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Aging effects on the mobility of Pb in soil: Influence on the energy requirements in electroremediation

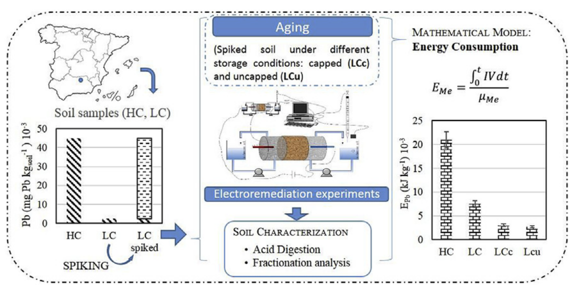
Maria Villen-Guzman*, Ana Garcia-Rubio, Juan M. Paz-Garcia, Carlos Vereda-Alonso, Cesar Gomez-Lahoz, Jose M. Rodriguez-Maroto

Chemical Engineering Department, Faculty of Sciences, University of Malaga, 29071 Malaga, Spain

HIGHLIGHTS

- Aging of spiked soil is compared with real contaminated soil.
- No aging effects on Pb mobility in spiked soil has been observed after 5 years.
- The behavior of Pb from spiked and real soils under electric field is analyzed.
- Soil mineralogy and other environmental factors should be considered in EKR studies.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper studies the possible differences in the behavior of lead as a contaminant in soil samples when it is present as "naturally-aged" for decades after the contamination, and when it has been spiked in the laboratory. This behavior differences are stablished mainly in two ways: as changes in the fractionation analysis obtained after a sequential extraction procedure (SEP) and as changes in the efficiency of the acid-enhanced electroremediation (EKR) technique. Additionally, aging effects have been studied for almost five years. In the case of the lead-spiked soil the influence of storage conditions on contaminant behavior have also been explored: 1) samples stored in capped containers at constant moisture conditions, and 2) samples in containers open to the atmosphere, with periods of water flooding and drying.

Lab-spiked and the "naturally-aged" contaminants show very different behavior with respect not only to SEP analysis but also to EKR experiments. The soil spiked with a soluble lead salt presents a higher percent in the more mobile fractions. Regarding storage conditions, some changes were observed in the lead distribution along the vertical soil profile for samples stored in uncapped containers. The EKR results were also in agreement with those from fractionation analysis. Energy requirements for the remediation were estimated by a mathematical model with important differences obtained for the different soil samples. Results are indicating that it will be very unreliable to draw estimations for the "naturally-aged" soils from contaminant-spiked samples.

1. Introduction

Electrokinetic Remediation (EKR) is probably the only *in-situ* technology to recover polluted soils with low permeability (Acar

* Corresponding author.
E-mail address: mvillen@uma.es (M. Villen-Guzman).

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et al., 1995). The electric field applied between electrodes inserted in the porous media mobilizes contaminants such as heavy metals or organic compounds by means of diffusion, electromigration, electroosmosis and electrophoresis (Acar et al., 1993; Alshawabkeh, 2009). The main goal of the early laboratory research on EKR was studying the fundamentals of the technique (Hamed et al., 1991; Acar et al., 1992; Acar and Alshawabkeh, 1996; Coletta et al., 1997). Many of these works were carried out using spiked kaolinite, as a first step toward the development of EKR technique for real soils. Today, still many papers in this field are using spiked model soils as kaolinite which presents a very limited variety of sorption sites for heavy metals. This, among other shortcomings, makes it difficult to extrapolate the results obtained in this kind of study to real soils (Ottosen et al., 2006).

The use of a wide variety of soil types in EKR studies demonstrates that soil and contaminant characteristics have an important influence on the effectiveness of the treatment (Gomes et al., 2015). The use of spiked real soils have been widely accepted in these studies (Yang and Lin, 1998; Reddy and Chinthamreddy, 2004; Zhou et al., 2004; Boulakradeche et al., 2015). Nevertheless, in early studies Reddy et al. (1997) found that effects of the mineralogical composition of soils together with the presence of natural substances should be considered to successfully use of the EKR technique in actual field applications. Concerning this kind of soils, Smolders et al. (2015) concluded that the behavior of toxic trace metals in field is not simulated by the toxic traces metals in soil freshly spiked with soluble metal salts.

