Influence of injection conditions on EDDS-flushing of metal-contaminated soil

Irene M.C. Lo [a,*], Daniel C.W. Tsang [b], Theo C.M. Yip [a], Fei Wang [a], Weihua Zhang [c]

[a] Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Hong Kong, China
[b] Department of Civil and Natural Resources Engineering, University of Canterbury, Canterbury, New Zealand
[c] School of Environmental Science and Engineering, Sun Yat-Sen University, 135 Xingang Road West, Guangzhou 510275, China

ARTICLE INFO

ABSTRACT

This study evaluated the design of step-gradient, single-pulse, multi-pulse, and continuous injection of biodegradable EDDS ([S,S]-ethylene-diamine-disuccinic acid, under the same total dosage) and the significance of pore-water velocities during in situ soil flushing. In view of the metal breakthrough and extraction efficiency of each injection mode, single-pulse injection was found to be the least effective for all metals. Multi-pulse injection was consistently more effective than single-pulse injection, although the efficiency of second and third pulse injections significantly diminished. Continuous injection offered a simple operation and the greatest Ni and Cu extraction, whereas step-gradient injection was the best option for Zn and Pb extraction because it mitigated the influence of metal exchange. Moreover, a rinsing step with a background solution following the initial injection of the multi-pulse injection removed newly formed metal–EDDS complexes from soil pores effectively before further EDDS-flushing. A decrease in pore-water velocity provided a longer residence time for greater Ni and Cu extraction, but also enhanced the rate-limited metal exchange of Zn–EDDS and Pb–EDDS complexes and thus hindered Zn and Pb extraction. These results suggest a slower and continuous injection for the best Ni or Cu removal, but a faster and step-gradient injection for Zn or Pb removal.

Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.

1. Introduction

Chelants have been used to facilitate metal extraction from contaminated soils, which can be performed in situ as soil flushing, phytoextraction and electrokinetics, or ex situ as soil washing and heap leaching [1–3]. In addition to the determination of extraction efficiency of target metals, recent research efforts have advanced our understanding in a diverse range of aspects: kinetic interactions of chelants and metal speciation [4–6], adsorption mechanisms of chelants on mineral surfaces [7,8], influences of geochemistry and operational conditions [9–13], and modelling of extraction kinetics [14,15]. Such knowledge could be applicable for both ex situ and in situ remediation technologies.

Compared with ex situ technologies, in situ soil flushing has received less attention, although it may be less energy-intensive and more economical. While in situ soil flushing can minimize the disturbance to neighbouring communities and the air pollution due to metal-laden fine particles, its application is hindered by the lower predictability in treatment effectiveness and undesirable metal leaching. Thus, previous studies on soil flushing focused on metal mobilization from soil columns, the cumulative metal

removal and flushing volume required, as well as the associated dissolution of soil minerals and organic matter [16–20]. The transport of metal–chelant complexes were then modelled with the modified advection-dispersion transport equations, which enabled the simulation of subsurface metal transport and potential metal leaching [21–24]. However, most of the soil flushing studies only applied continuous injection of the chelant at a constant concentration and did not consider possible the variation of injection modes which might optimize the metal extraction.

In view of the available batch findings, the multi-step washing process enabled renewal of the extracting solution after each washing stage and thus improved the metal extraction efficiency [25–28]. The enhancement could be as effective as applying a longer reaction time and a higher chelant dosage in single-step washing. In phytoextraction studies, single- or multi-pulse additions were both used to provide the same total dosage of chelant [29,30], although the influence of additional modes was not studied. In recent heap leaching studies, the amounts of metal extraction in each step of multi-step leaching using different chelant concentrations were investigated. It was found that multiple chelant dosages were more effective than a large single dose, while the extraction efficiency decreased with each step of multi-step leaching [31–33]. On the other hand, an extraction preference among different metals (due to metal lability, extraction kinetics and complex stability) was shown under the continuous addition of a low chelant concentration, but not under a single-pulse addition of a high chelant

* Corresponding author. Tel.: +852 2358 7157; fax: +852 2358 1534.
E-mail address: cemclo@ust.hk (I.M.C. Lo).

Table 1
Soil properties and metal contamination.

Sand/silt/clay (%)	96/3.6/0.4
Soil pH	5.55
CEC (meq g^{-1})	17.9
Organic carbon (%)	0.15
BET surface area (m^2 g^{-1})	7.25
Mineralogy	Fe/Cr oxides
Fe/Al/Ca/Mn (mmol kg^{-1})	399/4845/121/1.91
Amorphous Fe/Al/Mn oxide (mmol kg^{-1})	9.1/20/0.15
Ni (mmol kg^{-1})	17.2
Cu (mmol kg^{-1})	14.1
Zn (mmol kg^{-1})	1.1
Pb (mmol kg^{-1})	1.5
Cr (mmol kg^{-1})	15.1

concentration [34]. Furthermore, rinsing with deionized water after chelant addition was shown to play a significant role in metal extraction [35].

These previous findings suggested that varying the chelant injection conditions may significantly influence the effectiveness of the soil flushing process. Therefore, this study aims to investigate the metal transport (breakthrough curve) and cumulative extraction efficiency under four injection modes (step-gradient, single-pulse, multi-pulse, and continuous) using different chelant concentrations (1–20 mmol L^{-1}) and pore-water velocities (2–18 cm h^{-1}) in typical application ranges. Because biodegradable EDDS (S,S-ethylene-diamine-disuccinic acid) has been proposed as a substitute for EDTA (ethylene-diamine-tetraacetic acid) that is persistent and mobile in the natural environment, this study focused on the influence of injection conditions on EDDS-flushing, and compared the result with EDTA-flushing under continuous injection.

2. Experimental methods

2.1. Soil characteristics and chelant solutions

Field-contaminated soil samples were collected from an electroplating site in Guangzhou, China, which had been contaminated by Ni, Cu, Zn, Pb, and Cr for decades. The soil was taken from 25 to 50 cm below the ground surface, air-dried, and passed through a 2-mm sieve. The particle size distribution was determined by sieving and hydrometer methods. The soil pH was measured at a 1:2 soil-to-water ratio and the cation exchange capacity was determined by NH$_4$–Na exchange. The soil organic carbon content was measured by a total organic carbon analyzer-solid sample module (Shimadzu TOC-SSM-5000A). The BET surface area was determined by nitrogen gas adsorption (Micromeritics ASAP2010). Major mineralogy was found using X-ray diffraction analysis (Philips PW1830) and the amount of amorphous Fe/Al/Mn oxide content was measured by ammonium oxalate extraction. Total metal concentrations were

measured by acid digestion with HNO$_3$–HCl–HF in a microwave digester. Table 1 summarizes the soil properties and metal contamination.

