Zirconium organophosphonates as high capacity, selective lanthanide sorbents

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ABSTRACT

Novel and versatile zirconium organophosphonate coordination networks have been developed as sorbent platforms via simple, low-temperature hydrothermal reactions of zirconium propoxide with amino tris(methylene phosphonic acid) (ATMP). The resulting materials exhibited hierarchical porosity and possessed exceptional selectively for lanthanide elements over mono- and divalent metal ions during competitive sorption experiments in 0.1 M HNO_3, as well as modest intra-lanthanide selectivity. As such, the present materials have potential as solid phase extractants for lanthanide separations in applications including mining, radioactive waste treatment and environmental remediation. Lanthanide sorption was shown to occur via uncoordinated P—O groups in the ATMP molecule. The structure, porosity and sorption properties of the coordination network platform could be tuned through varying the molar ratio of phosphorus to zirconium. Interestingly, the sample with the lowest surface area (<2 m^2/g) demonstrated the highest sorption capacity. Optimal compositions demonstrated europium sorption with fast kinetics and very high capacities of up to 0.63 g/mg min and 60 mg/g respectively. As such, these highly stable zirconium organophosphonates, prepared from inexpensive precursor chemicals using one-pot methods, perform comparably to costly commercially available polymer resins.

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1. Introduction

Lanthanide elements (LN) have come to be considered among the most critical of materials due to their importance in the clean energy technologies of the future such as wind turbines and electric vehicles as well as their increasing industrial importance in applications such as catalysts, electronics and phosphors [1,2]. Lanthanides are also important in the context of the nuclear fuel cycle because they are produced during the fission of uranium and are hence present in radioactive wastes [3]. As well as being fission products, LN can be used as non-active mimics to determine the expected behaviour of the long-lived, radiotoxic minor actinides (MA) in used nuclear fuel due to their chemical similarity [3,4]. Elements within the LN series are also very chemically similar, so technologies for the efficient separation of LNs are highly desirable to a multitude of industries [5]. Overall, it is clear that development of LN separation and purification technologies would be advantageous for management of radioactive wastes, renewable energy technologies of the future, mining industries as well as environmental remediation and pollution control [6].

Although LNs were originally extracted using techniques such as fractional crystallization and ion exchange [7,8], the current dominant technique for their separation is solvent extraction (SX) [5]. Despite the dominance of SX in the LN industry, solid–liquid extraction using selective sorbents does have some attractive features. For example, less secondary waste generation (as no organic solvents are required) and faster kinetics in many cases [9]. In addition, the extractant molecule does not need to be soluble in an organic phase, a phase modifier is never required and there is no possibility of third phase formation. Thus, depending on the properties and performance of the solid-phase sorbent, solid–liquid extraction may reduce the complexity of processing relative to SX, which in turn reduces the number of unit processes, time and cost required. As such, it was of interest to develop solid phase sorbent materials for selective LN extraction.

Phosphate and phosphonate groups are well known to display a powerful affinity for LN and actinide cations and a myriad of organophosphorus compounds have been studied as extractants in SX systems (eg. tributylphosphate TBP, octylphenyl-N,N-diisobutylcarbamoylmethylphoshine oxide CMPO, tri-n-octylphosphine

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oxide TOPO and diidodecylphosphoric acid DIDPA) [10]. In fact, the organophosphorus extractant di(2-ethylhexyl)phosphoric acid (HDEHP) acts to selectively separate LN from MA in the well-known TALSPEAK process [11]. Comparatively less attention has been given to phosphonates as solid phase extractants. However, extraction chromatography resins have been developed and typically consist of macroreticular ion exchange resins such as Amberchrom resins as polymeric supports for organophosphonic acids [12–14]. A drawback of purely organic resins for separations in nuclear applications is their low tolerance to ionizing radiation which degrades the resins and makes them less efficient [15,16]. In addition, since the extractant is not covalently bonded to the polymer matrix, extractant loss may occur over time [17]. Radiation effects and extractant leaching may result in more frequent resin replacement and the generation of volumes of secondary wastes. Finally, the most common polystyrene based resins also have the drawback of potential exothermic reactions with nitric acid solutions [18], which are commonly used for the dissolution of used nuclear fuel [10].

Inorganic and hybrid ion exchangers might therefore offer advantages in terms of radiolytic and hydrolytic stability, as well as disposition since they offer the prospect of direct conversion to stable crystalline phases from which radionuclides cannot be leached [19]. This makes such materials suitable for direct disposition in deep underground repositories that have come to be accepted as the standard method for the disposal of long-lived heat-producing radionuclides [20]. Therefore, this study focused on zirconium organophosphonate materials due to their excellent hydrolytic [21] and radiolytic [22] stability, which is superior to other metal phosphonates [23], silica sorbents [24] and polymer sorbents [15,16]. This provides a distinct advantage for separations in a nuclear context. In addition, zirconia and phosphate based materials should be particularly amenable to being converted into stable ceramic waste forms after adsorption for immobilisation of the radionuclides [22,25,26].

