



A sequential extraction procedure to evaluate the mobilization behavior of rare earth elements in soils and tailings materials



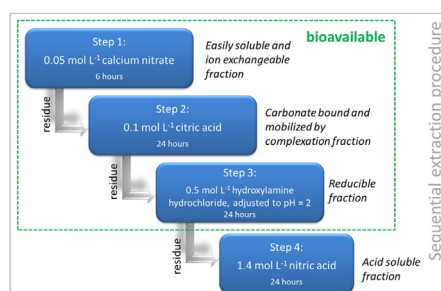
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HIGHLIGHTS

- Novel sequential extraction method for rare earth elements is presented.
- Detailed differentiation of bioavailable REE fractions is enabled.
- Better results for REE's are yield than by the common BCR procedure.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel sequential extraction method for evaluation of the mobilization behavior of rare earth elements in soils and mine tailings materials is presented. The sequence consists of the following four steps: 0.05 mol L⁻¹ calcium nitrate (easily soluble and ion exchangeable fraction), 0.1 mol L⁻¹ citric acid (fraction mobilized by complexation and carbonate bound), 0.05 mol L⁻¹ hydroxylamine hydrochloride (pH = 2) (reducible fraction), 1.4 mol L⁻¹ nitric acid (acid soluble fraction). The procedure was optimized with a certified soil material and a mine tailings material and was applied to eight samples of a soil profile. The different results obtained by using either the developed method or the widespread used BCR-Method for comparison are discussed. There were clear advantages using the newly created sequential extraction procedure in getting more detailed information about the bioavailable fraction and a fraction addressing REE phosphates.

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1. Introduction

Rare earth elements (REE) are mainly used for high-tech applications, e.g. light emitting devices, optical glasses and lenses, high performance magnets (Nd₂Fe₁₄B), catalysts and medical

applications like MRI contrast agents (Natrajan and Langford Paden, 2013). The discharge of gadolinium (Gd) into the environment is estimated to be more than 1000 kg per year in Germany (Kümmerer and Helmers, 2000). As a consequence, elevated concentrations of Gd are observed in sewage and surface water all over the world (Kulaksız and Bau, 2011) and might be a source of soil contamination. Furthermore, contamination by cerium (Ce) is reported from broken automotive catalytic converters (Helmers,

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1996). Low levels of the REE are able to stimulate organisms as a short-term effect, but higher levels result in toxicity symptoms, due to their similarity to calcium (Hirano and Suzuki, 1996). Stimulation of vegetable and animal organisms is the main reason for usage of REE as fertilizer or food supplements in animal production, respectively (Xu et al., 2002; Miller, 2006). Recent findings contradict stimulation of plants by REE (Saatz et al., 2015), but large amounts of REE were applied in China into the environment (Tyler, 2004). Chronic effects of long-term exposure with REE are hard to estimate and still lacking research. Other anthropogenic sources for REE input into the environment could be mining activities, especially dumped tailings materials from mines where REE occur but are not in the focus of the activity.

Sequential extraction methods are used to estimate the mobilization behavior of interesting elements from soils, sludge and sediments simulating different leaching conditions. Especially the mobilization behavior of heavy metals is in the focus to assess the risk potential of contaminated media. Hardly mobile or inertly bound elements pose a lower risk compared to easily soluble fractions. In sequential extraction methods the sample is successively suspended in extraction solutions of increasing strength and the mobilized amount of analytes is quantified. The assignment to different chemical surroundings and species is thereby operationally defined (Gleyzes et al., 2002; Hass and Fine, 2010).

Only a few studies have dealt with the mobilization behavior of REE from soils and sediments. Most studies adopt methods for REE which were developed for heavy metals, mainly the BCR method (Li et al., 1998; Rauret et al., 1999; Wang et al., 2003; Rao et al., 2010; Mihajlovic et al., 2014) and the sequence proposed by Tessier et al. (1979) (Zhang et al., 1998; Xinde et al., 2000; Wang et al., 2009; Šmuc et al., 2012; Xu et al., 2012). Sanematsu et al. (2011) developed a method especially for REE in rock minerals, focussing on differences in the binding to mineral phases.

