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 $P_2O_7^{4-}$.

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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 ± 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.
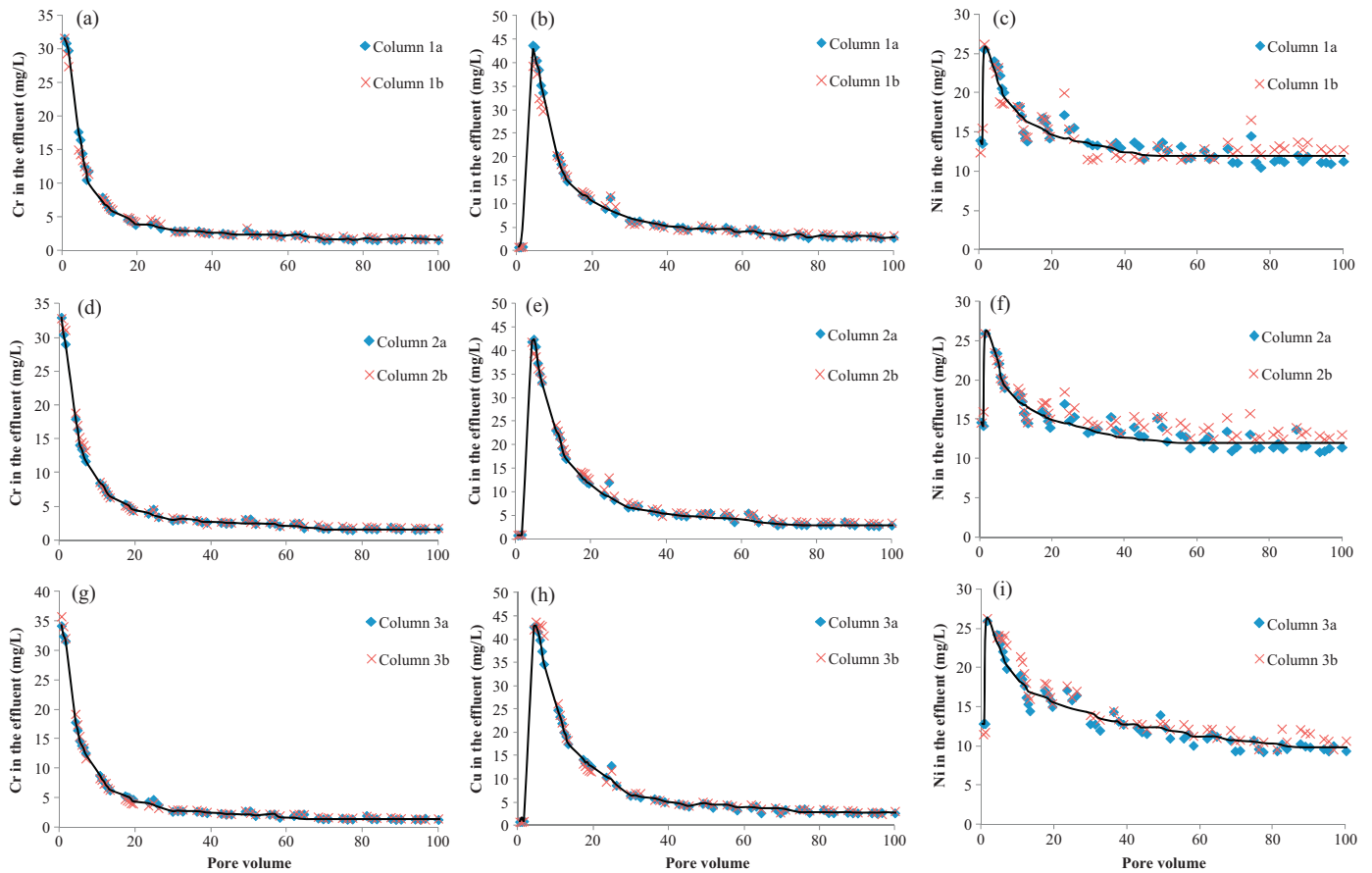
Fig. 1. Metal extraction using EDDS: (a) Cr; (b) Cu; (c) Ni extraction in the absence of humic acid; (d) Cr; (e) Cu; (f) Ni extraction in the presence of 2 mg/L of humic acid as DOC; (g) Cr; (h) Cu; (i) Ni extraction in the presence of 10 mg/L of humic acid as DOC (× and ♦ represent the duplication of column pairs). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The concentration decreased gradually to 12 mg/L at pore volume 100.