The EDDS solution was prepared by mixing the Na$_3$EDDS solution (30% [S,S]-EDDS, Innospec Ltd., HK) with 10 mM sodium nitrate background solution, buffered with 2 mM MES [2-morpholinoethane-sulfonic acid] and adjusted to pH 5.5 by 0.1 M NaOH and HNO$_3$. To avoid photodegradation and biodegradation, the EDDS solutions contained sodium azide (1 g L^{-1}) and were kept in the dark at 4 °C. Various concentrations of EDDS (1, 1.4, 10, and 20 mM, respectively) were used for different injection modes: step-gradient, single-pulse, multi-pulse, and continuous (Table 2). The EDTA solution (1.4 mM Na$_2$EDTA, Sigma–Aldrich) was similarly prepared for comparison under the continuous injection condition.

2.2. Column experiments and injection conditions

Column experiments were performed in 3.6-cm internal diameter and 15-cm long columns at room temperature (21 ± 1 °C). Approximately the same amounts of the soils were packed in small incremental steps to obtain homogeneous columns with uniform bulk density. The soil columns were slowly saturated and pre-conditioned with up-flowing background solution at 2 cm h^{-1} for two weeks, which was sufficient to maintain a stable pH and displace the entrapped or loosely bound metals.

After the pre-conditioning phase, EDDS or EDTA solutions were applied under step-gradient (set 1), single-pulse (set 2), multi-pulse (set 3), or continuous (sets 4–7) injection modes, as shown in Fig. 1. The chelant concentrations and corresponding pore volumes of each injection mode were designed to result in the same total amount of chelant dosage, which was equal to the molar sum of the heavy metals (Ni, Cu, Zn, Pb, and Cr) in the soil.

Continuous injection has been widely studied because of its ease of operation (68.5 pore volume of 1.4 mM EDDS). Step-gradient injection provided a short period of flushing at a high EDDS concentration, followed by flushing with lower concentrations for longer time. Single-pulse injection provided an intensive flushing at a high EDDS concentration (4.8 pore volume of 20 mM EDDS,) and then with background solution (4.8 pore volume of 0 mM EDDS). Multi-pulse injection provided several pulses of intensive EDDS flushing followed by background solution flushing (1.6 pore volume of 20 mM EDDS followed by 1.6 pore volume of 0 mM EDDS), which might allow EDDS-extracted metals to leach out before the next pulse of high EDDS input. Single-pulse and multi-pulse injection modes enable a shorter operation period and generate smaller volumes of flushing solution that require post-remediation of water treatment. On the other hand, under the continuous injection mode, three pore-water velocities (2, 8, and 18 cm h^{-1}) were employed to investigate the importance of pore water velocity. In set 7, EDTA was applied under the same conditions as set 4 (for EDDS) for com-
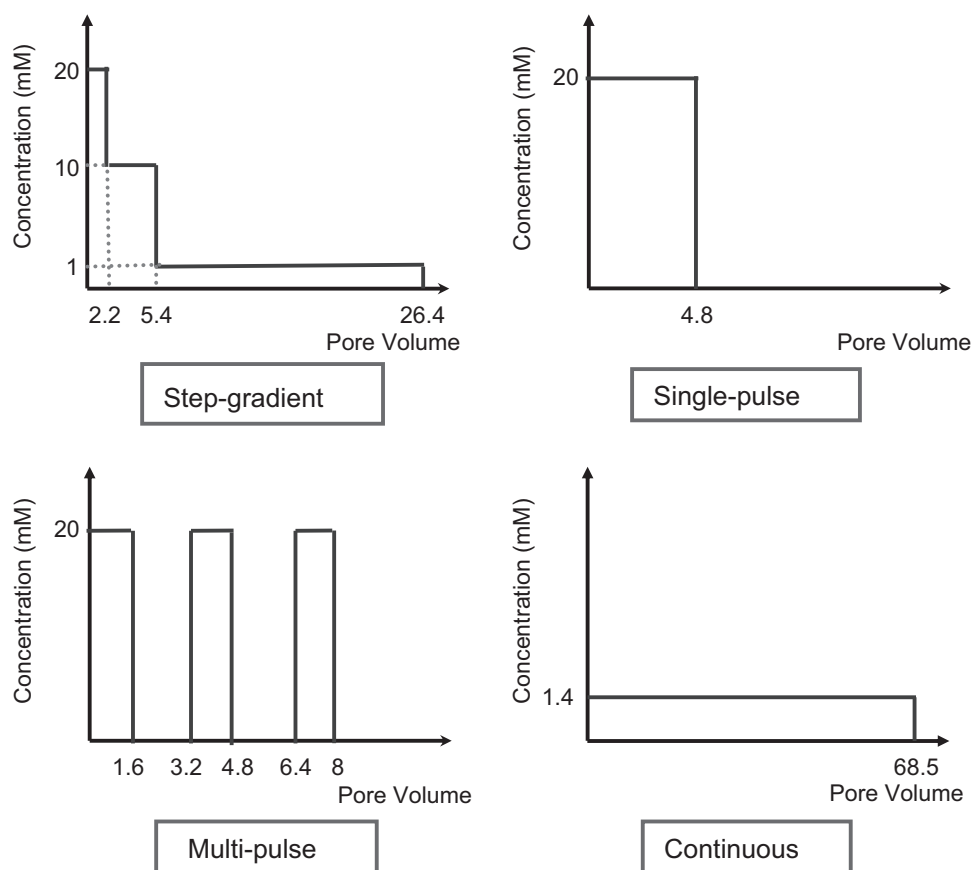
Table 2
Column operational conditions for various injection modes.

	Set 1	Set 2	Set 3
Chelating agent	EDDS	EDDS	EDDS
Chelant concentration	20 mM, 10 mM, 1 mM	20 mM, 0 mM	20 mM, 0 mM, 20 mM, 0 mM, 20 mM, 0 mM
Pore volume	2.2, 3.2, 20	4.8, 4.8	1.6, 1.6, 1.6, 1.6, 1.6, 1.6
Pore-water velocity	8 cm h^{-1}	8 cm h^{-1}	8 cm h^{-1}
Injection mode	Step-gradient	Single-pulse	Multi-pulse

	Set 4	Set 5	Set 6	Set 7
Chelating agent	EDDS	EDDS	EDDS	EDTA
Chelant concentration	1.4 mM	1.4 mM	1.4 mM	1.4 mM
Pore volume	68.5	68.5	68.5	68.5
Pore-water velocity	8 cm h^{-1}	2 cm h^{-1}	18 cm h^{-1}	8 cm h^{-1}
Injection mode	Continuous	Continuous	Continuous	Continuous

Fig. 1. Various EDDS injection conditions (total amounts of applied EDDS were equal to the sum of heavy metals in the soil in all four injection conditions; figures not to scale).

parison. Table 2 summarizes the different operational conditions applied for the four injection modes.

