



## Research paper

## Layered europium hydroxide system for phosphorous sensing and remediation

Cláudia C.L. Pereira<sup>a</sup>, João Carlos Lima<sup>a</sup>, Artur J. Moro<sup>a,\*</sup>, Bernardo Monteiro<sup>b,\*</sup><sup>a</sup> REQUIMTE, Dep. de Química, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal<sup>b</sup> Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 (km 139,7), 2695-066 Bobadela LRS, Portugal

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## ABSTRACT

A Layered Lanthanide Hydroxide (LLH) material based on europium (LEuH,  $\text{Eu}_8(\text{OH})_{20}\text{Cl}_4 \cdot 6\text{H}_2\text{O}$ ) was intercalated with 2,6-naphthalenedicarboxylate (NDC) yielding a material presenting the bright red luminescence characteristic of  $\text{Eu}^{3+}$ , both by direct excitation of europium and energy transfer from NDC. The material behaves as a sensor towards anions which display the ability to exchange with NDC. The sensor was tested with several anions (phosphate, sulphate, pyrophosphate, acetate, and tetraborate anions) and the changes in NDC ( $\lambda_{\text{em}} = 380 \text{ nm}$ ) and europium ( $\lambda_{\text{em}} = 615 \text{ nm}$ ) emission intensities upon excitation of NDC ( $\lambda_{\text{ex}} = 357 \text{ nm}$ ), were studied. Phosphate was found to have the highest degree of intercalation and displayed a strong increase (400% fold) on the fluorescence intensity of NDC. The presence of phosphate was further confirmed with Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Taking advantage of LEuH selectivity towards phosphate, its applicability in phosphorus remediation was studied presenting high sequestration capacity followed by controlled release of phosphate in three consecutive cycles and improved stability of the LEuH host material. These results highlight the significant potential of LLHs as new scavenging agents for inorganic phosphate.

## 1. Introduction

The urgency of building efficient and low cost anion sensors/scavengers, in particular for phosphate, arises from the heavy use of phosphate as a fertilizer by industrial agriculture. Since the discovery of phosphate rock in the 19th century, the rapidly increasing demand for mined phosphate rock has dominated global fertilizer production and has contributed to supplying food to billions of people. Phosphate rock are fossil sedimentary and igneous deposits that have accumulated over tens to hundreds of millions of years, and are therefore a finite resource on a human timescale. Production of high-quality phosphate rock is predicted to reach its peak this century, possibly as early as the next few decades, despite growing demand for phosphorus fertilizers (Neseta and Cordell, 2012). Because of the increased depletion of phosphate rock deposits, in the future they will contain lower phosphate concentrations and a higher content of impurities such as heavy metals, especially toxic cadmium associated with phosphate minerals. If such sources are used, the consequence will be a contamination of soil and ultimately food containing heavy metals (Mandel et al., 2013). Annually, only around 20–30% of phosphorous applied to agricultural land is exported directly out of the watershed (in runoff or removal in grain and animal

produce). The remaining 70–80% of applied phosphorus accumulates in soil, river sediments, groundwater, wetlands, riparian floodplains, lakes, and estuaries (Jarvie et al., 2013). Also, phosphorus is one of the major nutrients contributing to increased eutrophication of rivers and lakes (Wu et al., 2012). Numerous preventive actions tend to limit the use of products containing phosphorous, and curative treatments of waste water limit the eutrophication phenomena. In urban areas of industrial countries, the phosphate content in municipal wastewater is nowadays relatively well controlled, by the treatment of organic wastes especially using the activated sludge process (Ruby et al., 2015). and phosphate chemical precipitation with metal salts and subsequent removal with the sewage sludge. This precipitated metal phosphates have no fertilizer value, and phosphate has to be recovered from the sludge in a purer form which is a costly process with intensive chemicals consumption (Mandel et al., 2013; Niewersch et al., 2014). Such treatments, however, are generally not suitable for rural areas where the building costs and maintenance of wastewater treatment plants (WWTPs) would be too high and other collective sanitation systems are used such as lagoon based WWTPs and reed or sand bed filters. These passive systems consume very little energy and need little maintenance, but despite the fact that the organic matter release is generally

