Research Paper

Microscopic evidence for humic acid induced changes in lead immobilization by phosphate in a counterdiffusion system

Mei Wang [a,b], Zhuo Zhang [a,b], Jie Ren [a,b], Chao Zhang [b], Chunping Li [c], Guanlin Guo [b,*], Fasheng Li [a,b,**]

[a] College of Water Sciences, Beijing Normal University, Beijing 100875, China
[b] Department of Soil Pollution Control, State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[c] State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing Building Materirals Academy of Science Research, Beijing 100041, China

HIGHLIGHTS

- Effect of humic acid on lead immobilization was investigated.
- Fragmentation of Pb immobilization was induced by humic acid.
- Entrapped humic acid has influence on crystal growth of lead phosphates.
- Intuitive understanding of HA effect on lead immobilization was achieved.

GRAPHICAL ABSTRACT
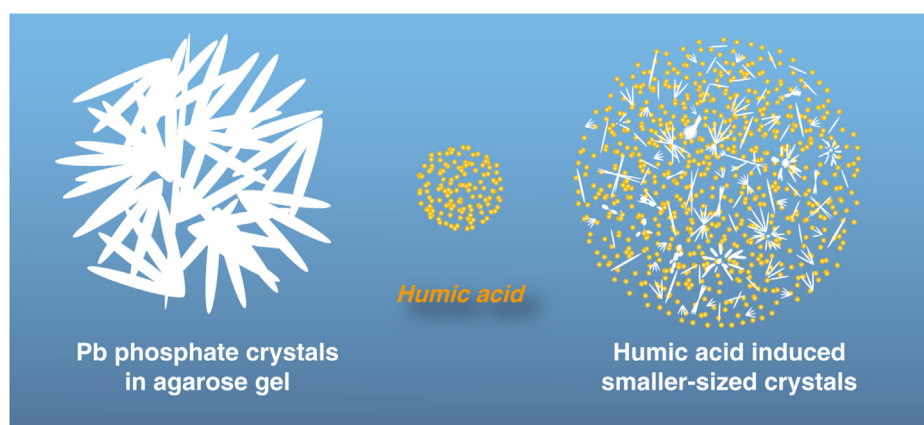
ARTICLE INFO

ABSTRACT

Abatement of lead (Pb) contamination in soil via chemical immobilization can reduce potential risks but is influenced by soil organic matter. The aim of this study was to observe and understand the influence of organic matter on Pb immobilization by phosphate. For this purpose, humic acid (HA) was introduced into a counterdiffusion system to mimic ionic reactions of the mineralization processes between the pollutant (Pb) and amendment agent (phosphate) in soil system, and were characterized jointly by in situ optical microscopy and ex situ XRD, SEM, TEM, and LSCM. The results indicate that lead immobilization in the counterdiffusion system involves a time-dependent crystallization process and that supersaturation occurs at nearly central region of the reaction zone. Entrapped HA had influence on crystal growth and size, causing more fragmented crystal morphology with increasing HA content, which can be explained by HA wrapping of the nucleation products and subsequent inhibition of reactions and crystal growth, as indicated by TEM and LSCM images. Mineral conversion from secondary lead orthophosphates to pyromorphite implies the promotion of more stable minerals. This approach provides evidence for a more intuitive understanding of the effects of HA on the immobilization of lead by phosphates.

© 2017 Elsevier B.V. All rights reserved.

* Corresponding author.
** Corresponding author at: College of Water Sciences, Beijing Normal University, Beijing 100875, China.
E-mail addresses: guogl@craes.org.cn (G. Guo), ligiulax@vip.sina.com, lifs@craes.org.cn (F. Li).

1. Introduction

Lead (Pb) arising from mining, smelting, and acid battery industrial processes is one of the hazardous pollutants in soils [1,2]. Lead species in soils include the minerals cerussite ($PbCO_3$), anglesite ($PbSO_4$), and crocoite ($PbCrO_4$); various lead oxides including litharge (PbO); Pb(II) adsorbed on calcite in calcareous soils; Fe/Mn oxides in noncalcareous soils; and complexes of lead oxide and soil organic matter (SOM), especially in clay soils [3,4]. Among these species, lead oxides, sulfates, and carbonates are all soluble under acidic and neutral conditions. In general, lead originally occurs in the form of PbO, and can be transformed into $PbCO_3$ under the influence of strong microbial activity in SOM with high CO_2 levels.

Phosphate immobilization has been considered one of the most cost-effective remediation technologies for lead-contaminated soils [5–7]. This remediation process involves an artificially enhanced mineralization process to promote the formation of relatively stable lead phosphate minerals such as the pyromorphite (PY; $Pb_5(PO_4)_3X$, where X is OH−, F−, or Cl−) group of lead phosphate minerals, which are much less soluble and are geochemically stable over a wide pH range. The solubility of lead phosphates was three orders of magnitude lower [8], and deemed to secure long-term stabilization in soils. Although Pb immobilization by phosphates has been extensively studied, there has been much less focus on the effect of real soil conditions. The effectiveness of lead remediation by phosphates in soils is not always satisfactory because of incomplete contact between the amendment agent and the contaminant, as well as the influence of environmental factors such as SOM and microorganisms [9]. X-ray Absorption Fine Structure (XAFS) confirmed that ~70% of soil Pb was not stabilized to pyromorphite, even if more phosphate was added, and proved that SOM-bound Pb is the persistent form in soils [9]. SOM plays important roles in Pb chemistry and transport [10]. Negatively charged dissolved organic matter (DOM), as the most active SOM, can chelate heavy metals and inactivate Pb, especially in clay particles [3], which would influence the chemical reaction between Pb and phosphates. Xiong et al. studied complexation mechanisms and the effects of SOM on lead, and found significant complexation of dissolved Pb with hydroxyl, carboxyl, and amino functional groups [11]. It has been argued that Pb preferentially adheres to strong amine binding sites rather than phenol and carboxyl groups [12]. Adsorption involves chelation and electrostatic attraction, which can occur simultaneously.