2.3. Data analysis

The effluent samples were periodically taken from the top end and sampling was randomly replicated for quality assurance. The samples were filtered using polypropylene syringes with 0.2-μm membrane filters and stored in amber vials at 4 °C prior to chemical analysis. The effluent pH varied by at most 0.3 during the column experiments. Dissolved metal concentrations (target metals: Ni, Cu, Zn, Pb, and Cr; mineral cations: Al, Ca, Mn, and Fe) were measured by an inductively coupled plasma-optical emission spectrometer (Perkin-Elmer Optima 3000XL). The effluent metal concentrations (mM) were plotted against flushing pore volume to construct the breakthrough curves. Cumulative metal extraction ($mmol\,kg^{-1}$) and mineral dissolution ($mmol\,kg^{-1}$) from the soil columns were calculated based on mass balance (i.e., integrating the area under the breakthrough curves). Comparable results were obtained in the re-run of selected columns, indicating data reliability and reproducibility. The EDDS concentrations were measured by colorimetric analysis at 670 nm absorption peak using UV–visible spectrophotometer (Milton Roy Spectronic 3000) as described in earlier studies [5,6]. Dissolved organic carbon (DOC) concentrations were measured by TOC analyzer (Shimadzu TOC-5000A), from which carbon concentration resulting from EDDS and buffer was subtracted. Dissolved organic matter (DOM) concentrations, calculated by multiplying the DOC concentrations by two, were found to be about $0.7\,mg\,L^{-1}$ throughout the column experiments.

The program Visual MINTEQ version 2.53 [36] was used to calculate the EDDS and metal speciation in the column effluent solutions.

Input parameters were the measured EDDS concentrations, dissolved metal concentrations, DOM concentrations, solution pH, and background ions (Na and NO_3^-). The stability constants for metal–EDDS complexation and EDDS protonation were obtained from previous studies [4–6,37]. The composition of DOM was assumed to be 50% fulvic acid and 50% humic acid; and metal binding to DOM was modelled using the NICA-Donnan model with generic parameters [38]. Possible precipitation of $Al(OH)_3$ and amorphous $Fe(OH)_3$ was considered in the speciation calculation [4–6].

3. Results and discussion

3.1. Step-gradient, single-pulse, multi-pulse, and continuous injection

It is widely recognised that chelants can enhance metal extraction as well as mineral dissolution. Fig. 2 illustrates the breakthrough curves of the target metals (Ni, Cu, Zn, Pb, and Cr) and the mineral cations (Fe, Al, Ca, and Mg) under step-gradient, single-pulse, and multi-pulse EDDS injection (as shown in Table 2). In general, the extracted amounts of Ni and Cu were more substantial than that of Zn and Pb, mainly due to higher initial metal loadings (Table 1). However, because Cr primarily existed as Fe/Cr oxides in this soil, its marginal extraction was associated with Fe dissolution and thus not discussed herein.

Comparing the breakthrough curves, it is noted that a prolonged step of 20 mM EDDS single-pulse injection did not appear to improve metal extraction (comparing the area under the breakthrough curve of the first 4.8 pore volumes in Fig. 2a and b), but resulted in a greater amount of mineral dissolution (Fig. 2d and
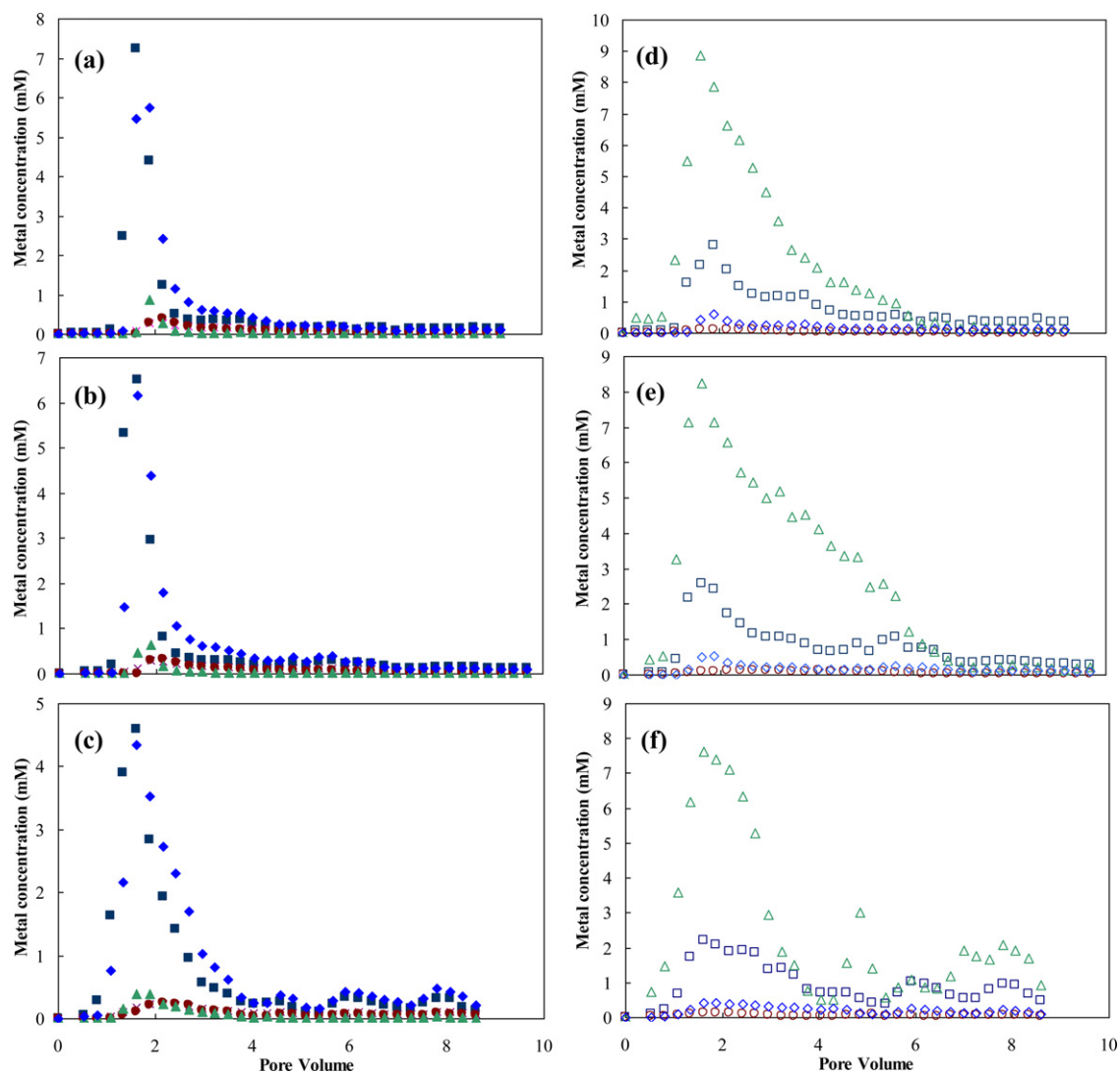
Fig. 2. Breakthrough curves of target metals and mineral cations under different EDDS injection conditions at pH 5.5: (a&d) step-gradient, (b&e) single-pulse, and (c&f) multi-pulse ((a-c) target metals: ■ Ni; ◆ Cu; ▲ Zn; ● Pb; ✕ Cr; (d-f) mineral cations: □ Al; ◇ Fe; △ Ca; ○ Mg; only the first ten pore volumes are shown for better comparison).

