



A versatile Zr(IV)-organophosphonate coordination polymer platform for the selective adsorption of lanthanides and actinides



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ABSTRACT

New coordination polymer materials based on the complexation of Zr(IV) by 1-hydroxy-2-(1H-imidazol-1-yl)ethane-1,1-diyl bisphosphonate (zoledronate) have been prepared by the hydrothermal reaction of $ZrOCl_2 \cdot 8H_2O$ with zoledronic acid. The materials were prepared with different compositions by varying the P/(P + Zr) mole fraction of the reactants. All compositions were X-ray amorphous and had virtually no open porosity which is consistent with the formation of a random gel-type network. The extraction of elements by these materials from solutions containing a range of lanthanide elements in addition to major and minor actinides and other typical fission product elements was investigated at different total cation concentrations. Through variation of the composition of the gels it was possible to tune the adsorption properties. Materials with high phosphorus mole fractions were found to have very high selectivity for lanthanides and Th^{4+} and low selectivity for typical fission product elements (Cs^+ , Sr^{2+} and Co^{2+}) in 0.10 M HNO_3 solution. In contrast materials with lower phosphorus mole fractions did not sorb lanthanides strongly while they continued to extract Th^{4+} quantitatively from acid solutions. The materials with lower mole fractions of phosphorus were incorporated into polyacrylonitrile beads and the adsorption properties of the composites explored in greater detail. The kinetics, capacity and acid dependency of this composite were investigated. The present versatile coordination polymer adsorbent platform can be used for the selective extraction of Th^{4+} and possibly other major actinides from complex mixtures containing a variety of lanthanides in the HNO_3 concentration range 0.5–0.01 mol/L. The group extraction of the remaining lanthanides could then be accomplished with a change in composition of the adsorbent. The ability to convert the Th-saturated adsorbent materials directly into sodium zirconium phosphate (NZP) adds an additional dimension to the utility to the materials since sorbed Th, or other actinides, could be converted into one of the most versatile and stable phosphate ceramic materials for the immobilization of actinides.

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1. Introduction

The actinides uranium and thorium are primordial elements whose abundance in the earth's crust ranks alongside that of the lanthanides, or rare earth elements (REEs) as they are sometimes also known. These primordial actinides are indeed often found together with lanthanides in phosphate rocks containing mineral phases such as bastanite, monazite and xenotime. The major primordial isotopes of both uranium and thorium are ^{235}U , ^{238}U and ^{232}Th . Uranium-235, which is fissionable, is found in 0.7% natural abundance and forms the basis of contemporary nuclear electricity generation. On the other hand, ^{238}U and ^{232}Th are both fertile isotopes. Uranium is extracted commercially from a variety of ores for use in the nuclear reactors that produce about 16% of world electricity. In some cases uranium is extracted as a by-product during the production of other valuable elements such as copper, gold and silver. Although the

use of ^{232}Th as a nuclear fuel has been extensively researched, its contemporary use has been rather limited and is currently restricted to countries such as India and China where full implementation has not yet been reached (Anantharaman et al., 2008). There is however increasing interest in the use of thorium because it is at least four times more abundant than uranium and because its use could significantly reduce the generation of long-lived, high heat-generating and extremely radiotoxic radionuclides such as those of plutonium and minor actinides (Lung and Gremm, 1998). For these reasons a number of new thorium energy projects are being initiated. An example is the FUJI molten salt reactor project development (Furukawa et al., 2008). In addition to interest as a nuclear fuel, the management of thorium containing wastes represents a major problem in REE production (Collier et al., 2001). In fact, in most REE-containing ores, such as monazites, the abundance of thorium is up to ten times higher than that of uranium (Hughes and Singh, 1980; Eyal and Olander, 1990).

It would clearly be desirable to develop new materials with advantageous properties that could form the basis of an efficient technology for

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the selective separation of valuable lanthanides and actinides from mineral processing solutions, in environmental decontamination, nuclear waste management, and fuel recycling. In these applications the predominant technology, liquid–liquid extraction, which is based entirely on organic solvents and extractants, has a number of drawbacks. These include low inherent selectivity for the species of interest often necessitating a large number of extraction stages, the generation of secondary waste streams including degraded solvent and extractants, and the hazards associated with handling highly combustible materials within nuclear fuel cycle installations. Thus, there has been increasing interest in the development of alternative approaches including solid-phase extraction employing different organic, inorganic and hybrid materials.

Extensive commercial use is made of porous materials for applications in the extraction of heavy metal ions and the separation and storage of gases as well as in catalysis. The toolbox of solid-phase extraction materials has expanded greatly over the past several decades and includes materials such as the traditional porous gels and macroreticular polymeric resins, carbons, silicas, aluminas, crystalline microporous aluminosilicates (zeolites), phosphates, titanates (Shehee et al., 2012; Nyman and Hobbs, 2006), titanosilicates (Zheng et al., 1995, 1996) and related totally inorganic mixed framework microporous oxides. One may now also include as part of this toolbox more developmental, yet promising, hybrid materials such as non-functionalized and organic functionalized mesoporous metal oxides (Feng et al., 1997), extraction chromatographic resins (Horwitz et al., 1993; Horwitz et al., 1990), and most recently, coordination polymers such as metal organic frameworks. The use of such solid-phase extractants as alternatives to liquid-phase extractants in the abovementioned areas therefore warrants detailed consideration. Lanthanides and minor actinides are generally found in the trivalent oxidation state and are classified according to Pearson as hard ions. They are thus most likely to form strong complexes with hard ligands containing highly electronegative elements such as F^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} and OH^- (Wood, 1990).