The study of time-dependence of the soil pollutants, typically denoted as “aging”, has been widely carried out as an important part of works using soil spiked with soluble metal salts. Some papers highlight the importance of the aging effects on the fractionation of heavy metal (Alexander, 2000). The increased retention of heavy metals with time is known as fixation. This process takes place by different mechanisms such as the slow diffusion of metals into Fe-oxides and by precipitation in carbonates and other stable components (Jalali and Khanlari, 2008). It has been reported that heavy metals tend to incorporate from more mobile fractions into more stable fractions (Ottosen et al., 2006; Jalali and Khanlari, 2008; Lu et al., 2009; Wang et al., 2015). Fajardo et al. (2015) concluded that the removal of Cd and Pb was not affected by soil age, whereas removal of Cu, Ni and Zn was higher in soils that had been aged for a shorter time. Hansen et al. (2013) performed studies with mine tailings of similar composition but different age. They concluded that age has a direct influence on the EKR performance.

In order to assess the heavy metals mobility, fractionation by means of sequential extraction procedures (SEP) are widely used. Therefore, this kind of fractionation should provide a good tool to establish the changes produced by aging. Tessier et al. (1979) presented the first influential SEP. It was applied to freshwater sediments and used as a tool for the assessment of potential bioavailability, risk, and remobilization. Currently, the procedure proposed by Standards, Measurements and Testing Program of the European Union (SM&T, formerly known as BCR), is the most used. This sequential extraction scheme classifies the total metal content into three fractions: acid soluble, reducible and oxidizable (Mester et al., 1998; Rauret et al., 1999, 2000). However, it is accepted that the SEPs present certain limitations. For example: for soils rich in carbonates, the incomplete dissolution of carbonates during the first step of fractionation analysis entails the overestimation of the next steps (Bacon and Davidson, 2008). Some studies suggest repeating the extraction steps before progressing to the next one, together with a careful monitoring of the pH to enhance the dissolution efficiency (Sulkowski and Hirner, 2006; Subirés-Muñoz et al., 2011; Villen-Guzman et al., 2015a).

In this work, the aging effects together with the influence of storage conditions on fractionation of lead in a spiked real soil and in a real contaminated soil during five years has been explored. With the aim of obtaining a better understanding of the contaminant behavior, EKR experiments have been performed. The results help to understand the reliability of the extrapolation of conclusions obtained from spiked soils to naturally-contaminated soils.

2. Materials and methods

2.1. Initial soil characterization

The soil samples used for this study were collected from the mining district of Linares (Andalusia, Spain) where galena has been mined for centuries. The samples were taken from two different zones, one of them with a very high lead concentration (labelled HC) and the other one with a lower lead concentration (LC) (Martínez López et al., 2008). The main properties of the soil (Table 1) were stablished using the following normalized methods: particle size distribution (ASTM-D 422), dry soil density (ASTM-D 854), hydraulic conductivity (EPA 9100), organic matter (ASTM-D 2974), pH (ASTM-D 4972), humidity (ASTM-D 2216), carbonate content (ISO 10693) and Pb concentration (EPA 3051A). The cation exchange capacity (CEC) was obtained using the barium method at pH 8.2 buffered by triethanolamine (Pansu and Gautheyrou, 2007).

According to the International Soil Science Classification (Prescott et al., 1934), the particle size distribution corresponds to a clay-loam soil for the HC soil, and to a sand-loam soil for the LC soil. Other main characteristics of these soils are a low organic matter content, a medium cation exchange capacity (CEC), a large carbonate content, and a very low hydraulic conductivity (Freeze and Cherry, 1979).

2.2. Spiking and aging procedure

In order to study the aging effects on the fractionation of Pb in a spiked real soil, the soil with the lower Pb concentration, LC, was spiked with an aqueous solution of $Pb(NO_3)_2$ to obtain a soil with a total concentration of Pb $\approx 41\,000$ mg kg_{soil}^{-1}, the same order of magnitude as the HC soil.

The spiked LC samples were placed in different containers and aging was studied using two different storage conditions: some soil containers were capped (LCc) and others uncapped (LCu). In order to approach the natural conditions, several episodes of flooding/drying were simulated by watering the LCu samples and then letting then dry at lab conditions. To study the possible influence of the CO_2 contact on the soil and other possible effects, the LCu samples were divided into three vertical sections, labelled from top to bottom LCu-a, LCu-b and LCu-c.

Regarding the total concentration of metals, it should be highlighted the very high Pb concentration in the HC soil. On the other hand, although the lead concentration is lower in LC soil, this value is well above the reference range value (275 mg kg_{soil}^{-1}) for the urban and rural land in Andalusia (BOJA, 2005).

2.3. Sequential extraction procedure (SEP)

A three-step protocol, as proposed by Standards, Measurements and Testing programme (SM&T) of the European Union, was applied for the fractionation of Pb in soil samples. This procedure uses three sequential steps to obtain different fractions of each metal present in the soil. First, the soil sample was treated with acetic acid to release the exchangeable and the acid-extractable metals known as the weak acid soluble fraction, labelled in this paper as WAS. Then, the remaining solid phase was separated by centrifugation and a solution of hydroxylamine hydrochloride was