e). As most of the extractable metals (i.e., the major peaks) were mobilized during the first injection step, a longer pulse of high EDDS concentration in single-pulse injection only provided a larger amount of free EDDS for promoting mineral dissolution. Under multi-pulse injection (Fig. 2c and f), a shorter initial pulse produced less sharp peaks while the following pulse injections led to multiple minor peaks. This indicates that metal extraction and mineral dissolution took place in response to subsequent pulse injections, but to a lesser extent compared with the first pulse of the same EDDS concentration. On the contrary, continuous injection of a low EDDS concentration (1.4 mM) resulted in much lower and broader peaks (with maximum metal concentrations of only 0.03–0.4 mmol L^{-1}, figures not shown) and demonstrated an obvious preference in metal breakthrough due to metal exchange [5,12].

As biodegradation of EDDS was negligible in the presence of sodium azide in the solution, the retarded breakthrough of EDDS and the difference of influent/effluent EDDS concentrations (Fig. 3) reflected EDDS adsorption on the soil, which was also observed in previous studies [4,6,19,39]. Nevertheless, at least a significant part of EDDS adsorption was weak and reversible as shown by overshoot (i.e., desorption) of EDDS concentrations when the influent EDDS concentration was reduced in step-gradient injection

(Fig. 3a) or when background solution was applied in single-pulse and multiple-pulse injections (Fig. 3b and c). This was consistent with recent spectroscopic evidence of outer-sphere complexation and hydrogen bonding of EDDS adsorption on mineral oxides [7,8].

