Process Safety and Environmental Protection 103 (2016) 174–182

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Extraction mechanism of lead from shooting range soil by ferric salts

Jong-Chan Yoo[a], Yeon-Jun Shin[b], Eun-Jung Kim[c], Jung-Seok Yang[b], Kitae Baek[a],[d],*

[a] Department of Environmental Engineering and Soil Environment Research Center, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju, Jeollabuk-do 54896, Republic of Korea
[b] Biomodulation Team, KIST Gangneung Natural Products Research Institute, 679 Saimdang-ro, Ganengung, Gangwon-do 25451, Republic of Korea
[c] Department of Environmental Engineering, Mokpo National University, 1666 Yeongsan-ro, Cheonggye-myeon, Muan-gun, Jeollanam-do 58554, Republic of Korea
[d] Department of Bioactive Material Sciences, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju, Jeollabuk-do 54896, Republic of Korea

ARTICLE INFO

Article history:
Received 18 November 2015
Received in revised form 26 May 2016
Accepted 6 July 2016
Available online 15 July 2016

Keywords:
Ferric chloride
Fractionation
Inorganic acid
Lead
Soil washing
Soil quality

ABSTRACT

The conventional soil washing process uses inorganic acids to extract metal from contaminated soils; however, soil structure disturbance is a negative by-product of the process using the acids. To minimize the adverse effects of soil washing, the use of alternative extractants is needed. Ferric chloride has a low pK_a value, and anionic chloride ligand can enhance the extraction of toxic cationic metals from soils. In this study, a soil washing process using ferric chloride and ferric nitrate was applied to a Pb-contaminated model and field shooting range soils, and the outcome was compared to the use of conventional inorganic acids. The extraction of Pb from both soils was mostly dependent on the equilibrium solution pH regardless of the extractants used, and chloride could not significantly enhance that. Ferric iron enhanced the extraction of Pb compared to the inorganic acid treatment because ferric could generate continuously hydrogen ions by the equilibrium reaction between ferric ions and ferric hydroxide. Ferric chloride may be an attractive alternative extractant for the soil washing of Pb-contaminated soils. However, although Pb concentration in soil was significantly decreased by washing process, soil enzyme activity and plant growth was inhibited by severe soil acidification. Additionally, ferric salt-based washing showed similar seed germination test using tomato (*Solanum lycopersicum*) with HCl-based washing. Therefore, ferric salt based soil washing could remove more Pb from the shooting range soil with similar quality of soil compared to inorganic-based washing.

1. Introduction

Metal contamination of soil has increased due to industrial developments and human activities including abandoning mines and the refinery of metals. It is well known that heavy metals are significantly harmful to human health and have disastrous effects on the ecosystem. Several soil remediation techniques have been applied to treat heavy-metal contaminated sites, with stabilization/solidification as the most common choice (Ahmad et al., 2012a, 2012b; Moon et al.,

---

* Corresponding author at: Department of Environmental Engineering and Soil Environment Research Center, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju, Jeollabuk-do 54896, Republic of Korea. Tel.: +82 63 270 2437; fax: +82 63 270 2449.
E-mail address: kbaek@jbnu.ac.kr (K. Baek).

http://dx.doi.org/10.1016/j.psep.2016.07.002

2013). However, this technique is not suitable in Korea because the Korean government has regulated soil quality based on the pseudo-total content of metals after *aqua regia* extraction since 2009 (Yoo et al., 2013). Therefore in Korea, separation or extraction techniques such as soil washing, phytoremediation, and electrokinetic remediation have been used to restore metal-contaminated soils (Kim et al., 2013b, 2011, 2014; Moon et al., 2012; Oh et al., 2012; Ryu et al., 2011). Among them, *ex situ* soil washing has been the most widely applied because of its high removal efficiency, short treatment time, effective volume reduction of soils as well as contaminants, and relatively simple treatment process (Dermont et al., 2008; Yoo et al., 2013).