The extraction behavior of Cr, Cu and Ni from field contaminated soil by using EDDS appears to be affected by the initial metal distribution. From the sequential extraction results, about 27, 28 and 11% of Cr, Cu and Ni, respectively, was initially distributed in the exchangeable and carbonate fractions of the soils (Supplementary data Fig. S1a–c), and could be effectively extracted by EDDS due to their weakly metal binding strengths, compared with those located in the organic matter and residual fractions [13,19]. As a result, the extraction of Cr, Cu and Ni was rapid in the first 5 pore volumes, but the extraction rates subsequently slowed down. It should be noted that the competitive effect of mineral complexation by EDDS on heavy metals extraction was negligible in this part of the study as the mineral dissolution from the soil was insignificant, with maximum Al and Fe dissolutions of 0.6 and 0.8%, respectively (data not shown). In addition, the extent of extraction for Cr, Cu and Ni was different. The extraction of Cu and Ni was more notable owing to a higher preference for forming metal complexes based on their higher stability constants (i.e., 18.5 for Cu and Ni, Supplementary data Table S3). Furthermore, the mobilization of Cr is possibly facilitated by the formation of Cr(III)–EDDS complexes [16] and anion exchange between EDDS and chromate from the soil, although the amount of extraction was less than that of Cu and Ni. It should be noted that the difference in stability constants between Cr(III)–EDTA and Cr(III)–EDDS is insignificant (i.e., 12.7 and 11.1 for Cr(III)–EDTA and Cr(III)–EDDS, respectively, Supplementary data Table S3). Therefore, the affinity between EDTA and Cr, as well as between EDDS and Cr should be comparable [20]. In view of the rate of extraction, a maximum Cr concentration of 33 mg/L was

observed at pore volume 1. It can be elucidated by the natural leaching of Cr which is favorable under low pH conditions [21]. This evidence was supported by visual observation of the effluent which had a yellow color immediately after the column saturation with the background solution at pH 5.5, prior to the application of EDDS.

