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Enhancing radium solubilization in soils by citrate, EDTA, and EDDS chelating amendments

C. Prieto [a], J.C. Lozano [a], P. Blanco Rodríguez [b], F. Vera Tomé [b,*]

[a] Departamento de Física Fundamental, Universidad de Salamanca, 37008 Salamanca, Spain
[b] Natural Radioactivity Group, Universidad de Extremadura, Avda. Elvas s/n, 06071 Badajoz, Spain

HIGHLIGHTS

- The aim was to optimize radium solubilization for the purposes of remediation.
- The most important factor in radium solubilization was found to be the pH.
- Radium release increases with the reagent concentration.
- The largest release of radium is obtained with 50 mmol kg^{-1} of citrate, at pH acid, and 4 days after incubation.
- The best conditions for the release of radium are the same as for uranium.

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ABSTRACT

The effect of three chelating agents (citrate, EDTA, and EDDS) on the solubilization of radium from a granitic soil was studied systematically, considering different soil pH values, chelating agent concentrations, and leaching times. For all the chelating agents tested, the amount of radium leached proved to be strongly dependent on the pH of the substrate: only for acidic conditions did the amount of radium released increase significantly relative to the controls. Under the best conditions, the radium released from the amended soil was greater by factors of 20 in the case of citrate, 18 for EDTA, and 14 for EDDS. The greatest improvement in the release of radium was obtained for the citrate amendment at the highest concentration tested (50 mmol kg^{-1}). A slightly lower amount of radium was leached with EDTA at 5 mmol kg^{-1} soil, but the solubilization over time was very different from that observed with citrate or EDDS. With EDTA, a maximum in radium leaching was reached on the first day after amendment, while with citrate, the maximum was attained on the fourth day. With EDDS, radium leaching increased slightly but steadily with time (until the sixth day), but the net effect for the period tested was the lowest of the three reagents.

1. Introduction

The use of plants to remediate contaminated soils (phytoremediation) has attracted considerable attention over the past 20 years. These techniques have been applied to a broad range of contaminants, both organic and inorganic, including metals and radionuclides, although with varying results. For success in phytoremediation, it is necessary that contaminants be available for their absorption by roots, and such bioavailability depends on the solubility of the pollutants in the soil solution. In order to improve the phytoextraction yield, many workers have investigated the addition to the soil of chelating agents that enhance metal uptake by plants [1–7]. The formation of chelates prevents the precipitation and sorption of metals, thereby maintaining their availability for plant uptake [8]. However, the action of a complexing agent is metal- and soil-dependent. Any given chelating agent is not specific to one metal, but is subject to many interferences from other cations present in the soil at higher concentrations [3]. A well established conclusion is that chemical speciation is fundamental for the solubilization of metals in the soil, and consequently for their bioavailability [9,10].

Chelating agent-assisted phytoextraction has been widely applied not only to heavy metal phytoextraction, but also to enhancing the uptake of radionuclides (especially uranium) by plants. Ebbs et al. [11] and Huang et al. [12] studied the combined effect of chelating agents and acidification on the solubilization of uranium. Vandenhove et al. [13] tested the effect of citric acid in the phytoextraction of uranium. Shahandeh and Hossner [14] screened the addition of chelating agents and organic acids on uranium uptake. Duquène et al. [15] compared the efficiency of EDDS and other organic acids in uranium extraction.

* Corresponding author. Tel.: +34 924289524; fax: +34 924 289651.
E-mail address: fvt@unex.es (F.V. Tomé).

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^{226}Ra is a member of the ^{238}U radioactive chain, and hence both nuclides are present simultaneously in the soil. Owing to its chemical similarity to calcium, radium may be bioaccumulated by plants and animals and transferred to humans through the food chain. In spite of the volume of work devoted to studying the influence of chelating amendments on the leaching of uranium, to the best of our knowledge their influence on the release of ^{226}Ra from the bulk soil to the soil solution has yet to be determined. In a recent work [16], the authors carried out a systematic study to assess the influence of pH and organic amendments on the release of uranium in a granitic soil. That study forms part of a global work whose main goal is to determine the factors that influence the process of the release of radionuclides from a granitic soil to the soil solution, and their uptake and translocation in the plant. Following the same line of enquiry, the present work aims to ascertain the role of the same factors in the solubilization of radium. It is well known that pH plays a key role in chemical speciation, and hence in the bioavailability of metals in soils. The present work reports a study of the combined action of pH and chelating agents on the amount and rate of radium leached from a granitic soil. Three chelating agents were tested: citrate, EDTA (ethylenediaminetetraacetic acid), and EDDS ([S,S]-stereo-isomer of ethylenediaminedisuccinic acid). They were chosen not only because of their known potential for increasing the uptake of metals by plants, but also because of the degree of degradability of these chelating agents themselves and of their metal complexes. Citrate, which improves the uptake of uranium and radium by plants [17,18], appears to degrade within a few days to CO_2 and water [19]. The efficiency of EDTA in increasing metal uptake by plants has been widely documented [2,20], but its poor biodegradability limits its large-scale application [9,21,22]. In recent years, the effect of other more biodegradable chelating agents, such as EDDS, has been compared with that of EDTA. EDDS, a naturally occurring substance, has proved to be effective in enhancing the uptake of several metals, including uranium [3,6,15,16,21]. Grčman et al. [3] have reported a half-life of 2.5 days for EDDS. Despite its persistence, EDTA was also chosen to study because it is a referential chelating agent for comparative purposes, and it forms relatively stable compounds with Ra, an element which is not easily complexed owing to its basic character [23,24].