Speciation calculation was then performed using the measured concentrations of EDDS, metal and DOM in the effluent solution (Fig. 3). Because of limited dissolution of organic matter from the soil columns (about 0.7 mg L^{-1}), DOM–metal binding played an insignificant role in this study. It was found that Al and Fe precipitation as well as EDDS complexation with Ca, Mn and Mg were unimportant; only a small amount of Al(OH)$_{3(s)}$ might exist for a short period of time at the beginning of flushing process. There was a substantial decrease of uncomplexed EDDS in the first two pore volumes along with the major peaks of metal extraction. Under step-gradient and single-pulse injections (Fig. 3a and b), uncomplexed EDDS was present throughout the flushing process and thus all metals (Ni, Cu, Zn and Pb) were complexed with EDDS. As expected, single-pulse injection resulted in a longer period of high proportion of uncomplexed EDDS, representing an inefficient use of EDDS input for metal complexation. On the contrary, under multiple-pulse injection, there was little or no uncomplexed EDDS before the second EDDS injection step, resulting in a portion of Ni,
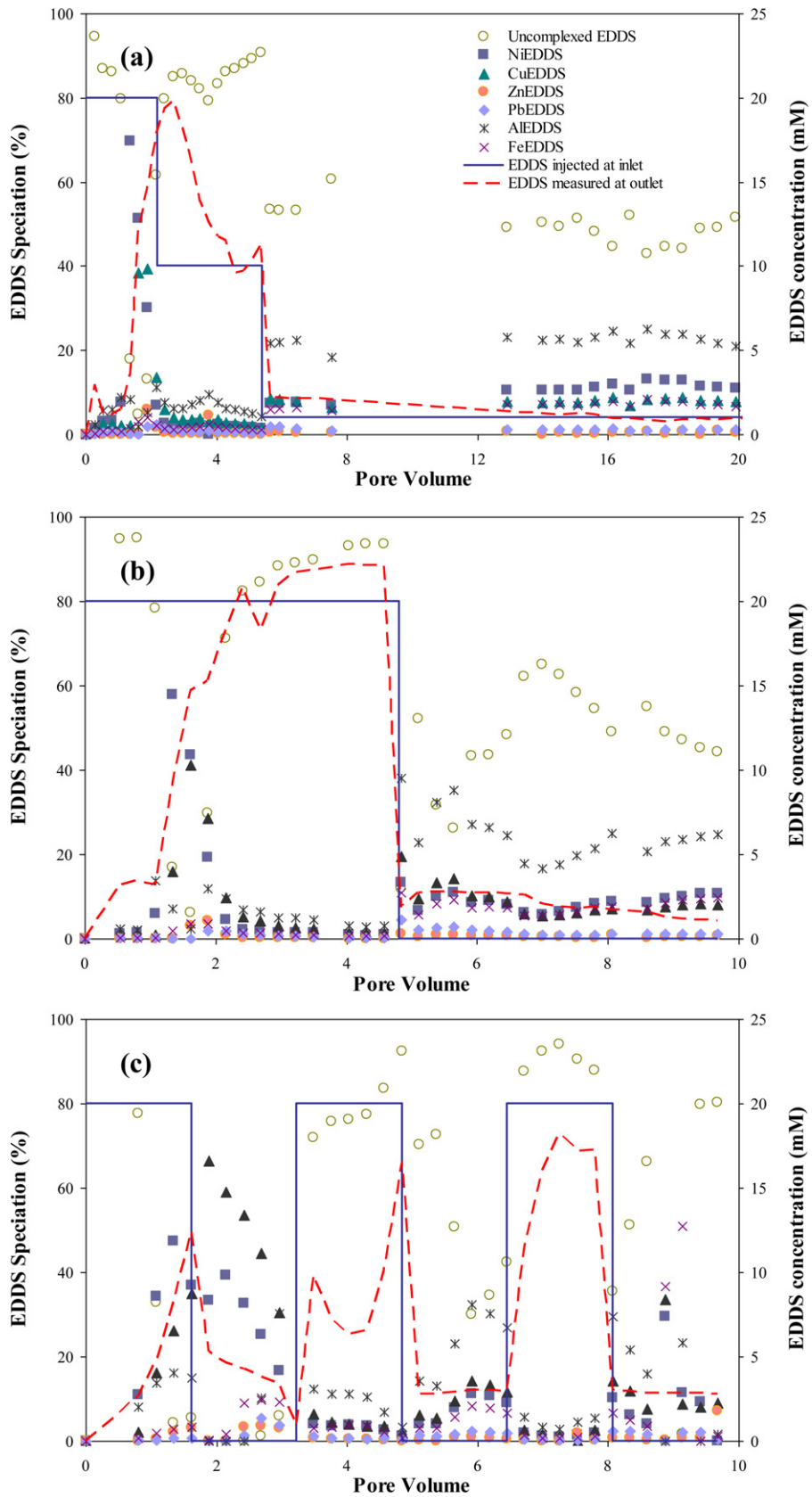
Fig. 3. EDDS concentration and speciation in the column effluents under different EDDS injection conditions: (a) step-gradient, (b) single-pulse, and (c) multi-pulse.
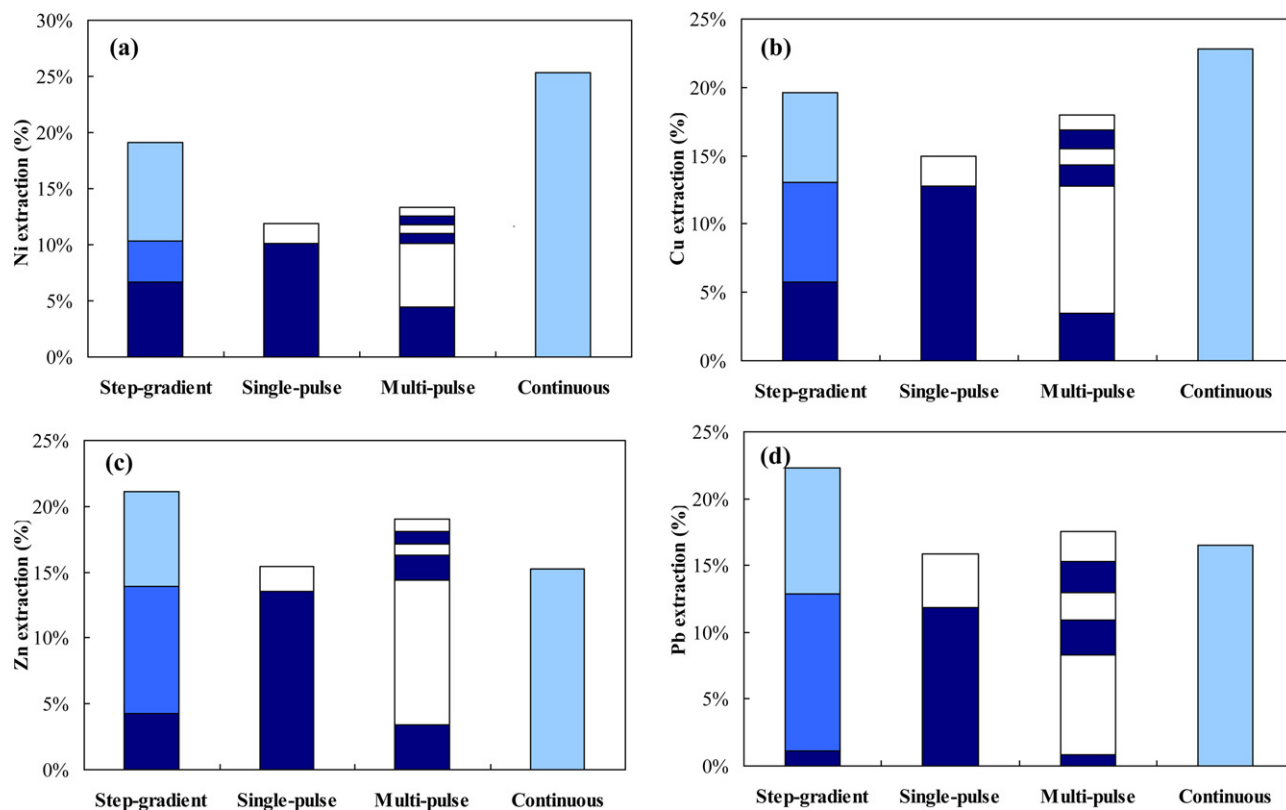
Fig. 4. Metal extraction by individual steps of step-gradient, single-pulse, multi-pulse, and continuous EDDS injection using the same total EDDS dosage: (a) Ni, (b) Cu, (c) Zn, and (d) Pb (■ 20 mM EDDS; ■ 10 mM EDDS; ■ 1 or 1.4mM EDDS; o 0 mM EDDS (i.e., background solution).

Zn and Pb being uncomplexed with EDDS (figure not shown), probably due to metal exchange [5,6,39]. After the second and third injection steps, weakly adsorbed EDDS and metal–EDDS complexes were partially extracted by background solution.

Based on mass balance calculations under the metal breakthrough curves, the extraction efficiency of individual steps of different injection modes (under the same total EDDS dosage) are compared in Fig. 4. While single-pulse injection offers advantages in requiring a shorter operation time and less flushing solution, it does not provide a sufficiently long flushing time for rate-limited extraction of less labile metal fractions on the soil. It was found that the extraction kinetics of Ni, Cu, Zn and Pb were significantly slower from oxides and organic matter fractions than from exchangeable and carbonate fractions [15,40]. As a matter of fact, the overall metal extraction for step-gradient injection was higher than single-pulse and multi-pulse injections mainly owing to the efficiency of the prolonged final step of 1-mM EDDS flushing. Moreover, multi-pulse injection was consistently more effective than single-pulse injection, although the differences might be quite small in some cases (Ni and Pb), which is in agreement with previous results [33].