3.2. Effect of flushing duration, EDDS dosage and humic acid concentration

Fig. 2a–c shows the concentrations of Cr, Cu and Ni in the effluent after flushing the columns at total pore volumes of 200. The extraction efficiencies of Cr, Cu and Ni at pore volumes 100 and 200 are presented in Table S4 (Supplementary data). The effect of flushing duration on metal extraction can be seen in columns 1a, 2a and 3a in which the MR of EDDS was fixed at 1. The extraction efficiencies of Cr were 20.7, 21.1 and 21.1% at pore volume 100 for columns 1a, 2a and 3a, respectively, and were further increased to 26.9, 27.9 and 26.8%, respectively, at pore volume 200. However, the increments were less significant, with only an additional 6.2, 6.8 and 5.7% of Cr extracted for columns 1a, 2a and 3a, respectively. In addition, an insignificant enhancement in Cu extraction was also observed from pore volume 100 to 200, and the corresponding increase in Cu extraction efficiencies for columns 1a, 2a and 3a were 8.0, 9.1 and 9.9%, respectively. Compared with Cr and Cu, much higher enhancements in Ni extraction efficiency were found for pore volumes 100–200, with values 22.5, 25.2 and 20.7% for columns 1a, 2a and 3a, respectively.
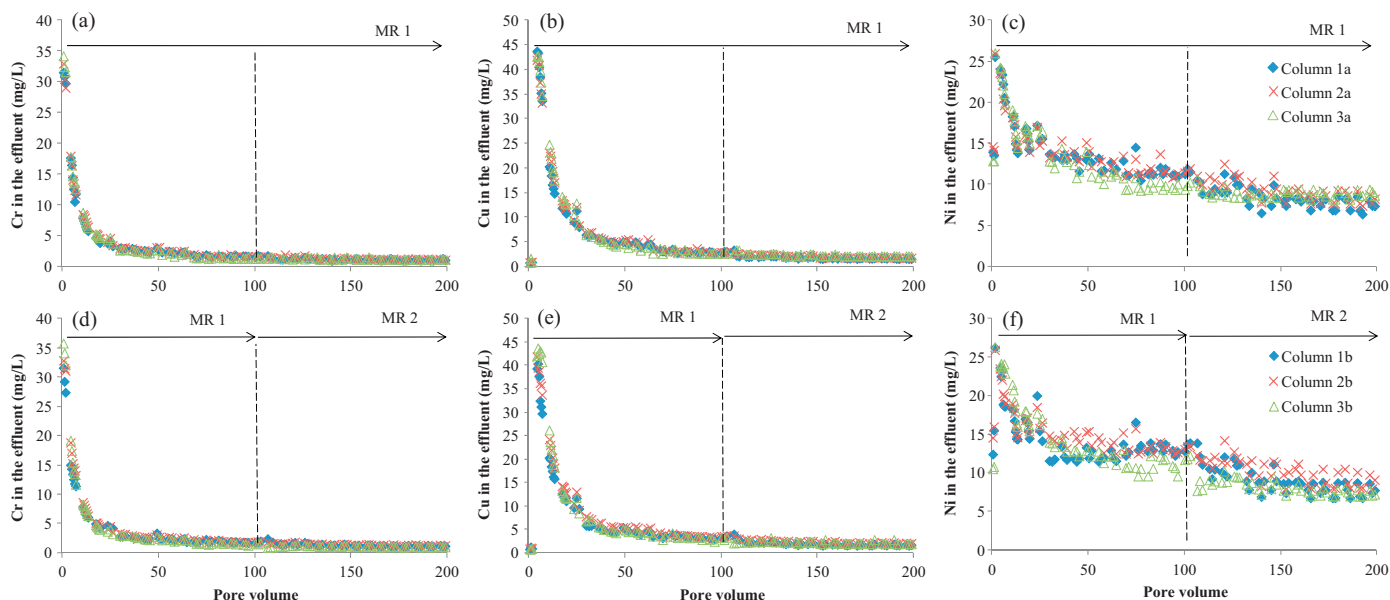
Fig. 2. The influences of flushing duration, EDDS dosage and humic acid on metal extraction: (a) Cr; (b) Cu; (c) Ni extraction at constant EDDS MR 1 (◆, without humic acid; ×, 2 mg/L of humic acid as DOC; △, 10 mg/L of humic acid as DOC); (d) Cr; (e) Cu; (f) Ni extraction with EDDS MR increased to MR 2 at pore volume 100 (◆, without humic acid; ×, 2 mg/L of humic acid as DOC; △, 10 mg/L of humic acid as DOC). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Furthermore, the dosage effect of EDDS is illustrated in Fig. 2d–f for columns 1b, 2b and 3b, with an increase of EDDS-to-metal molar ratios from 1 to 2 at pore volume 100. The concentrations of Cr in the effluent were 1.7, 1.8 and 1.6 mg/L at pore volume 100 for columns 1b, 2b and 3b, respectively, and they gradually decreased to 1.1, 1.2 and 1.0 mg/L at pore volume 200. The concentrations of Cu were 3.2, 3.5 and 3.6 mg/L at pore volume 100 for columns 1b, 2b and 3b, respectively, and they slowly decreased to 1.7, 2.0 and 1.8 mg/L at pore volume 200. Similarly, the concentrations of Ni were 12.8, 13.1 and 11.7 mg/L at pore volume 100 for column 1b, 2b and 3b, respectively, and they gently decreased to 7.7, 9.1 and 7.2 mg/L at pore volume 200. Unexpectedly, there was no increase in the metal concentration in the effluent after doubling the EDDS dosage.

