



# The effect of different extractants on lead desorption from a natural mineral



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## ABSTRACT

Natural minerals, such as quartz, clinoptilolite and calcite, are useful as sorbents for various applications, but their content of heavy metals ions is the most problematic obstacle to their application. Before their (re)use, the minerals must be purified. In this work, the subject was desorption of lead from a natural multi-component mineral sample consisting of a mixture of silicates (mainly quartz and clinoptilolite) and calcite formations. Besides deionized water, different extraction solutions were tested: NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, HCl, HNO<sub>3</sub>, EDTA, EDTA/HCl, EDTA/NaOAc–HOAc, HOAc, NaOAc and NaOAc–HOAc. Several parameters were varied in order to obtain the optimal conditions for the desorption process: the concentration of the extraction solution, the ratio of the mass of the sample and volume of the extractant, and the pH value of the suspension. The best purification effect in one desorption cycle was obtained when 0.1 M EDTA, at a pH value of 3.5 (0.2 M EDTA was mixed with 0.01 M acetic buffer, at pH value 3.0, in ratio 1:1) was applied. Sequential extraction (5 consecutive iterations) was performed to provide a more efficient purification process. The lead content (58.20 mg/kg) was decreased by: 20% (using HOAc), 21% (using EDTA) and by more than 50% (using EDTA/NaOAc–HOAc). The pH value and conductivity were measured at all critical points to clarify the mechanism of the desorption process. The formation of Pb–EDTA complex is the result of two parallel phenomena, complexing and ion–exchange. An enhanced adsorption capacity and an improved microelement profile for the purified samples were also attained. The mineralogical and radiochemical performances of the sample were determined by the X-ray diffraction and gamma spectrometry techniques. Microelement analyses of the native and purified samples were performed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

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## 1. Introduction

Minerals are naturally occurring substances, distinguished by various physical and chemical properties. These properties are influenced by the geological environment during the formation of the mineral [1]. The main feature of these covalently bound materials is their ability to adsorb pollutants, especially heavy metals [2]. Silicates are the most abundant class of natural minerals, presented by 84 mass% in the Earth's crust. They are classified into different subgroups by the degree of polymerization of the silica tetrahedral, [SiO<sub>4</sub>]<sup>4-</sup>, base unit [3]. Aluminosilicates or 'framework silicates' consist of three-dimensional networks (lattice) of tetrahedra. This

offers a large internal and external surface area for adsorption and ion–exchange processes. They possess some net negative structural charges due to the isomorphous substitution of cations in the mineral lattice [4]. Quartz is the only group of the silica family that is chemically in the form of oxides. It is made up of a continuous framework of silicon–oxygen tetrahedra, in which each oxygen atom is shared between two tetrahedra, giving an overall formula SiO<sub>2</sub>. The use of quartz as a natural sorbent is dominant for different heavy metal uptakes [5]. Calcites present a large class of natural minerals and are the main constituent of rocks (petrogenic minerals). The ubiquity and reactivity of calcite in natural systems and the high affinity of Pb for a calcite sorbent is essential for the prediction of the mobility of this metal and, thus, its potential bioavailability [6].

Faced with more and more stringent regulations, nowadays heavy metals are deemed pollutants of concern, POCs [7]. Among all heavy metals, lead is important due to its high toxicity and influence

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on human health, even at extremely low concentrations (15 ppb in drinking water) [8]. Thus, this heavy metal should be removed from the water and soil basin to the level of the effluent regulations of the EPA (EPA 833-B87-202, December 1987). Dissolved lead is well attracted onto aluminosilicates and clays, better than other heavy metals [9–11]. The enhanced mobility of  $\text{Pb}^{2+}$ -ion through the crystalline structure is due to its smaller hydrated ion radius compared to  $\text{Al}^{3+}$ -,  $\text{Fe}^{3+}$ -,  $\text{Cr}^{3+}$ -,  $\text{Ni}^{2+}$ -,  $\text{Cu}^{2+}$ -,  $\text{Zn}^{2+}$ -,  $\text{Co}^{2+}$ -,  $\text{Fe}^{2+}$ -,  $\text{Cd}^{2+}$ - and  $\text{Sr}^{2+}$ -ions [3]. Despite significant adsorption, the reverse process, *i.e.*, the release of lead is 20 to 50 times inferior [12,13]. In many separation studies, desorption is mentioned in terms of leaching or regeneration tests, but only briefly. A profound understanding and a more detailed interpretation of the application of desorption is crucial for the development of new analytical procedures. Some of desorption approaches, such as acid washing with HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  have been developed and adopted as standard methods for the pretreatment of zeolites and clays [10,14] (in order to remove surface dust and impurities) or as an activation process (to increase the specific surface area) [15–17]. Recently, different chemical reagents (NaCl, KCl, HCl,  $\text{NaNO}_3$ ,  $\text{NaCO}_3$ , and NaOH) were applied for heavy metal extraction from natural minerals [14,18–21]. The purification and regeneration processes enable multiple use of the same material. Another application of desorption is related to the modification of surface of a mineral. The use of anionic surfactants conditioned by adsorption–desorption processes results in a net change in the surface charge and enhanced removal of cationic pollutants [22].

Not much data exist in the literature related to lead desorption from natural sorbents [21,23,24]. The aim of this study was to investigate the optimal purification solution for lead extraction from a mixture of mineral components. The topic was focused on a naturally occurring sample because of its prevalence in soil and sediment may control its ion exchange and surface properties, and in particular to its application in environmental remediation technologies. Furthermore, the objective was to enlighten the possible mechanisms and optimal conditions of the reactions. Conductivity and pH value measurements of the suspensions were examined under a variety of desorption processes. The applied purification treatments showed two remarkable benefits: a decrease in the content of heavy metal(s) in the native material (expressed in mg/kg) and an enhanced sorption capacity (expressed in mg/g). These improvements of natural minerals open more possibilities for their use as low cost and widely available natural sorbent materials.

