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Pyrophosphate coupling with chelant-enhanced soil flushing of field contaminated soils for heavy metal extraction

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ABSTRACT

This study investigated the influence of flushing duration, [S,S]-ethylenediaminedisuccinic acid (EDDS) dosage, humic acid and various combinations of ethylenediaminetetraacetic acid (EDTA), EDDS and tetrasodium pyrophosphate ($Na_4P_2O_7$) on metal extraction during soil flushing, through column experiments. A lesser extent of enhancement in metal extraction efficiencies was found when the flushing duration and the dosage of EDDS was doubled, compared to their efficiencies measured at pore volume 100. Metal extraction efficiency was mainly influenced by the initial metal distribution in the soils rather than the flushing duration and the EDDS-to-metal molar ratio. Humic acid of less than 10 mg/L as dissolved organic carbon (DOC) posed an insignificant effect on metal extraction during EDDS enhanced soil flushing. The extraction rate of Ni by EDTA and EDDS was time dependent, and was initially fast in the case of EDDS, whereas it was slow for EDTA. However, the overall Ni extraction efficiency by EDTA was higher when the flushing time was longer. $Na_4P_2O_7$ promoted the mineral dissolution which enhanced the metal extraction as a result of soil disruption. The order of metal extraction by $Na_4P_2O_7$ was Ni > Cr > Cu, probably be due to the different affinities between metals and $P_2O_7{}^{4-}$.

1. Introduction

Chelant-enhanced soil flushing has shown promising results over soil remediation in extracting heavy metals [1,2] from contaminated sites, as it is generally more economical and safer than soil washing [3,4]. In particular, [S,S]-ethylenediaminedisuccinic acid (EDDS) has recently been investigated since the extraction efficiency for various heavy metals is comparatively high [5] and most metal–EDDS complexes can be biodegraded in soils [1,6]. This results in less residual effects on the environment [7] and less toxicity to plants, fungi and microorganism [8].

The flushing duration and EDDS dosage are of primary engineering concern in soil flushing. It has been reported that a batch study of metal extraction from contaminated soils by EDDS is time dependent and attains equilibrium within 2 d during the ex situ soil washing [9]. However, the EDDS flushing duration should also be studied in order to give a better insight into the in situ soil flushing. On the other hand, the metal extraction efficiency was found to be mainly dependent on the metal distribution under EDDS excess [9], in which an adequate dosage of EDDS has to be applied in order to achieve efficient soil flushing.

Moreover, dissolved organic matter (DOM) can increase the metal extraction from the soil minerals or soil surfaces by forming dissolved metal–humic substance complexes [10]. Batch experiments with high concentrations of humic acid have been conducted to investigate the effect on metal extraction from multi-metal contaminated soils under both EDDS-deficiency and EDDS-excess conditions [10]. The results showed that metal extraction was enhanced during soil washing by the formation of additional metal–humate complexes under EDDS-deficiency conditions, while more metals were dissolved from the soils due to the disruption of the soil structure under EDDS-excess conditions. On the other hand, a steric blocking of soil surfaces by humic acid was also reported which restricted the access of the sorbed metals for EDDS complexation [11]. Nevertheless, it is still not known whether the metal extraction by EDDS from contaminated soils would be enhanced or worsened with a continuous flushing of humic acid.

Besides EDDS, ethylenediaminetetraacetic acid (EDTA) is one of the most efficient chelating agents for solubilizing soil-bound Pb [12]. Stronger complexation of Pb by EDTA and higher extraction from soils was reported when compared to EDDS [13]. In view of the high extraction efficiency for some of the heavy metals, the application of EDTA was also included in this study, although it is non-biodegradable and may induce adverse health and environmental impacts. In addition, a combined application of EDDS and EDTA was found to increase metal extraction from soils, especially for Pb [7]. A synergistic performance of the EDDS and EDTA mixture under a chelant-deficiency condition was observed, that probably

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resulted from the change of chemical speciation and thus gave less competition among other metals [11]. Hence, an optimum composition of the chelant mixture should be considered taking into account the effectiveness and associated environmental impact. In view of the remediation goals, the Cr extraction by both EDDS and EDTA was quite unsatisfactory for a solution pH above 4, even with an excess amount of chelants [14–16]. In order to enhance the metal extraction efficiency from contaminated soils, tetrasodium pyrophosphate ($Na_4P_2O_7$) was selected in this study because it had been reported to remove metals, especially chromium, from exchangeable, precipitated, and organic fractions in soils [17].

The objectives of this column study were to investigate: (i) the effect of flushing duration and EDDS dosage, (ii) the influence of DOM on metal extraction using EDDS, (iii) the effect of different combinations of EDTA and EDDS, and (iv) the enhancement in metal extraction by $Na_4P_2O_7$.

2. Experimental

2.1. Soil characteristics

Field contaminated soil was obtained from a demolished electroplating plant located in a northern district in Guangzhou, China. The soil was collected from the upper soil layer at levels 0.5–1.0 m below the ground surface, and was air dried and passed through a 60 mesh sieve. The soil characteristics are summarized in Table S1. The field contaminated soil was polluted by five heavy metals in which only Cr, Cu and Ni were of particular interest in this study, because their contamination levels in the soil (i.e., 743, 913 and 1456 mg/kg, respectively) were high compared with Pb and Zn (i.e., 166 and 85 mg/kg, respectively), and exceeded the China Environmental Quality Standard for soils (GB 15618-1995). The metal concentrations were measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Optima 3000XL, Perkin Elmer). The metal distribution of the soil sample was determined by sequential extractions according to the procedures reported in a previous study [9].