Considering the ease of metal extraction, Cr, Cu and Ni can be readily extracted from the exchangeable and carbonate fractions, which are classified as weakly sorbed fractions, whereas metals sorbed on the organic matter and residual fraction prove more difficult to be extracted. After the flushing with EDDS, less than 4% of Cr, Cu and Ni remained in the exchangeable and carbonate fractions (Supplementary data Fig. S1), indicating that already the three metals have mostly been extracted from the soil. Moreover, the extraction is suspected of being rapid, occurring within the first 5 pore volumes. As a result, metals sorbed on the Fe/Mn oxides fraction, being relatively less strongly bound compared with the organic matter and residual fractions, were then extracted by EDDS, with the extraction rate was still comparatively slower than for the first 5 pore volumes. The extraction of the three metals reached equilibrium at about pore volume 100, and the metal concentrations in the effluent remained almost constant afterwards (Fig. 2). After pore volume 100, the metal extraction rate became even slower because the amount of extractable metals from the Fe/Mn oxides fraction was reduced with increasing time, and practically none of the metals could be extracted from the organic matter and residual fractions. As a result, extending the flushing duration after pore volume 100 only slightly increased the metal extraction efficiency. Similarly, doubling the EDDS dosage showed no increase in the metal concentration in the effluent after pore volume 100. In this study, the metal mobilization appears to be EDDS dosage independent

above MR 1. In regard to the three metals, a longer flushing duration was essential for Ni to reach its equilibrium compared with Cr and Cu, as more Ni was initially distributed on the oxide fraction in the soil (32, 45 and 67% for Cr, Cu and Ni, respectively, Fig. S1).

The presence of 10 mg/L of humic acid as DOC, or less, during the application of EDDS suggests that there is a possibility of metal extraction enhancement by forming metal–humate complexes, as has been postulated in a previous batch study [11]. However, the formation of metal–humate complexes, which was expected to aid metal extraction, was not significant in this study because it was estimated to have about 97% of humic acid to be adsorbed onto the soil at pore volume 200. The total amount of humic acid injected in 200 pore volumes was only slightly higher than the soil adsorption capacity of humic acid of about 0.75 mg/g (equilibrium adsorption data not shown). As a result, no obvious steric blocking of the soil surfaces was observed and thus the metals were extracted by EDDS with an insignificant influence from the presence of humic acid. However, the metal extraction efficiency may be affected significantly after the soil is saturated with humic acid. It should be noted that direct measurement of humic acid concentration as DOC by a total organic carbon analyzer was not possible because of the presence of EDDS in the effluent.