It is also interesting to evaluate the extraction efficiency of the rinsing steps (with background solution) of multi-pulse injection. The first rinsing step was remarkably effective in removing newly formed metal–EDDS complexes, which might otherwise be entrapped in soil pores or weakly re-adsorbed on the soil surfaces until further EDDS-flushing [5,32,35]. This was corroborated by the speciation calculation (Fig. 3c) that both EDDS-complexed and uncomplexed Ni, Zn and Pb were observed during the first rinsing step. The combined efficiency of the first pulse injection and rinsing step of multi-pulse injection was comparable to the efficiency of single-pulse injection, although only one-third of total EDDS amount was applied. However, there was a diminishing efficiency in the following rinsing steps because the extractable amounts of metals decreased with the second and third pulse injections. It was also reported that the first one to three pore volumes of rinsing with water removed most mobile metals that were left behind after soil leaching [35].

Comparing the overall extraction (Fig. 4), single-pulse injection was the least effective for all metals; continuous injection outperformed the other modes for Ni and Cu extraction, whereas step-gradient injection was the best for Zn and Pb extraction. Metal exchange of newly formed Zn–EDDS and Pb–EDDS complexes with other sorbed metals (Ni and Cu), which was shown to suppress Zn and Pb extraction [5,12], might have occurred under continuous injection because EDDS was applied at a low concentration throughout the flushing process. Nevertheless, step-gradient injection extracted a significant portion of easily extractable Ni and Cu during the initial flushing step with high EDDS concentration, thus reducing the degree of metal exchange and producing higher Zn and Pb extraction efficiencies in the subsequent flushing steps (Fig. 4c and d).

It should also be noted that there are other concerns in designing the injection conditions. Using high chelant dosages could lead to phyto-toxicity (e.g., necrosis and loss of dry weight were observed at 25 mM [30]), mineral dissolution and pore clogging due to soil dispersion [16,17,20]. However, using low chelant dosages would require longer operation times and larger volumes of flushing solution, i.e., higher remediation costs [20,28]. In view of the above concerns and the results of this study, continuous injection is preferred for its simple operation if Ni or Cu is the major contaminant, while step-gradient injection is suggested if Zn or Pb is the priority target. Furthermore, step-gradient injection could possibly be improved with an additional water-rinsing step of a few pore volumes following the initial step of high EDDS concentration.
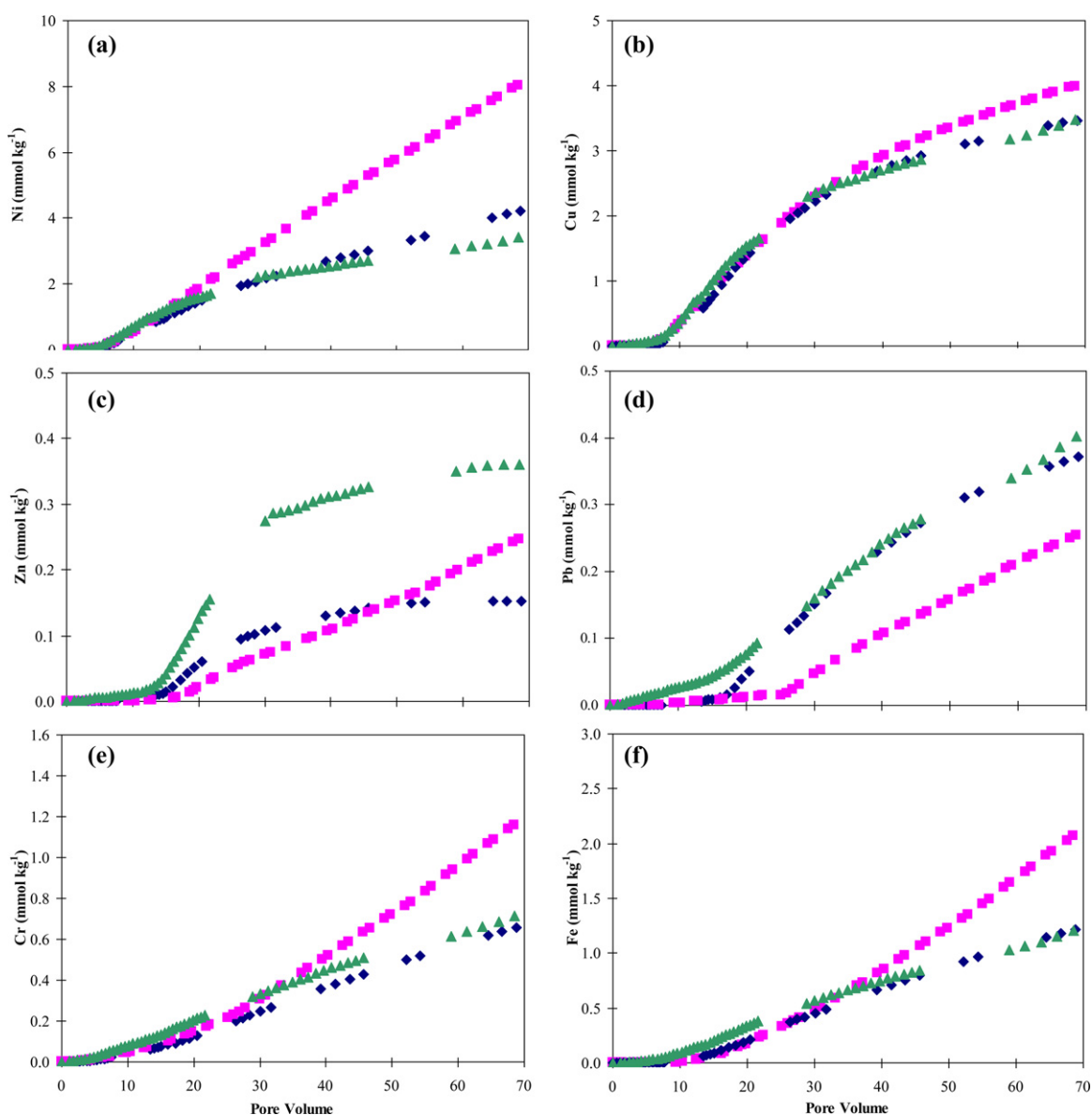
Fig. 5. Metal extraction by continuous EDDS-flushing at different pore-water velocities: (a) Ni, (b) Cu, (c) Zn, (d) Pb, (e) Cr, and (f) Fe (■ 2 cm h-1; ◆ 8 cm h-1; ▲ 18 cm h-1).