It has been shown that SOM can affect precipitation and mineralization rates and thus interfere with immobilization [13]. Contaminated soils wiped out the organic matter would subdue the immobilization effectiveness [14]. One study revealed that high SOM concentrations could inhibit mineralization by forming organic Pb complexes and preventing the growth of crystal seeds [13]. SOM may compete with phosphates for adsorption sites, leading to changes in phosphate availability [15]. In addition, low-molecular-weight organic acids could increase the bioavailability of Pb and enhance the formation of pyromorphite, but could also intensify Pb release from pyromorphite [16,17]. The effect of SOM depends on the pH and organic matter conditions and may involve three mechanisms: chelation; adsorption; and reaction with functional groups. Lack of knowledge regarding the effect of SOM on immobilization limits our ability to interpret, predict, and control the efficiency of heavy metal remediation. The mechanism by which SOM affects the effectiveness of immobilization thus requires further investigation.

Immobilization, which mainly occurs at the boundary between a polluted solid and a solution, first involves desorption from unstable Pb minerals and then reaction in the solution [18]. The reactions are mainly driven by desorption and diffusion, and abundant SOM has an affinity for destabilized Pb minerals. Some studies have investigated the influence of SOM, most frequently in liquid. Lang and Kaupenjohann [13] investigated the effects of DOM on Pb-P reactions in solution. They found that DOM inhibits Pb-P reactions and reduces the size of precipitated products, and DOM wrapping of crystals and the soil environment influence the availability of amendment phosphates. However, the precipitation reaction in solution is too fast to capture. In situ observation of crystal growth is constrained in opaque soil systems, so it is difficult to determine the influence of humic acid (HA) on the extent of Pb immobilization. Although there are no conclusive results on the effect of HA on Pb immobilization, such information is urgently needed for real site remediation.

We simulated diffusion-controlled immobilization to investigate the impact of DOM on Pb immobilization. The study is aimed at elucidating the immobilization reaction in a counterdiffusion gel system and help to understand the complex reaction system in soil. Visual observation and characterization techniques were applied to investigate the immobilization process and the impact of HA on Pb immobilization by phosphate.

2. Materials and methods

2.1. Materials

$Pb(NO_3)_2$, KH_2PO_4, and NaCl reagents (analytical grade) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Commercial HA (CAS 1415-93-6; Aldrich, Milwaukee, USA) was used as the DOM standard. Agarose (Biowest, Spain) with a 1% gel strength of $750 \, g/cm^2$ was used as the gel medium. Other reagents were of analytical grade and were used as purchased. All solutions were prepared using deionized (DI) water (Millipore Milli-Q $\geq 18.2 \, M\Omega$ cm; Merck, Germany). All glassware was washed in 1 M HNO_3 for at least 24 h and rinsed with DI water before use.

To prepare stock solutions, HA was dissolved in 50 mM NaOH buffer (pH 10) under magnetic stirring for 10 min. Then HCl was added dropwise under stirring to reach pH 6.5–8.5. The solution was filtered three times through a 0.45-μm membrane to remove impurities and then transferred to a brown volumetric flask and made up to volume. The stock solution (final concentration 800 mg C/L measured using a TOC instrument) was sealed and stored at 4 °C [19].

2.2. Gel system and immobilization experiments

A U-tube consisted of a 90 mm horizontal tube and two vertical tubes was designed for counterdiffusion experiments (dimensions shown in Fig. 1) as in crystallographic analyses of proteins and minerals [20]. Agarose powder was completely dissolved in hot water at 90 °C to prepare a 0.4 wt.% stock solution, and was then mixed with the required volume of heated DI water in a water bath at 50 °C to obtain 0.2 wt.% agarose solution. DOM stock was added to aliquots of this solution to yield DOM concentrations of 0, 20, 40, and 80 mg C/L, followed by vortexing for 1 min. Then 5 ml of the agarose gel was slowly introduced into the horizontal tube and cooled until the gel condensed.

Immobilization experiments were accessed by diffusing reagents from two ion source reservoirs in the U-tube. Equivalent amounts (0.05 M) of KH_2PO_4 and $Pb(NO_3)_2$ solutions were prepared, and aliquots (1.0 ml) of the two reaction reagents were injected into the two vertical branches of the tube, which were then sealed. Cation and anion solutions counterdiffused through the horizontal tube filled with curdy agarose and entrapped varying levels of DOM until immobilized precipitation took place. During experiments, we measured the waiting time (t_w), the point at which precipitation started (x_0), and the crystal growing space