3.3. Metal extractions under various combinations of EDTA and EDDS

The metals concentrations of Cr, Cu and Ni in the effluent after flushing the soil with different combinations of EDTA and EDDS are presented in Fig. 3. Similar trends are observed for Cr and Cu extraction as those described in the previous section. The extraction efficiencies of Cr at pore volume 100 were in the range of 20.1–20.9% (Supplementary data Fig. S4) for columns 4–8, whereas those of Cu were in the range of 33.2–34.8% (Supplementary data Fig. S4). The finding that there were no significant differences in extraction suggests that the capabilities of EDTA and EDDS for the extraction of Cr and Cu from the studied soils are almost equal. The maximum dissolution of soil Al and Fe among for all conditions at pore volume
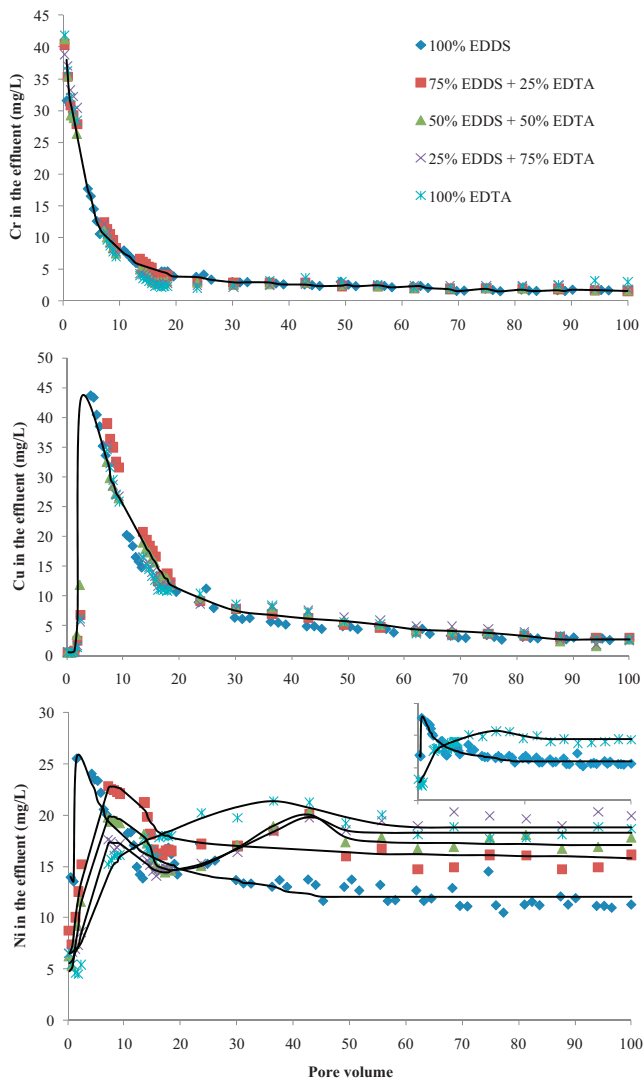
Fig. 3. Metal extraction using various combination of EDTA and EDDS: Cr; Cu; Ni extraction (◆, 100% EDDS; ■, 75% EDDS + 25% EDTA; ▲, 50% EDDS + 50% EDTA; ✕, 25% EDDS + 75% EDTA; ✳, 100% EDTA). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

100 only contributed 0.7 and 1.7%, respectively, of the indigenous soil mineral content (data not shown). The dissolved mineral effect on Cr and Cu extraction was therefore insignificant due to such a low level of mineral dissolution.

On the other hand, the extraction of Ni by EDTA and EDDS was comparatively distinct in terms of the extraction pattern (Fig. 3c) and efficiency. Ni was extracted dramatically by EDDS in the first 1.6 pore volume with a maximum concentration of 42 mg/L, after which the rate of extraction decreased, reaching 12 mg/L at the end of flushing. In contrast, the rate of Ni extraction by EDTA mildly increased before reaching a maximum concentration of 20 mg/L, which was lower than that of EDDS at pore volume 36.5, after which the rate declined slowly with a concentration of 18.7 mg/L at pore volume 100. The extraction patterns for Ni by multifarious combinations of EDTA and EDDS appear to be constituted according to the superposition of the Ni extraction trends under sole EDTA and EDDS flushing. In view of the efficiency, the overall Ni extractions followed an ascending order from 38.2 to 49.4% (Supplementary data Fig. S4) which increased with increasing EDTA concentration.Ni extraction by EDTA and EDDS appears to