3.2. Variation in pore-water velocities and comparison with EDTA-flushing

As both EDDS-enhanced metal extraction and metal exchange of metal–EDDS complexes are rate-limited in the order of hours [5,8,15], a variation of pore-water velocity, as well as the resulting residence time, was suspected to affect the metal breakthrough and extraction effectiveness of EDDS-flushing. Fig. 5 illustrates the cumulative metal extraction as a function of pore volume of continuous flushing. As expected, Ni and Cu extraction was more significant at $2 \, cm \, h^{-1}$ than at 8 and $18 \, cm \, h^{-1}$ (Fig. 5a and b) because of longer residence time. Similar trends were observed for Cr and Fe dissolution (Fig. 5e and f). However, the discrepancies at different pore-water velocities did not appear until the later stage of flushing, suggesting that Ni/Cu extraction and Fe/Cr dissolution were not rate-limited in the early stages. It was likely that Ni and Cu were first extracted from labile fractions, while Cr and Fe were initially dissolved from amorphous oxides (Table 1), thereby manifesting fast kinetics. Moreover, Ni/Cu extraction and Fe/Cr dissolution were similar at 8 and $18 \, cm \, h^{-1}$, reflecting a lower sensitivity to residence time in this range.

On the contrary, Zn and Pb extraction was retarded and reduced with decreasing pore-water velocity (Fig. 5c and d). It has been shown that a part of the newly formed Zn–EDDS and Pb–EDDS complexes were dissociated due to metal exchange and re-adsorbed onto the soil surfaces [5,19]. The tendency of a metal–EDDS complex to undergo metal exchange was negatively correlated with the complex stability and positively correlated with the sorption affinity of the metal centre [5,11,24]. Hence, Zn–EDDS and Pb–EDDS complexes were more prone to metal exchange than Ni–EDDS and Cu–EDDS complexes. The significance of metal exchange was also found to be greater with a lower chelant-to-metal molar ratio [12], at a longer travel distance, or in a soil containing larger amounts of labile (weakly sorbed) metal fractions [39]. The results of this study further suggest that the influence of metal exchange of Zn–EDDS and Pb–EDDS complexes was more substantial at a lower pore-water velocity (i.e., longer residence time) because of the rate-limitation of the exchange reaction.

To compare EDDS-flushing with EDTA-flushing, Fig. 6 illustrates the cumulative metal extraction and mineral dissolution under a continuous chelant injection mode. The effectiveness was comparable for Cu and Zn extraction, while EDTA-flushing was more
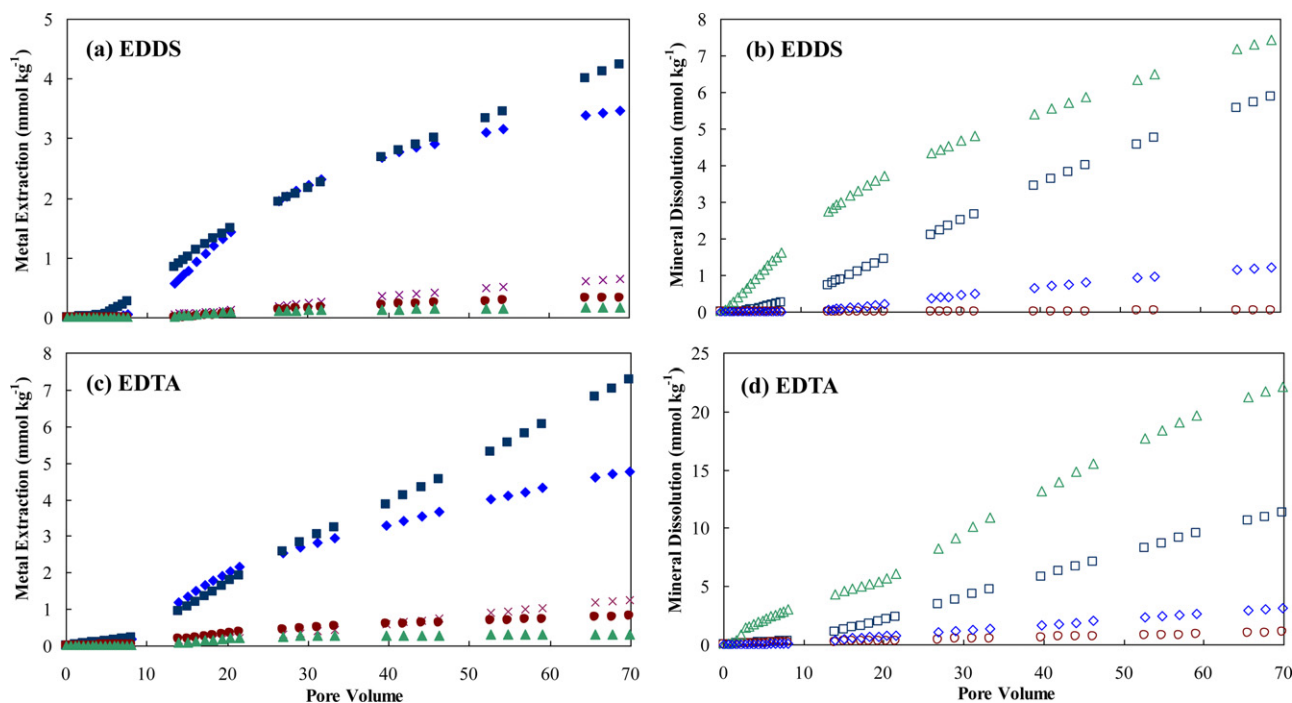
Fig. 6. Metal extraction and mineral dissolution by continuous EDDS- or EDTA-flushing: (a) metal extraction by EDDS-flushing, (b) mineral dissolution by EDDS-flushing, (c) metal extraction by EDTA-flushing, and (d) mineral dissolution by EDTA-flushing (■ Ni; ◆ Cu; ▲ Zn; ● Pb; ✕ Cr; □ Al; ◇ Fe; △ Ca; ○ Mg).

efficient for Ni and Pb extraction. Previous studies also reported that EDTA could achieve better Pb extraction than EDDS [9,13]. This could primarily be attributed to the difference in complex stability [37]. Recent ATR-FTIR results revealed that ring structure of zwitterionic EDDS is formed with stable intramolecular hydrogen bond, while protonated amine of zwitterionic EDTA forms hydrogen bonds with two neighbouring carboxyl groups (intensifying their negative charge) [7,8], accounting for the discrepancy in their metal extraction efficiency. As Ni and Pb can form stronger complexes with EDTA than EDDS, they became more extractable and less prone to subsequent metal exchange during EDTA-flushing. However, it should be noted that mineral cations were also dissolved to a greater extent by EDTA-flushing (nearly doubled) because of higher complexing ability of EDTA.