## 2. Materials and methods

### 2.1. Material preparation and characterization

A natural raw mineral sample, originating from Central Bosnia and Hercegovina in South Eastern Europe (the Balkan area) was the subject of the investigation. The light grey, sandy and partially gritty sample with particle sizes in the range of 0.5–2 mm could be described as a heterogeneous material. Before the use, the sample was washed by deionized water, dried 2 h at 105 °C and placed in desiccators before further analytical procedure. The dry sample was homogenized using pestle and mortar. The aim was to subject the material to minimal processing considering possible future practical applications.

The sample was characterized by X-ray diffraction (XRD) and element chemical analyses. Radiochemical analysis of the mineral sample was performed because of the vicinity of the territorial source to coal deposits, known to be enriched with radionuclide components.

The X-ray diffraction method was used for qualitative mineralogical analysis, employing an ENRAF NONIUS FR590 XRD (Bruker AXS, MA, USA) diffractometer with  $\text{Cu K}\alpha$  1,2 radiation and a

step/time scan mode of 0.05°/1 s. The XRD pattern of the natural mineral sample was compared with the diffraction powder file (PDF2) for silicate (reference pattern: 70–1859, 72–1386, 78–1254, 82–1572, 80–2157), and calcite (89–1305).

Element chemical analysis was performed to determinate the micro (expressed in mg/kg) and macro (expressed in %) contents of elements in the natural mineral. The samples were dissolved by the acid digestion method using MW CEM MARS 5 system A solid sample (0.5 g) was digested using a mixture of 6.0 mL  $\text{HNO}_3$ , 4.0 mL HCl and 2.0 mL HF (Sigma–Aldrich, St. Louis, MO, USA). Microwave heating was applied a 15-min ramping time to a pressure of above 250 psi and 15-min hold time. After digestion, the liquor media (mixture of the used acids and leached metals) were decanted from the remaining solid sample into centrifuge vessels. Phase removal was performed by centrifugation (IEC Centra CI3, Thermo Scientific) at 1200 rpm for 5 min and the concentrations of the metal ions in the supernatant were determined by inductively coupled plasma optical emission spectroscopy analysis, ICP-OES.

The radioactivity measurements were performed using an ORTEC-AMETEK (PA, USA) HPGe gamma-ray spectrometer (49% relative efficiency and 1.85 KeV FWHM for  $^{60}\text{Co}$  at 1.33 MeV, 8192 channels) shielded with 10 cm lead internally lined with 2 mm copper foil. The activity of each sample was measured for 60,000 s. The activity of  $^{226}\text{Ra}$  was evaluated from the 609.3 keV gamma ray peak of  $^{214}\text{Bi}$  and the 351.9 keV peak of  $^{214}\text{Pb}$ , while the 911.2 and 969.1 keV gamma-ray lines emitted by  $^{228}\text{Ac}$  and the 238.6 keV peak emitted by  $^{212}\text{Pb}$  were used to determine the activity of  $^{232}\text{Th}$ . The activity of  $^{40}\text{K}$  was determined using its 1460.8 keV gamma-ray line. Gamma Vision 32 was used to process the obtained spectra.

### 2.2. Desorption experiments

#### 2.2.1. Reagents

Various chemical reagents, in different concentrations, were tested for lead extraction from the natural mineral sample. Selected desorption solutions were: (i) deionized water; (ii) inorganic chemicals: sodium, potassium, calcium and magnesium chloride salts – NaCl, KCl,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , hydrochloric acid, HCl and nitric acid,  $\text{HNO}_3$ ; (iii) organic reagents: ethylenediaminetetraacetic acid disodium salt (EDTA) or complexone III, acetic acid, HOAc, acetic buffer, NaOAc–HOAc and sodium acetate, NaOAc. Chemicals of analytical grade NaCl, KCl,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  were supplied by Merck (Darmstadt, Germany) and  $\text{HNO}_3$  and HCl from Sigma–Aldrich (St. Louis, MO, USA). The others EDTA, NaOAc and HOAc were supplied by Zorka (Šabac, Serbia). Ultra-pure water (resistivity less than  $18 \text{ M}\Omega \text{ cm}^{-1}$ ) obtained from a Millipore Milli-Q system was used throughout the experimental work.

#### 2.2.2. Extraction procedure

Desorption studies were performed by batch technique and all experiments were carried out in 100 mL glass flasks. Prior to use, samples were washed with deionized water to remove surface dust and dried for 24 h at 80 °C. The raw silicates sample (2.5 g) was weighed to a four-digit accuracy (Radwag model mza5.3y, Radom, Poland) and placed in a flask with the desorption solution. The solid mass and solution volume were varied in the ratios 1:10 and 1:20. The desorption process was stimulated by magnetic stirring at 170–200 rpm (MTS basicC, Ika, Chelmsford, UK) at room temperature ( $22 \pm 1$  °C) for 2 h. The solution and solid sample were separated through a standard filter designed for a wide range of laboratory applications (MF-Millipore membrane filter, mixed cellulose ester, 0.45  $\mu\text{m}$ ). The filtrate deposits were dried at 105 °C for 2 h. The concentration of  $\text{Pb}^{2+}$ -ions in the supernatant was further subjected to spectroscopic analysis. Concentration of extracted lead was measured in both: (a) the dried filtration deposits (after the acid digestion procedure) and (b) in the filtrates, to provide a

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