be time dependent in the early stage of soil flushing. It has been reported that the initial Ni mobilization from soil by EDDS was higher than EDTA, but was overtaken by EDTA over a longer period of time [22]. The extraction of Ni by EDTA was found to be a slow process [23], especially from the Fe oxide fraction. According to a previous study [24], Ni extraction by EDTA consists of 2 phases, and the fast extraction rate of Ni only occurs during the first 0.25 h which is indicative of slow extraction of Ni throughout the whole experiment. The dissolution of Fe by forming Fe-EDTA took place in conjunction with Ni extraction which abated the amount of free EDTA for Ni extraction, as Fe–EDTA is formed preferably due to its high stability constant (i.e., 19.5 and 26.5 for Ni–EDTA and Fe–EDTA, respectively, Supplementary data Table S3). Although Fe dissolution would also occur by forming Fe–EDDS, the preference of a complex formation between Ni and Fe with EDDS is insignificant owing to the comparable stability constants for Ni–EDDS and Fe–EDDS (i.e., 18.5 and 20.6, respectively, Supplementary data Table S3). Hence, the first phase of Ni extraction was longer and the extent of extraction was higher for EDDS with less influence caused by Fe dissolution. Nevertheless, more Ni can be extracted by EDTA if sufficient time is allowed because the stability constant of Ni–EDTA (i.e., 19.5) is slightly higher than that of Ni–EDDS (i.e., 18.5), denoting that EDTA is more favorable in Ni extraction. The results were also supported by a batch study in which the Ni extraction was higher for EDTA than EDDS at equilibrium (Fig. S2). Although the affinity of Cu is comparable to that of Ni, the rate of extraction of Cu by EDTA was fast. This was because more Cu was initially distributed on the exchangeable and carbonate fractions, and was easily extracted by both EDTA and EDDS, thus the rate of extraction was not significantly affected by the dissolution of Fe.

3.4. Metals extraction enhancement by $Na_4P_2O_7$

Column 9 was selected as being representative in studying the enhancement in metal extraction by replacing 50% of EDTA and 50% of EDDS solution with $Na_4P_2O_7$ after pore volume 100. Fig. 4 illustrates the metal concentration enhancement after the injection of $Na_4P_2O_7$ at pore volume 100. The concentration of Cr in the effluent rose again from 1.9 to 14.9 mg/L within 26 pore volume after the injection of $Na_4P_2O_7$ and decreased with time until reaching 10.4 mg/L at pore volume 200. The concentration of Cu increased again to reach a peak of 13.2 mg/L, followed by a drop until reaching 7.0 mg/L at the end of flushing. However, Ni increased to its maximum value of 30.8 mg/L followed by a decrease to a final concentration of 16.5 mg/L. In view of the extraction efficiency, additional increases of 50.6, 30.4 and 51.7% were recorded for Cr, Cu and Ni, respectively, compared with their extraction efficiencies at pore volume 100. The substantial increases in metal extraction are probably attributable to the mineral dissolution after the addition of $Na_4P_2O_7$, which may induce soil disruption and promote the complexation between the metals and pyrophoshate. Pyrophosphate is often used to extract Al and Fe, as well as metals sorbed on the organic matter fraction in soils [25–27]. In this study, the percentages of Al and Fe dissolution rose from 0.7 to 4.6% and 0.9 to 4.7%, respectively, from pore volume 100 to 200. Under detrimental mineral dissolution, the soil structure would be disrupted which, in turn, would enhance the metals from the soils dissolving into solution, which could aid the extraction of metals by $Na_4P_2O_7$. On the other hand, it was reported that $Na_4P_2O_7$ could extract metals from soils by forming complexes with $P_2O_7^{4-}$ [28,29]. The extraction of metals by $Na_4P_2O_7$ was reported to be significant, even though the amount of metals located on the organic matter fraction was rather small, as metals from the oxide fraction can also be extracted [26]. From Fig. 4, the additional increase in metal extraction followed the order Ni > Cr > Cu and was probably due to their different affinities with $P_2O_7^{4-}$. Their stability constants follow the