The same agents have been used by the authors to study the release of uranium from the soil [16]. This should make it possible to establish whether the conditions necessary to enhance the availability of ^{238}U are also adequate for ^{226}Ra, which are respectively associated as precursor and daughter in the 4n + 2 radioactive family.

2. Materials and methods

2.1. Soil characterization

A soil sample was collected from the "Los Ratones" mine, a disused mine located in the region of Extremadura in the south-west of Spain. Mining activities ceased in 1974, and restoration works were carried out in 1999. This mine area has been well characterized in previous studies [25]. The sampling point was selected attending to the high activity concentration of natural radionuclides, mainly from the ^{238}U series.

The soil sample was collected from the topmost layer (10 cm depth) with an EIJKELKAMP split-tube sampler. The sample was oven-dried at 80 °C to constant weight, and sieved to a particle size of 2 mm. It was then homogenized and quartered carefully in such a way that resulted in selecting representative aliquots from the original bulk soil sample [26].

Physical and chemical variables such as texture, field capacity, loss on ignition (LOI), moisture content, organic matter, available N and P, cation exchange capacity (CEC), and pH were determined. For the textural analyses, the sieved soil samples were classified using Robinson's pipette method into three categories: sand, silt, and clay. Table 1 lists the main chemical and physical characteristics of the samples.

Table 1
Soil sample properties.

Soil parameter	Values	Method [Reference]
Fraction < 2 mm	78.3%	Mechanical sieving
Texture		Robinson's pipette method [27]
Sand	71.9%	
Silt	19.85%	
Clay	8.25%	
Loss on ignition (LOI)	4.93%	At 550 °C [27]
Organic matter	3.47%	K-dichromate oxidation [28]
pH (1:1 water)	5.58	(1:1) soil–water [27]
Soil moisture	12.3%	At 105 °C [27]
CEC	1.4 cmol kg^{-1}	1 M ammonium acetate and ICP-OES [29]
Ca^{2+}	386 mg kg^{-1}	
Mg^{2+}	42 mg kg^{-1}	
K^{+}	104 mg kg^{-1}	
Available P	80.2 mg kg^{-1}	Bray II method [30]
Nitrogen	0.194%	Kjeldahl method [31]
Field capacity	27.5%	At 33 kPa [32]
^{226}Ra	(838 ± 37) Bq kg^{-1}	Radiochemical [33]
^{238}U	(3385 ± 108) Bq kg^{-1}	Radiochemical [16]
^{234}U	(3652 ± 78) Bq kg^{-1}	Radiochemical [16]

Previous studies of soils in this area [34] had revealed that ^{226}Ra was mainly associated with the most resistant phase of the soil (47–51%), while the more labile fractions [35] had the following percentages: 13–19% associated with the organic fraction; 22–28% with carbonates, and a slight association of 1–3% with oxides.

2.2. Soil pH titration and pH-preconditioning

A pH titration process was implemented to determine the acid–base buffer capacity of the soil, and the amounts of acid (HCl) or alkali (KOH) required to obtain predefined pH values.

20 g of dry and sieved soil was suspended in 40 mL of solution. This solution was prepared with 20 mL of 10 mM $CaCl_2$ mixed with variable volumes of 0.06 M KOH or 0.06 M HCl in order to achieve the final molarity. The final concentrations obtained were between 6 and 30 mmol kg^{-1} dry soil of HCl, and between 6 and 30 mmol kg^{-1} dry soil of KOH. Finally, de-ionized water was added to bring the volume up to 40 mL. The containers were covered with a double cap to avoid volume reduction due to evaporation. The bottles were shaken continuously during the test using a HEIDOLPH, Mod. Rotamax 120, orbital shaker. The whole system was maintained in the dark.

Daily pH measurements were made over a period of 7 days in order to observe the evolution of pH with time. The instruments used were a HANNA, Mod. HI1285-5, combined electrode and a HANNA, Mod. HI9811-5, pH-meter with automatic temperature compensation.

2.3. Leaching tests

The effects of three chelating agents (citrate, EDTA, and EDDS) on the solubilization of radium were tested. In each case, the influence of pH, the test time, and the initial concentration of reagent were considered using three different concentrations of each chelating agent acting on soils with 3 preconditioned pH values. After the addition of the complexing agent, samples were withdrawn for analyses at test times of 24, 48, 96, and 144 h. One group without