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Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils

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Abstract

Ethylenediaminetetraacetic acid (EDTA) was used as a reference chelating agent in column experiments to investigate the effectiveness of chelant-enhanced flushing of soils artificially contaminated under various conditions (low/high Cu loading, and aging). The associated soil dissolution issues were of particular concern. Dissolution of indigenous Fe/Al oxides, Ca carbonates and organic matter was monitored over the course of flushing. Regardless of contamination condition, above 85% extraction efficiency could be accomplished by 10^{-2} and 10^{-3} M EDTA-flushing, but not 10^{-4} M. The Cu extraction kinetics positively correlated to EDTA concentration but inversely to Cu loading in soils. In addition to extraction from weakly sorbed fractions, a large portion of Cu was extracted from oxide, organic matter and residual fractions, which appears to derive from soil dissolution. Cumulative dissolved amounts of Fe, Al, and Ca were found to reach as high as hundreds of mg kg^{-1}, which were comparable to Cu contamination. Soil organic matter, which is known to strongly interact with Fe and Al oxides, was also mobilized. The rate and extent of these soil dissolutions were also positively correlated to EDTA concentration. Therefore, the co-extraction of soil minerals and organic matter during chelant-enhanced flushing, which would alter both physical structure and chemical properties of the soils, is detrimental to future land use and deserves greater attention. The concentration of chelating agent is the most crucial factor for an effective soil flushing with minimal damage.

Keywords: Chelating agent; Dissolution; EDTA; Organic matter; Fe/Al oxides; Soil flushing

1. Introduction

A large number of sites contaminated by heavy metals have been reported in the United States and Europe; Cu is one of the heavy metals most often encountered (Peters, 1999; Sun et al., 2001). Chelant-enhanced soil washing/flushing is gaining popularity. In situ flushing technologies, for which soil excavation is not required, are generally more economical and safer than soil washing (Heil et al., 1999; Hauser et al., 2005). EDTA (ethylenediaminetetraacetic acid) has been widely proposed and studied, because of its attributes of high efficiency of metal extraction, weak adsorption on soils, and effective recovery and reuse (Di Palma et al., 2003; Lo and Zhang, 2005). However, it should be emphasized that, in consideration of its low biodegradability and high mobility in subsurface environment, EDTA was employed as a reference chelating agent in this study to examine the effectiveness and, more importantly, the coupled soil dissolution issues of chelant-enhanced flushing of contaminated soils. These findings can stimulate relevant concern about the recently proposed use of easily biodegradable chelating agents (e.g., SS-EDDS (S,S-ethylenediaminedisuccinic acid)) in soil washing/flushing/pytoextraction (Vandevivere et al., 2001; Kos and Lestan, 2003; Tandy et al., 2004; Hauser et al., 2005; Santos et al., 2006).

It has been shown that the source and form of metals can affect the extraction efficiency of chelating agents (Kim et al., 2003; Tandy et al., 2004). Past research showed that the forms of metal precipitates (artificially added) determined the efficiency of EDTA extraction for neutral

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or alkaline soils with very high heavy metal contamination (i.e., several thousands of mg kg^{-1}) (Davis and Singh, 1995; Davis and Hotha, 1998). For acidic soils, however, the distribution of sorbed metals, which depends on contamination condition, appears to be the most influential factor (Sun et al., 2001). The metal loading (Barona et al., 2001) and 30–400-d contamination age (McBride et al., 1998; Gao et al., 2003) were found to influence the extraction efficiency of EDTA. Therefore, soils artificially contaminated under different conditions (i.e., metal loading and aging), which can minimize the ambiguity of contamination source and heterogeneity in soil properties, were used to examine the relationship between metal distribution and EDTA extraction efficiency. The extraction efficiency was, however, expected to be higher than that of field-contaminated soils.