Regarding tailings materials and soils, there are natural processes for REE mobilization; firstly, rain water or pore water will make REE mobile by dissolution of REE-bearing minerals or ion exchange. Secondly, plants will make REE bioavailable by root exudation of low molecular organic acids (Ryan et al., 2001). Dividing the first step of the BCR-Sequence into the fractions easily soluble and ion exchangeable and a fraction mobilized by complexation and carbonate bound will allow determining these separately. A third important process is the mobilization under reducing conditions by changing either the oxidation state of the element or the host mineral elements (like iron ore manganese hydroxides), which will promote mobility. This process can be caused by weathering as well as microbial and root activities (Marschner, 1995). Typical REE-bearing minerals are the phosphates. These minerals have a very low solubility, and mobilization will only occur under strong acidic conditions. (Oelkers and Poitrasson, 2002; Cetiner et al., 2005) Under acidic mine drainage large quantities of REE might be mobilized (Nordstrom, 2011). These amounts of REE will therefore not be available for plants under usual environmental conditions, but may be important regarding acid mine drainage and other strong acidic conditions.

The aim of this study was to develop a sequential extraction procedure directed to the mobilization of REE from tailing materials and soils which allows prediction of their environmental behavior with special emphasis on the bioavailability.

2. Materials and methods

2.1. Chemicals and apparatus

The following chemicals were used to prepare the leaching solution in p.a. or higher purity: 0.05 mol L⁻¹ calcium nitrate

(Ca(NO₃)₂ · 4H₂O; MERCK), 1 mol L⁻¹ ammonium acetate (MERCK), 1 mol L⁻¹ acetic acid (Th. Geyer), 0.05 mol L⁻¹ EDTA (Na₂EDTA · 2H₂O; MERCK), 0.1 mol L⁻¹ malic acid (Th. Geyer), 0.1 mol L⁻¹ citric acid (MERCK), 0.1 mol L⁻¹ oxalic acid pH = 3 ((NH₄)₂oxalate, MERCK), 0.05 mol L⁻¹ hydroxylamine hydrochloride, pH = 2 (MERCK) and nitric acid in concentrations of 0.1 and 1 mol L⁻¹ (1 M FIXANAL, FLUKA) and 1.4 mol L⁻¹ (diluted by a factor of 10 from 65%, MERCK). The pH value of the extraction solutions was adjusted as named before with nitric acid.

All extraction solutions were freshly prepared using de-ionized water (Milli-Q, Millipore).

All laboratory-ware were soaked overnight in 4% nitric acid, rinsed repeatedly with distilled water and dried before being used. Extractions were performed using a horizontal shaker (HS-250 basic, IKA Labor Technik; Germany) at 90 rpm and at room temperature. Centrifugation was carried out at 4000 rpm for 10 min (Rotana 460, Hettich Zentrifugen; Germany). Samples were stored prior to analysis in a fridge at 4 °C or they were measured immediately.

2.2. Sample materials

The certified reference material SRM 2710 (National Institute of Standards and Technology; USA) was chosen as soil sample for the optimization of the procedure. Additionally a tailings material with elevated REE concentrations was tested.

Several soil samples were collected from a weathering profile in 2012 from a lead contaminated forest soil at Teutoburger Wald; Germany (Lorz et al., 2010). The profile reached from +10 cm to -70 cm and could be divided into the horizons Oh₁, Oh₂, Aeh, Ahc, Bh, Bs and Cv. Soils at the investigation site are extremely poor, shallow podzols. The organic layers are raw humus. The sample materials from every horizon were dried and milled (Retsch MM 200, with zircon oxide materials) before usage.

2.3. Microwave assisted aqua-regia digestion

An aliquot of the dried and ground samples of 250 mg were weighed into the digestion vessels and 4.5 mL fuming hydrochloric acid (MERCK) and 1.5 mL concentrated nitric acid (MERCK) was added. The microwave digestion device (Multiwave, Anton Paar; Austria) was used to enhance the yield of digestion. The following program was used: 0–8 min from 500 to 800 W, 8–11 min from 800 to 1000 W and finally for another 20 min at 1000 W. After cooling down to room temperature the volume was adjusted to 50 mL using deionized water. The made-up solution was centrifuged to separate remaining particles from the supernatant, which was used for analysis without further treatment.

2.4. Single batch extractions

Single batch extractions were performed with the sample materials SRM 2710 and the tailings material using a sample-to-solvent-ratio (SSR) of 1:200 and the solutions listed in chapter 2.1. To 50 mg of sample material, 10 mL of extraction solution was added and shaken for 24 h at room temperature. Samples were centrifuged before the supernatant was analysed by ICP-MS. Before and after extraction, the pH-value was controlled using a pH-Electrode (pH-Meter pH 539 equipped with Sentix Mic[®]-Electrode, WTW; Germany). In case suspended particles were visible, the extractant was filtered using 45 µm syringe filters from regenerated celluloses (Minisart RC 15, Sartorius; Germany). All extractions were performed as triplicates.

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