2.2. Materials and solution preparation

The EDDS solution was prepared by mixing 30% Na_3EDDS solution (Innospec Ltd., UK) with 0.2 g/L of sodium azide to circumvent biodegradation, while the EDTA solution was prepared from Na_2EDTA salt (Sigma–Aldrich). The different concentrations of EDTA and EDDS used were 1.44 and 2.88 mM, respectively, prepared corresponding to a EDDS-to-metal molar ratios (MR) of 1 and 2, defined as the ratio of the total number of moles of EDDS to the initial total number of moles of the sorbed metal (i.e., Cr, Cu, Ni, Pb and Zn) in the contaminated soils, for 100 pore volumes of flushing. The humic acid was obtained from Aldrich Chemicals with the dissolved organic carbon (DOC) concentration measured by a total organic carbon analyzer (Shimadzu TOC-5000A). The $Na_4P_2O_7$ solution was prepared from sodium pyrophosphate decahydrate salt obtained from Aldrich Chemicals. All influent solutions were prepared in the presence of 10 mM $NaNO_3$ to provide a constant background electrolyte, adjusted to pH 5.5 by 10 mM $NaOH/HNO_3$, and buffered with 2 mM 2-morpholinoethane-sulfonic acid (MES).

2.3. Column experiments

Column experiments were performed in 3.6 cm internal diameter and 15 cm long columns. The columns were packed with 200 ± 3 g of the contaminated soil in 10 incremental steps, in which each 20 g of the soil was compacted to obtain a uniform bulk density of $1.310 \pm 0.020\ g/cm^3$, corresponding to a porosity of 0.506 ± 0.004. Filter papers (0.45-μm nominal pore size) were placed at both ends of the soil columns to ensure that the effluent was free of turbidity. The soil columns were oriented vertically and slowly saturated in an upward flow direction for 1 pore volume at a pore-water velocity of 2 ± 0.3 cm/h with a background solution of 10 mM $NaNO_3$ and 2 mM MES at an initial pH 5.5.

Following the soil saturation, the influent solution was switched according to the experimental conditions summarized in Table S2 (Supplementary data). The initial samples were collected at the effluent after soil saturation. For the first 100 pore volumes, columns 1a and 1b, columns 2a and 2b, columns 3a and 3b were paired and run in duplicate to show the repeatability of the experiments. From 0 to 200 pore volumes, column 1a was flushed with EDDS at MR 1 without humic acid, whereas column 2a was flushed with EDDS at MR 1 containing 2 mg/L of humic acid as DOC and column 3a with 10 mg/L of humic acid as DOC, in order to study the effect of flushing duration and humic acid on the metal extraction. On the other hand, the concentration of EDDS was doubled (i.e., 2.88 mM) from 100 to 200 pore volumes for columns 1b, 2b and 3b in order to study the concentration effect of the EDDS dosage on metal extraction. After the column tests, the soil columns were sliced horizontally into 5 even portions and 1 g of the soil sample was collected from the center of each portion. The soil samples were then freeze-dried and sequential extractions were carried out to determine the Cr, Cu and Ni distribution in different soil components after flushing. The sequential extraction procedures adopted were as described in a previous study [18].

Furthermore, the effect of different combinations of chelating agents on metal extraction was also studied through columns 4–8 for 100 pore volumes of flushing. Columns 4 and 8 were flushed with 100% of EDDS and 100% of EDTA by molar concentration at MR 1. The flushing solution for column 8 contained 75% of EDDS and 25% of EDTA, while that of column 7 contained 25% of EDDS and 75% of EDTA at MR 1. The flushing solution was prepared with 50% of EDDS and 50% of EDTA for column 6. For column 9, the flushing solution was the same as column 6 in the first 100 pore volumes and afterwards, the EDDS and EDTA solution was replaced by 10 mM $Na_4P_2O_7$ from 100 to 200 pore volumes in order to study the enhancement in metal extraction using $Na_4P_2O_7$.

3. Results and discussion

3.1. Column repeatability and metal extraction behaviors

Fig. 1 shows a high repeatability for each pair of columns, indicating consistency and reliability of the experiments. In the absence of humic acid, the relative standard deviation (%RSD) of the concentrations of Cr, Cu and Ni in the effluent from the soil columns after flushing with EDDS at MR 1 were 13.6, 12.8 and 10.6%, respectively (Fig. 1a–c). On the other hand, when flushing the soil columns with EDDS, the %RSD for Cr, Cu and Ni in the presence of 2 mg/L of humic acid as DOC were 11.3, 12.5 and 12.4%, respectively (Fig. 1d–f), whereas in the presence of 10 mg/L of humic acid as DOC were 13.4, 11.9 and 11.4% for Cr, Cu and Ni, respectively (Fig. 1g–i).

As seen in Fig. 1, the general trends of metal extraction are similar for various concentrations of humic acid (i.e., 0, 2 and 10 mg/L of humic acid as DOC). Around 34 mg/L of Cr in the effluent was recorded at pore volume 1. The concentration then dropped drastically to 4.0 mg/L and slowly reached equilibrium at 2 mg/L. In contrast, almost no Cu was initially detected in the effluent but rapidly reached a peak concentration of 42 mg/L at pore volume 4. A decreasing trend was then observed until its equilibrium was reached at pore volume 40, and a final concentration of 3 mg/L was measured at pore volume 100. A similar trend was observed for Ni, in which the initial effluent concentration was about 14 mg/L and there was a sharp increase to a peak of 26 mg/L at pore volume 1.6.