The aforementioned organic functionalized high surface area mesoporous metal oxides are prepared by anchoring of organic molecules such as organo-silanes and organo-phosphonates to the surfaces of materials with high porosity such as the supramolecularly templated mesoporous metal oxides. Such materials offer considerable tailorability since there is a scope to vary both the organic and inorganic components and the porosity of the oxide. The use of high surface area supports is generally considered as a means of maximizing the number of surface active sites and therefore capacity. Indeed our group and others have shown considerable potential of such functionalized mesoporous oxides for the adsorption of lanthanides and actinides (Griffith et al., 2010; Luca et al., 2007; Sizgek et al., 2008, 2009; Polednak et al., 1983; Fryxell et al., 2004, 2005).

One of the limitations of such functionalized porous oxide materials however is the relative fragility of the coupling between metal oxide and the functional organic group. Another limitation is the fact that the loading of functional organic groups on the pre-assembled metal oxide is generally low hence compromising the capacity of the adsorbent. The co-assembly of a functional open framework metal oxide in the presence of surfactants is an approach that can be realized in one pot and has the potential to achieve higher loading of organic. Such co-assembly has been undertaken and extensively reported on in the case of functionalized mesoporous materials (Stein et al., 2000).

Another class of promising materials is the coordination polymers that result from the coordination of metal cations by multifunctional organic ligands to form compounds that extend continuously in 1, 2 and 3 dimensions and that may or may not be crystalline. The hexacyanoferrates can be regarded as traditional members of this class of compound and their ion exchange properties are well documented and have been extensively explored. That the couplings of group IV metal cations and organic moieties can yield polymer-like porous materials was demonstrated by Clearfield and others as early as the mid-nineties (Poojary et al., 1994; Alberti

et al., 1996). Nowadays the one-step hydrothermal reaction between reactive metal salts or organometallic precursors and complexing polyfunctional organic molecules with or without the use of a template to form a coordination polymer network is yielding an ever expanding array of new and exciting compounds (Kitagawa and Matsuda, 2007). If these coordination polymers consist of crystalline open frameworks then they are known as metal organic frameworks (MOFs). Like mesoporous metal oxides generated through supramolecular self-assembly, MOFs can have enormous surface areas. Their utility for the adsorption and separation of gases is being studied intensively and impressive capacities and selectivities for different gases have been demonstrated. Particularly relevant to the present work are materials prepared through the coupling of organo polyphosphonates with Zr^{4+} since many extractants in both liquid–liquid and solid-phase extraction are known to be particularly effective at complexing lanthanides and actinides and since zirconium salts are generally quite insoluble in highly acidic and alkaline solutions.

The general objectives of the present program of research are to develop high capacity, novel coordination polymer adsorbent materials via simple template- or porogen-free methods with the potential to selectively separate actinides and minor actinides from complex solutions containing fission products, including radio lanthanides. In particular, the focus of this communication is on materials with high selectivity for the actinide thorium in the presence of lanthanides and high stability in corrosive solutions. Although many previous studies have addressed the separation of thorium by different adsorbents, most of these have employed simple solutions with near neutral pH, in many cases, containing few if any competing ions (Chen et al., 2007a).

In a previous related study with similar objectives (Velisek-Carolan et al., 2014) we focused on coordination polymers prepared through the coupling of Zr(IV) to the trisphosphonic acid amino trimethylene phosphonate (ATMP) under hydrothermal conditions. The present study addresses the preparation of novel coordination polymer networks from zirconium(IV) and 1-hydroxy-2-(1H-imidazol-1-yl)ethane-1,1-diyl bisphosphonic acid (zoledronic acid). Being one of a family of bisphosphonic acids that is used for the treatment of osteoporosis, zoledronic acid is commercially available. This acid could potentially coordinate to the zirconium(IV) via either one or both of the phosphonate groups and/or the nitrogen donor atoms on the imidazole group forming a coordination polymer network or MOF. Alternatively the predominant coordination to Zr(IV) could be via the phosphonate groups leaving the imidazole function free to bind cations from aqueous solution. The adsorption properties of the materials have been assessed here by using mixed cation solutions containing Th^{4+} as a representative of the major actinide series, rare earths and other major fission product elements expected to be present during separations at the back-end of the nuclear fuel cycle and in mineral processing. Despite the involvement of complex equilibria in multi-element solutions the study has concentrated on such solutions since they are more relevant to expected applications for the materials.

Since the materials of interest here are zirconium phosphonates another objective of this work is to determine if the actinide loaded phosphonate can be converted to a durable ceramic phase.

2. Experimental

Zirconium(IV)-zoledronate coordination polymer samples were prepared by dissolving zoledronic acid (Gador S.A., Argentina) in water and adding sufficient 8.0 M NaOH to achieve dissolution of the acid. Zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) was then dissolved in this solution and the transparent homogenous solution was then reacted for 48 h in a PTFE-lined autoclave at 160 °C. Materials were prepared with P/(P + Zr) mole fractions of 0.8, 0.7 and 0.6. The products are designated zirconium(IV)-zoledronate, $ZrZ-x$, where x is the mole fraction of phosphorus in the precursor solution.

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