\* Corresponding authors at: Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 (km 139,7), 2695-066 Bobadela LRS, Portugal.  
 E-mail addresses: [ajm12769@fct.unl.pt](mailto:ajm12769@fct.unl.pt) (A.J. Moro), [bernardo.monteiro@ctn.tecnico.ulisboa.pt](mailto:bernardo.monteiro@ctn.tecnico.ulisboa.pt) (B. Monteiro).

satisfactory, the rate of dephosphatation remains too low (Drenkova-Tuhtana et al., 2016). Nanometric crystal sized iron oxyhydroxides such as ferrihydrite, or mesoporous spheres, present particularly high phosphate adsorption capacity but present problems of water clogging and release of rust colored water (Ruby et al., 2015). Thus, recovery of phosphate from wastewater not only prevents loss of a scarce resource but also protects natural waters from pollution. The standard method for measuring soluble phosphate in water is a colorimetric technique developed in the 1960s. This colorimetric approach is difficult to adapt for on-line measurements, uses specific reagents which require safe disposal and thus incurs significant costs to the water industry when carried out on a large scale. However no sensor based technology has, so far, been validated and replaced the standard colorimetric technique for determining the phosphate content of environmental water. The need for an effective sensing solution is a significant opportunity, although the phosphate anion's lack of electrochemical activity, together with its high hydration energy, makes direct detection and transduction challenging (Warwick et al., 2013). Thus fundamental research is still needed.

Layered lanthanide hydroxide (LLHs) compounds are materials of great interest due to a unique combination of the lanthanide (Ln) cations in the host layer and a rich anion exchange chemistry (Geng et al., 2008a; McIntyre et al., 2008). The compositional flexibility of such materials, where the cation and anion can be controlled to target a specific application enables these materials to be extremely appealing for potential applications like CO<sub>2</sub> adsorbents, catalysts, or directly as ion exchange hosts, fire retardant additives, polymer/LDH nanocomposites, drug delivery hosts, and as cement additives (Wang and O'Hare, 2012). LLHs have a general chemical formula of Ln<sub>2</sub>(OH)<sub>5</sub>A<sup>-</sup>*n*H<sub>2</sub>O, where A<sup>-</sup> represents interlayer anions. The crystal structure is built up along the *c*-axis via an alternative stacking of the host layer, composed of edge-shared [Ln(OH)<sub>7</sub>(H<sub>2</sub>O)] and [Ln(OH)<sub>8</sub>(H<sub>2</sub>O)] polyhedra, with each hydroxyl acting as a μ<sub>3</sub>-bridge connecting the lanthanide centers and the anions are intercalated between the layers for charge balance (Geng et al., 2008b). Inorganic luminescent materials based on Ln compounds, have been widely used in high-performance luminescent devices (Hasegawa et al., 2002), including LLHs (Yang et al., 2011; Wang et al., 2011; Yoon et al., 2010), due to their excellent electronic, optical, and chemical characteristics resulting from the lanthanide 4f electrons. Nevertheless, despite the rich anion exchange properties of LLHs, to the best of our knowledge, a study of these materials for anion sensing and scavenging has never been reported.

The strategies used for anion detection (in particular PO<sub>4</sub><sup>3-</sup>), are commonly based on supramolecular recognition. The complex synthetic procedures of the supramolecular approach are usually a limitation, as well as the use of fluorophores with short fluorescence lifetimes, which fall in the range of nanoseconds (Choi and Hamilton, 2001; Kim et al., 2009). To overcome this obstacles, a high research interest has been focused on fluorescent sensors based on lanthanide complexes, taking advantage of the sharp emission lines arising from the characteristic 4f electronic transitions, and the analyte-induced hyperfine energy transfer or change of coordination environment mechanism to offer considerable virtues over typical luminescent complexes (Santos and Gunnlaugsson, 2009; Zhou et al., 2012; Li et al., 2013; Zhu et al., 2013; Han et al., 2014; He et al., 2014). Recently, lanthanide complexes based on a quinolinecarboxylate ligand presented a strong response in the Eu<sup>3+</sup> emitting behavior with a low detection limit of 15.3 and 8.3 nM, for HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> respectively, and a quick response time of < 30 s (Xu et al., 2015). The predominant equilibrium species of inorganic phosphate at physiological pH is H<sub>2</sub>PO<sub>4</sub><sup>-</sup> which have received increasing attention of late and the advances in fluorescent sensors have recently been reported by A. Martinez and coworkers (Zhang et al., 2014). Additionally, the use of a preorganized materials in substitution of a supramolecular complex (like LLHs) should add the advantage of preorganized cavities (essential to recognition) and easy of synthetic

procedure, in combination with luminescent changes upon anion exchange and the sensitivity gain of having multi-site anion binding per sensor particle which is also useful in anion scavenging. The composite materials herein presented intend to contribute to the development of low-cost phosphate scavenger/sensor in aqueous media.