Above all, the majority of literature has focused on demonstrating the remediation capabilities of chelating agents (e.g., Lim et al., 2004; Tsang et al., 2005), of which the extraction of heavy metals was shown to be faster and more complete with increasing the quantity of chelating agents (Kim et al., 2003; Tandy et al., 2004). This appears to favor the use of high-concentration solution on the grounds of shorter duration and smaller volume of solution. Nevertheless, to what extent and by how fast the soil components are influenced during chelant-enhanced flushing have seldom been investigated. Without taking into account the ligand-promoted mineral dissolution reactions, which destabilize the mineral structure and enhance the overall dissolution rate (Sposito, 2004), the calculation based on stability constants of metal complexes and solubility products of metal precipitates (Vandevivere et al., 2001) may not truly reflect the seriousness of soil dissolution. Previous studies have illustrated that tremendous amount of Ca dissolution from carbonates in calcareous soils significantly diminished the EDTA extraction effectiveness of the metal contaminants and resulted in a costly remediation (Papassiopi et al., 1999; Theodoratos et al., 2000). In non-calcareous soils, Fe dissolution from Fe oxides (e.g., goethite and hematite) and Al dissolution from Al oxides (e.g., gibbsite) and aluminosilicates (e.g., clay minerals) may be more crucial in view of their higher tendency for complexation with chelating agents (i.e., larger stability constants). Along with soil minerals, soil organic matter may also be mobilized (Vulava and Seaman, 2000; Yang et al., 2001). An extensive dissolution of soil minerals and organic matter would alter the soil physical and chemical properties, or even disintegration of soil structures, which can render the soil unfit for future use of vegetation or construction. Therefore, the rate and extent of soil dissolution is an issue of particular concern that demands extensive assessment during the course of chelant-enhanced flushing.

To achieve the foresaid objectives, soils of two Cu loading levels, fresh and aged contamination were flushed with various EDTA concentrations (10^{-4}–10^{-2} M) at two pore-water velocities. Sequential extraction scheme was applied to reveal the Cu distribution in soils and the fractions resistant to EDTA extraction. The effectiveness of EDTA-flushing was assessed in terms of the Cu extraction efficiency, volume of flushing solution, and EDTA consumption; and the associated soil dissolution issues were evaluated by tracing the cumulative amount of Fe, Al, Ca and organic matter dissolving from the soils.

2. Experimental methods

2.1. Soil characteristics

A soil sample, taken from 25 to 50 cm below ground surface in Hong Kong, was air-dried and passed through a 2-mm sieve. The soil was comparable to sandy loam (64% of sand, 20% of silt, 16% of clay by mass) according to particle size distribution obtained by sieving and hydrometer methods, and it contained 1.47% organic carbon content, measured by a total organic carbon (TOC) analyzer (Shimadzu TOC-5000A) with an infrared spectrometer after combustion in a furnace (total carbon) and acidification (total inorganic carbon). The soil pH was 7.6, measured at a 1:2 soil-to-water ratio. Measured by nitrogen gas adsorption (Micromeritics ASAP2010), the soil possessed a BET surface area of 7.04 $m^2\ g^{-1}$ and an unnoticeable micropore surface area. The cation exchange capacity of the soil was 34.9 meq 100 g^{-1}, as determined by NH_4-Na exchange. The clay-size particles separated by pipette method were determined with X-ray diffraction (XRD) analysis (Philips PW1830); the most abundant mineral was kaolinite. X-ray fluorescence (XRF) spectrometry (JEOL JSX-3201Z) was used to qualitatively compare different heavy metal contents in the soil. The relative mass percentages were 5.98% Fe, 25.0% Al, 3.07% Ca, 0.355% Mn, which were however calculated without taking into account some major elements of soils (i.e., C, H, O, and N) that cannot be accurately quantified by XRF. Therefore, amorphous and total (amorphous-plus-crystalline) oxides of the soil were determined by ammonium oxalate and DCB (dithionite–carbonate–bicarbonate) extractions. Amorphous Fe/Al/Mn oxides were 338 ± 2.5, 474 ± 6, and 45.9 ± 0.9 mg kg^{-1}, respectively. Total Fe/Al/Mn oxides were 6236 ± 112, 797 ± 17, and 124 ± 3.7 mg kg^{-1}, respectively. It has been shown that Mn-chelate complexes were significant in some soils (Sun et al., 2001; Hauser et al., 2005). In this studied soil, however, the amount of Mn oxides was much smaller than Fe/Al oxides, as shown by XRF and oxalate/DCB extractions. Preliminary 3-d batch extraction experiments (5:1 EDTA–metal molar ratio) showed that Mn dissolution was not significant. The Mn dissolution during EDTA-flushing column experiments was also found to be insignificant, and thus, its data were not reported. The indigenous Cu content of the soil was 17.4 ± 0.8 mg kg^{-1} (four replicates), determined by acid digestion with HNO_3-HCl-HF in a microwave oven (CEM MDS-2000). The metal concentrations of the above extraction/digestion samples were analyzed by flame-Atomic Absorption Spectrometry (AAS) (Hitachi Z-8200).