The *ex situ* soil washing technique is a combined process of physical separation and chemical extraction, and it is applicable to the removal of various contaminants (Dermont et al., 2008). In chemical extraction, the selection of extracting agents including organic/inorganic acids, chelating agents, and surfactants is most important to extract contaminants from the soil to the aqueous phase (Arwidsson et al., 2010; Di Palma et al., 2011; Lei et al., 2008). Metals are extracted from the solid phase by ion exchange with hydrogen ions or cations and metal-ligand complexations. It is well known that chelating agents including ethylenediaminetetraacetic acid (EDTA) and ethylenediaminedisuccinic acid (EDDS) bind strongly with metals and effectively extract metals via chelation (Fabbricino et al., 2013; Polettini et al., 2009). However, high cost is a barrier for the application of remediation agents on a field-scale. Though the recycling of EDTA has been applied to a pilot-scale soil washing process, a considerable amount of EDTA was required due to the presence of Fe-EDTA complexes, which have higher affinity than metal-EDTA complexations (Voglar and Lestan, 2012, 2013). Therefore, inorganic acids including hydrochloric acid (HCl), nitric acid (HNO_3) and sulfuric acid (H_2SO_4) are more frequently used to treat metal contaminants because of their low cost and high metal extraction capacities (Ko et al., 2005). Even though inorganic acids can extract toxic metals via dissolution and desorption, the issues of harmful effect on soil ecosystem by severe soil acidification should be solved for the general application of this technique. Recently, some researches using various salt solutions as an alternative extractant have investigated to enhance both metal removal and soil quality. Makino et al. (2006, 2008) and Li et al. (2015) reported that the extraction of Cd and Pb using cationic chloride solutions including $CaCl_2$, $FeCl_3$, $MgCl_2$, KCl, and NaCl from paddy and agricultural soils was influenced by extraction pH, metal-chloride complexations, and ion exchange between Al on soil surface and cations selectively. Among the Ca-, Mg-, Na-, K-, and Fe-based salts, ferric iron(Fe(III)) has a low pK_a value. Fe(III) can also form ferric (oxy)hydroxides, which are abundant minerals in soils, can dissociate water molecules, and can generate hydrogen ions during precipitation. The produced hydrogen ions then decrease the solution pH and enhance the metal extraction. The researchers reported that metal-chloride complexation enhanced the metal extraction, however, the mechanism of metal extraction by ferric salts is unclear because the stability constant between metals and chloride is not high enough to achieve the extraction.

In this study, soil-washing experiments using ferric salts and conventional inorganic acids were carried out to investigate Pb extraction characteristics using Pb-contaminated model soil. Based on these results, we evaluated the mechanism and potential of ferric salts on the removal of Pb from soil collected from contaminated shooting range soil to address its applicability to a real field situation. Usually, the easily extractable Pb including cerussite($PbCO_3$) and/or hydrocerussite($Pb_3(CO_3)_2(OH)_2$) is commonly found in shooting range soils (Cao et al., 2003; Lin et al., 1995), which are exchangeable fractions of Pb in soils. In addition, the soil quality via a seed germination test in a pot and soil enzyme activity test for urease before and after washing process using HCl and $FeCl_3$ was evaluated for field contaminated soil.

2. Materials and methods

2.1. Artificially Pb-contamination of kaolin and field shooting range soil

One model soil, kaolin, and field shooting range soil, were used to test soil-washing efficiency. Kaolin is a category of rock that is rich in kaolinite ($Al_2Si_2O_5(OH)_4$), most abundant clay mineral in Korea, and has a low shrink-swell capacity and a low cation exchange capacity (CEC). Pb-contaminated kaolin was prepared by mixing 1 kg of kaolin (Sigma–Aldrich Co. Ltd, MO, USA) and 3 L of 145 mM $Pb(NO_3)_2$ adjusted to pH 6.0 ± 0.1 with 0.1 M HNO_3 and NaOH. The mixture was stirred using a horizontal shaker at 100 rpm for 24 h at room temperature. Then, the final mixture was filtered using a vacuum pump and washed with deionized water to remove unattached Pb. The residual solid was dried at 75 °C and was used as the Pb-contaminated model soil. The original kaolin soil consisted mainly of kaolinite but also contained some impurities including Pb. The Pb content in the original kaolin soil was 2887 mg/kg. After the kaolin was artificially contaminated with additional Pb, the concentration of Pb was approximately 27 mg/g and the pH was 6.1.

The field Pb-contaminated soil was collected from a former shooting range in South Korea. The physicochemical properties of the Pb-contaminated shooting range soil are shown in Table 1. The particle size distribution was measured by wet-sieving, and the size distribution of the soil particles smaller than 75 μm was analyzed using a particle size analyzer (Accu-Sizer 780 SIS, PSS, USA). The soil pH and electrical conductivity

Table 1 – The physicochemical properties of the field Pb-contaminated shooting range soil.

Parameter	Value
pH	5.9
Organic matter (%)	5.6
CEC (meq/100 g)	15.5
Soil minerals identified by XRD	Quartz, feldspar, muscovite
Particle size distribution (wt%)	
>2.000 mm	0.0
0.075–2.000 mm	58.4
0.038–0.075 mm	5.8
0.002–0.038 mm	35.2
<0.002 mm	0.6
Initial concentration of elements (<0.075 mm)	
Pb (mg/kg)	5715.4 ± 2.5
Zn (mg/kg)	218.6 ± 0.7
Ni (mg/kg)	62.0 ± 0.1
Cu (mg/kg)	15.1 ± 0.1
Ca (mg/kg)	932.9 ± 0.1
Mn (mg/kg)	579.7 ± 1.4
Fe (g/kg)	37.4 ± 0.1
Al (g/kg)	38.0 ± 0.1
Mg (g/kg)	8.3 ± 0.0