## 2. Experimental

### 2.1. Materials and reagents

The starting materials EuCl<sub>3</sub>·6H<sub>2</sub>O (Aldrich), NaCl (Panreac), Hexamethylenetetramine (HMT) (Aldrich) and 2,6-Naphthalenedicarboxylic acid (Aldrich) were obtained from commercial sources and used as received. All solvents for spectroscopic studies were of spectroscopic or HPLC grade (Carlo Erba), and used without further treatment.

### 2.2. Synthesis

Both Eu<sub>8</sub>(OH)<sub>20</sub>Cl<sub>4</sub>·6H<sub>2</sub>O (LEuH) and Eu<sub>8</sub>(OH)<sub>20</sub>(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (LEuH-2,6-NDC) materials were prepared as reported previously for the dysprosium analogues (Monteiro et al., 2013; Monteiro et al., 2015).

#### 2.2.1. LEuH

Eu<sub>8</sub>(OH)<sub>20</sub>Cl<sub>4</sub>·6H<sub>2</sub>O was prepared by mixing EuCl<sub>3</sub>·6H<sub>2</sub>O (1.832 g; 5 mmol), NaCl (3.825 g; 65 mmol), and HMT (0.702 g; 5 mmol) in 1000 cm<sup>3</sup> decarbonated Milli-Q water, and the solution was heated at refluxing temperature overnight under continuous magnetic stirring and nitrogen gas protection. The obtained final product was recovered by filtration, washed with decarbonated deionized (DD) water and dried at room temperature under reduced pressure. Anal. Calcd. for Eu<sub>8</sub>(OH)<sub>20</sub>Cl<sub>4</sub>·6H<sub>2</sub>O: Eu, 67.32; H, 1.79%. Found: Eu, 67.28; H, 1.82%.

#### 2.2.2. LEuH-2,6-NDC

2,6-Naphthalene dicarboxylic acid was deprotonated with a solution of NaOH, 50% in water and, if necessary, pH was adjusted to 7 with a diluted solution of HCl. Excess (3 equivalents) of 2,6-naphthalene dicarboxylate was added to a suspension of LEuH in DD water and stirred for about 20 min. The mixture was sealed in a 25 mL teflon-lined stainless-steel autoclave and kept at 100 °C for 12 h. The reaction mixture was then cooled to room temperature and the product was recovered by filtration, washed with DD water, and dried at room temperature under reduced pressure. Anal. Calcd. for Eu<sub>8</sub>(OH)<sub>20</sub>(C<sub>12</sub>H<sub>6</sub>O<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O: Eu, 58.10; C, 13.78; H, 2.12%. Found: Eu, 58.01; C, 13.65 H, 2.28%.

### 2.3. Structural characterization procedures

Microanalyses for C and H were performed on a CE Instruments EA1110 automatic analyzer. To guarantee complete combustion of the samples, V<sub>2</sub>O<sub>5</sub> was added during the analysis. Eu and P were determined by ICP-AES at Laboratório de Análises, Faculdade Ciências e Tecnologias da Universidade Nova de Lisboa, solid samples were digested in aqueous nitric acid before measurements. FT-IR spectra (range 4000–400 cm<sup>-1</sup>) were collected as KBr pellets (Sigma-Aldrich, FT-IR grade) using a Jasco FT/IR-4100 spectrophotometer by averaging 64 scans at a maximum resolution of 4 cm<sup>-1</sup>. Conventional XRD data were collected at room-temperature on a Panalytical X'Pert Pro diffractometer, with a curved graphite monochromator (Cu Kα radiation, λ = 1.54060 Å), and a flat-plate sample holder, in a Bragg-Brentano para-focusing optics configuration (45 kV, 40 mA). Samples were step-scanned in 0.01° 2θ steps with a counting time of 2 s per step.

### 2.4. Absorption and fluorescence experiments

Absorption measurements were performed either in a Cary 100 or in

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