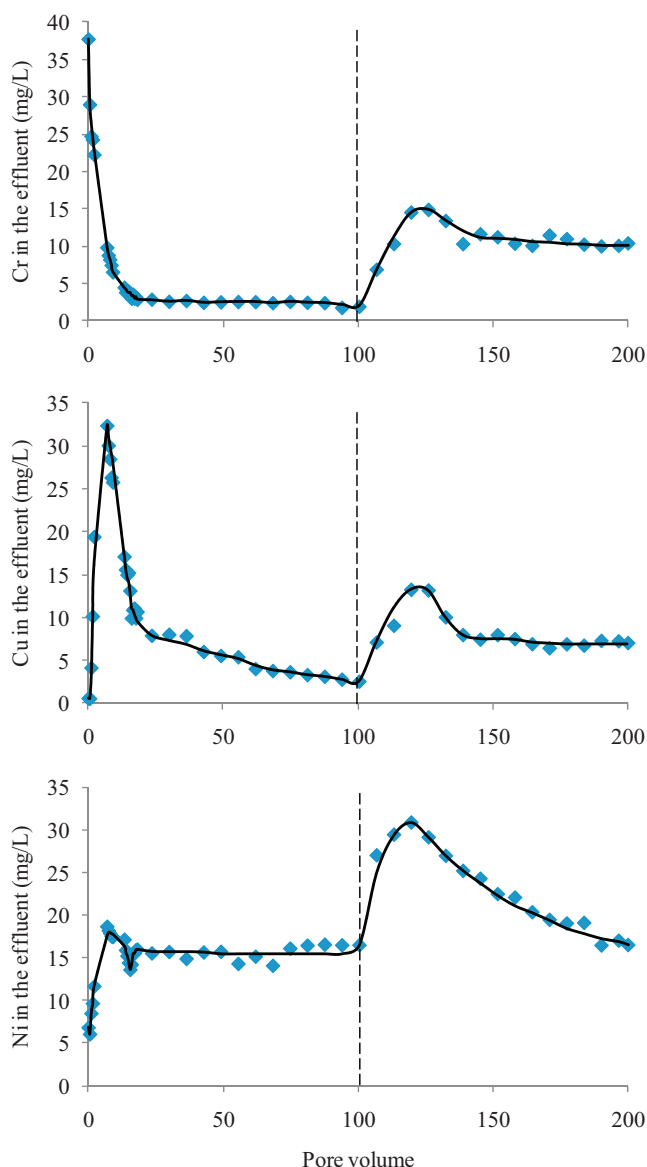**Fig. 4.** Enhancement of metal extraction after soil flushing with 50% EDTA and 50% EDDS using 10 mM $Na_4P_2O_7$: extraction of Cr; Cu; Ni.

order $Ni_2P_2O_7 > Cr_2P_2O_7 > Cu_2P_2O_7$ [30,31] which implies a higher preference for the extraction of Ni. Furthermore, it should be noted that the sequence of $Na_4P_2O_7$ injection is also important. Neither a mixture of $Na_4P_2O_7$ with EDTA and EDDS nor solely $Na_4P_2O_7$ would facilitate the metal extraction during soil flushing. This is because $Ca_2P_2O_7$, an insoluble precipitate, was formed during the flushing experiment and led to the clogging of the soils [32]. In this study, no soil clogging was found because some portions of Ca from the soils were already complexed with EDTA and left the column during the first 100 pore volume, which may prevent the formation of insoluble $Ca_2P_2O_7$ solids. Hence, the sequence of the $Na_4P_2O_7$ application has to be considered when dealing with calcareous soils.

4. Conclusion

Flushing duration and the EDDS dosage were thought to be the primary concerns during chemical enhanced soil flushing. However, the enhancement in metal extraction efficiencies was insignificant even though the flushing duration and the dosage of EDDS were doubled. Instead, it was found that the initial metal

distribution in the soils is more crucial in determining the metal extraction efficiency. On the other hand, the humic acid present in groundwater may not be able to enhance the metal extraction by forming metal–humate complexes if the soil is not yet saturated with humic acid. For the low levels of Ni contamination, EDDS is preferable due to its fast extraction rate; however, EDTA is recommended for high levels of Ni contamination as it can achieve higher Ni extraction efficiency if sufficient time is provided. $Na_4P_2O_7$ can be applied to promote the mineral dissolution which further enhanced metal extraction as a result of soil disruption, but it may also reduce the reusability of the soil after remediation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.10.054.

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