Since the pioneering work of Alberti and Clearfield on pillared Zr(IV) phosphonates [27,28], a wide range of other Zr(IV) metal organic frameworks based on phosphonate motifs have been developed having structures that range from amorphous to highly crystalline [29–36]. Most previously synthesised zirconium organophosphonates have used mono- or bis-phosphonates to form either amorphous porous structures [31,32] or crystalline layered/pillared structures [33–36]. However, in order to potentially provide more unbound phosphonate groups for LN binding from solution, the use of higher order polyphosphonates was targeted in this study. Recently a tris-phosphonate; amino tris(methylene phosphonic acid) (ATMP), was used to functionalise pre-assembled mesoporous zirconium titanium oxide. The ATMP imparted significant selectivity for LN and mitigated leaching of the framework elements [21]. However, these materials had a low phosphonate loading as the partially condensed metal oxide framework had only a limited number of coordinatively unsaturated surface sites to which phosphonates could bind. Hence they demonstrated a very limited capacity for LN [37]. Therefore in the present work, materials were synthesised with ATMP incorporated into the framework, giving a higher density of evenly distributed phosphonate groups. Similar materials have been synthesised previously but their LN sorption properties were either unexplored [29] or demonstrated to be inferior to the present materials [30].

Few studies have considered zirconium organophosphonate materials for the sorption of lanthanides or actinides [30,34–36] despite the known affinity of phosphonate based extractants for LN and actinide cations in solvent extraction processes [10]. The aim of the present study was to develop novel zirconium organophosphonate phases with high selectivity for LN and understand the relationship between their sorption properties and structures.

The effects of elemental composition, surface area and morphology of the zirconium organophosphonate materials on the selectivity, capacity and kinetics of LN sorption were explored. Investigation of the mode of cation binding was also undertaken by FTIR.

2. Materials and methods

2.1. Synthesis

All reactants were purchased from Sigma Aldrich and were reagent grade or higher. Reagents were used as supplied without further purification. Aqueous ATMP (50 wt%) was mixed with MilliQ water to make a total volume of 10.0 mL. Zirconium(IV) propoxide (70 wt% in 1-propanol) was then added. The pH was adjusted to between 4.2 and 4.6 by addition of potassium hydroxide solution (2.0 M). Specific synthesis conditions for each sample are listed in Table 1. The resulting suspension was then stirred at room temperature for 1 h in a plastic beaker before transfer to a parr reactor vessel for hydrothermal treatment at 160 °C for 24 h. After cooling, the products were vacuum filtered through qualitative filter paper, washed with MilliQ water and air dried. The resulting white solid was ground to a fine powder in a mortar and pestle. The materials are designated ZrP-x where x is the measured mole fraction P/(P + Zr).

2.2. Characterisation

X-ray diffraction (XRD) data were obtained on a Panalytical Empyrean diffractometer using Cu Kα radiation and a PIXcel 3D detector. Nitrogen adsorption–desorption isotherms for dried powders were obtained by multipoint nitrogen gas sorption experiments at 77 K after degassing at 200 °C on a Micromeritics ASAP 2420 porosimeter. Surface areas were estimated according to the Brunauer–Emmett–Teller (BET) method while pore volume and pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method based on the desorption branch. For elemental analysis, samples were digested in conc. H_2SO_4 for 48 h and the resulting solutions were diluted before ICP-MS analysis to determine the Zr and P contents. This methodology was validated by independent microanalysis (see below) to determine the percentage C, H, N and P in ZrP-0.50 and ZrP-0.76, which gave% P values within 1.2% of those determined by ICP-MS. C, H, N analysis was performed using the automatic analyser instrument, Carlo Erba 1106. The sample is combusted, and the gases, after scrubbing and reducing, are separated on a gas chromatography column and measured at the detector. Phosphorus determinations were made after oxidative digestion by comparative UV spectrophotometric measurements of the yellow vanadomolybdophosphate complex. A variety of methods are used for decomposition of the sample to minimise chemical interferences. Scanning electron microscopy (SEM) was performed on a Zeiss Ultra Plus electron microscope operating at 10–15 kV. Inductively coupled plasma-mass spectrometry (ICP-MS) for elemental analysis of solutions before and after sorption experiments was performed on a Varian 820-MS instrument. Samples for ICP-MS analysis were diluted 1:10 in 3%

Table 1
Synthesis conditions for ZrP materials.

Sample	Zr:P molar ratio added	2 M KOH (mL)	Final pH
ZrP-0.50	1:1	0.7	4.3
ZrP-0.54	3:4	1.0	4.5
ZrP-0.65	1:2	1.4	4.3
ZrP-0.71	1:3	2.4	4.6
ZrP-0.76	1:4	3.5	4.2