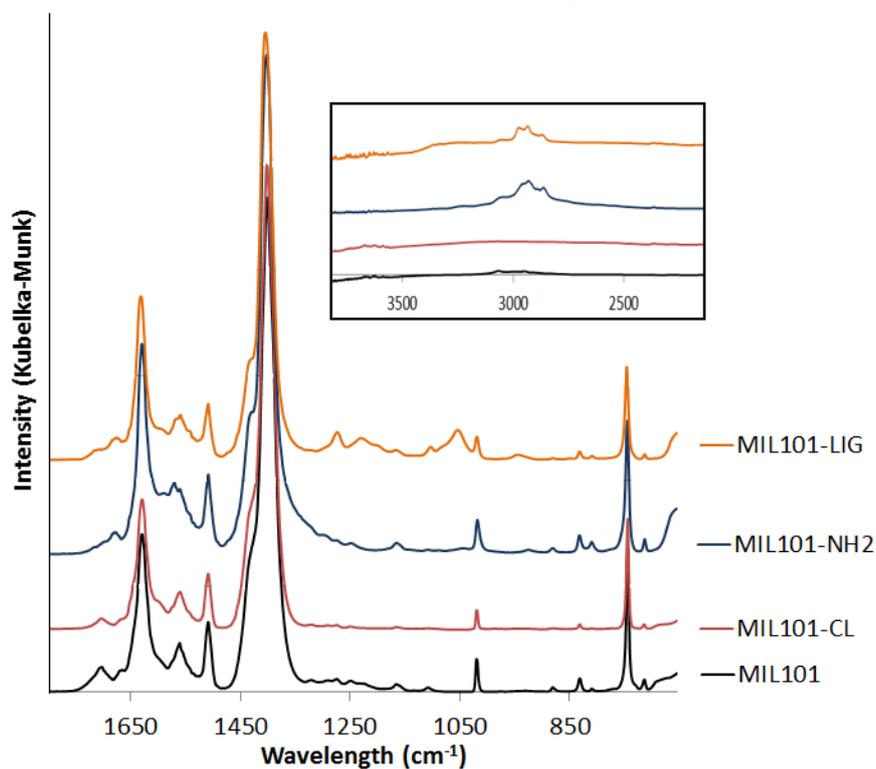


Figure 5: DRIFTS spectra of each step in the functionalization. Inset: zoom on the aliphatic stretch region.

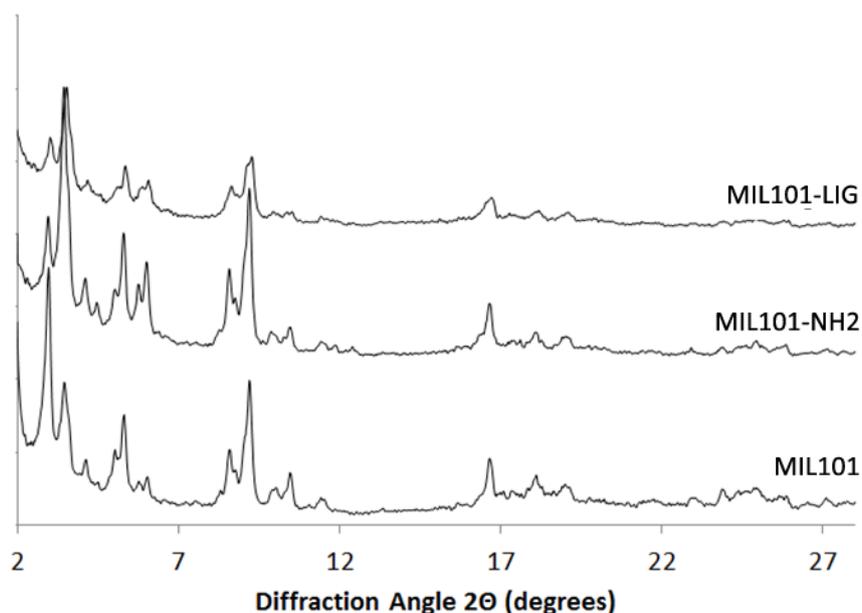


Figure 6: Powder XRD patterns of the (un)functionalised materials.

From the preservation of the XRD pattern and shape of nitrogen adsorption isotherm, it can be concluded that the MIL-101 perfectly maintains its structure throughout the different functionalization steps. Starting out at S_{Langmuir} : 3000 m²/g, the MIL-101 gradually decreases in specific surface area upon each functionalization step due to anchored species that fill up the cages and increase the weight of the material. In the DRIFTS spectra aliphatic CH stretches appear (2850 – 3000 cm⁻¹, inset), confirming the presence of diaminobutane in the aminated sample and the final adsorbent. An indication of amine groups is visible near 1550 and 1650 cm⁻¹, corresponding to primary-NH₂ scissoring. These do not appear as isolated peaks but partially overlap with vibrations originating from the MIL-101 structure. In the spectrum of the finalised adsorbent, vibrations are visible at 1040 cm⁻¹ and in the region between 1200 and 1260 cm⁻¹. These indicate the P-OR ester and the phosphine oxides or phosphonates vibrations, respectively. Presence of other characteristic peaks could not be proven unambiguously due to overlap with the MIL-101 structural vibrations and possible low loading.

XRF-analyses showed a phosphorous-loading of 0.7 mmol/g, which indicates that not all primary amines have been functionalised with the phosphonoacetic acid group. Current research focusses on increasing the yield of this solid-phase peptidization.

The CMPO functionalised MIL-101 was tested in the adsorption of europium. The unfunctionalised MOF as well as the aminated one were tested in the same conditions and were found to be inactive for the adsorption of Eu³⁺. The results of the final adsorbent are presented in table 1.

Table 1: Adsorption capacity of the CMPO functionalized MOF.

Material	Functional group	q_e (mg/g)	q_e (mmol Eu/g)
MIL-101-Full Ligand	-CMPO	17 (±2)	0.11 (±0.01)

The amount of europium adsorbed is calculated using the following expression:

$$q_e = \frac{C_0 - C_e}{m} \cdot V$$

where q_e is the equilibrium adsorption capacity of europium (mg/g), C_0 and C_e the initial and equilibrium Eu^{3+} concentration (mg/L) respectively, V the solution volume (mL) and m the adsorbent mass (mg). A total of 17 mg Eu^{3+} /g (0.11 mmol/g) is adsorbed with 0.7 mmol/g of CMPO ligands. This corresponds to six or seven ligands for every Eu^{3+} . The exact manner of coordination or the number of ligands coordinating to one europium, is not yet determined.

Conclusion

The MIL-101(Cr) is successfully functionalised and applied for the first time as a rare earth metal adsorbent in acidic aqueous solution. The solid is post-modified via three subsequent steps which resulted in a material with 0.70 mmol per gram of carbamoylmethylphosphine oxide ligands. The CMPO-functionalised MOF was used in preliminary experiments as a europium adsorbent and was able to adsorb ~17 mg Eu^{3+} /g. More in-depth europium adsorption experiments will be performed including regeneration of the CMPO functionalised MOF adsorbent.

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