4. Conclusions

In situ soil flushing can be performed using various chelant injection conditions; however, the design of flushing conditions is unclear. Therefore, this study investigated the effectiveness of step-gradient, single-pulse, multi-pulse, and continuous injection modes, and the significance of pore-water velocities. Single-pulse injection was found to be the least effective for overall extraction of all the metals considered. Multi-pulse injection was consistently more effective than single-pulse injection, but the differences were quite small for Ni and Pb extraction. Continuous injection outperformed other modes for Ni and Cu extraction and was preferred for its simple operation. Nevertheless, for Zn and Pb extraction, step-gradient injection was the best option because it mitigated the influence of metal exchange. In addition, a rinsing step with background solution following the initial EDDS injection of multi-pulse could effectively remove newly formed metal–EDDS complexes from the soil pores before further EDDS-flushing. Furthermore, the influence of pore-water velocity was metal-specific. A decrease in pore-water velocity provided a longer residence time for greater Ni and Cu extraction, but enhanced the rate-limited metal exchange of Zn–EDDS and Pb–EDDS complexes and thus hindered Zn and Pb

extraction. In consideration of these results, slower and continuous injection is recommended for Ni or Cu removal, while faster and step-gradient injection is suggested for Zn or Pb removal, depending on which metal removal priority in particular soil remediation projects.

References

[1] B. Nowack, Environmental chemistry of aminopolycarboxylate chelating agents, Environ. Sci. Technol. 36 (2002) 4009–4016.
[2] B. Nowack, R. Schulin, B.H. Robinson, Critical assessment of chelant-enhanced metal phytoextraction, Environ. Sci. Technol. 40 (2006) 5225–5232.
[3] D. Lestan, C.L. Luo, X.D. Li, The use of chelating agents in the remediation of metal-contaminated soils: a review, Environ. Pollut. 153 (2008) 3–13.
[4] G.F. Koopmans, W.D.C. Schenkeveld, J. Song, Y. Luo, J. Japenga, E.J.M. Temminghoff, Influence of EDDS on metal speciation in soil extracts: measurement and mechanistic multicomponent modeling, Environ. Sci. Technol. 42 (2008) 1123–1130.
[5] D.C.W. Tsang, T.C.M. Yip, I.M.C. Lo, Kinetic interactions of EDDS with soils. 2. Metal–EDDS complexes in uncontaminated and metal-contaminated soils, Environ. Sci. Technol. 43 (2009) 837–842.
[6] T.C.M. Yip, D.C.W. Tsang, K.T.W. Ng, I.M.C. Lo, Kinetic interactions of EDDS with soils. 1. Metal resorption and competition under EDDS deficiency, Environ. Sci. Technol. 43 (2009) 831–836.
[7] K. Noren, J.S. Loring, J.R. Bargar, P. Persson, Adsorption mechanisms of EDTA at the water–iron oxide interface: implications for dissolution, J. Phys. Chem. C 113 (2009) 7762–7771.
[8] T.C.M. Yip, D.C.W. Tsang, I.M.C. Lo, Interactions of chelating agents with Pb-goethite at the solid–liquid interface: Pb extraction and re-adsorption, Chemosphere 81 (2010) 415–421.
[9] S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin, B. Nowack, Extraction of heavy metals from soils using biodegradable chelating agents, Environ. Sci. Technol. 38 (2004) 937–944.
[10] W. Zhang, D.C.W. Tsang, I.M.C. Lo, Removal of Pb by EDTA-washing in the presence of hydrophobic organic contaminants or anionic surfactant, J. Hazard. Mater. 155 (2008) 433–439.
[11] M. Komarek, A. Vanek, J. Szakova, J. Balik, V. Chrastny, Interactions of EDDS with Fe- and Al-(hydr)oxides, Chemosphere 77 (2009) 87–93.

[12] D.Y.S. Yan, M.M.T. Yui, T.C.M. Yip, D.C.W. Tsang, I.M.C. Lo, Influence of EDDS-to-metal molar ratio, solution pH, and soil-to-solution ratio on metal extraction under EDDS deficiency, J. Hazard. Mater. 178 (2010) 890–894.

[13] T.C.M. Yip, D.Y.S. Yan, M.M.T. Yui, D.C.W. Tsang, I.M.C. Lo, Heavy metal extraction from an artificially contaminated sandy soil under EDDS deficiency: significance of humic acid and chelant mixture, Chemosphere 80 (2010) 416–421.

[14] D. Fangueiro, A. Bermond, E. Santos, H. Carapuca, A. Duarte, Kinetic approach to heavy metal mobilization assessment in sediments: choose of kinetics equations and models to achieve maximum information, Talanta 66 (2005) 844–857.

[15] T.C.M. Yip, D.C.W. Tsang, K.T.W. Ng, I.M.C. Lo, Empirical modeling of heavy metal extraction by EDDS from single-metal and multi-metal contaminated soils, Chemosphere 74 (2009) 301–307.

[16] M.A.M. Kedziorek, A.C.M. Bourg, Solubilization of lead and cadmium during the percolation of EDTA through a soil polluted by smelting activities, J. Contam. Hydrol. 40 (2000) 381–392.

[17] M.A. Mayes, P.M. Jardine, I.L. Larsen, S.C. Brooks, S.E. Fendorf, Multispecies transport of metal–EDTA complexes and chromate through undisturbed columns of weathered fractured saprolite, J. Contam. Hydrol. 45 (2000) 243–265.

[18] V.M. Vulava, J.C. Seaman, Mobilization of lead from highly weathered porous material by extracting agents, Environ. Sci. Technol. 34 (2000) 4828–4834.

[19] L. Hauser, S. Tandy, R. Schulin, B. Nowack, Column extraction of heavy metals from soils using the biodegradable chelating agent EDDS, Environ. Sci. Technol. 39 (2005) 6819–6824.

[20] D.C.W. Tsang, W. Zhang, I.M.C. Lo, Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils, Chemosphere 68 (2007) 234–243.

[21] M.A.M. Kedziorek, A. Dupuy, A.C.M. Bourg, F. Compere, Leaching of Cd and Pb from a polluted soil during the percolation of EDTA: laboratory column experiments modeled with a non-equilibrium solubilization step, Environ. Sci. Technol. 32 (1998) 1609–1614.

[22] J.C. Friedly, D.B. Kent, J.A. Davis, Simulation of the mobility of metal–EDTA complexes in groundwater: the influence of contaminant metals, Environ. Sci. Technol. 36 (2002) 355–363.

[23] D.C.W. Tsang, I.M.C. Lo, K.L. Chan, Modeling the transport of metals with rate-limited EDTA-promoted extraction and dissolution during EDTA-flushing of copper-contaminated soils, Environ. Sci. Technol. 41 (2007) 3660–3667.

[24] D.B. Kent, J.A. Davis, J.L. Joye, G.P. Curtis, Influence of variable chemical conditions on EDTA-enhanced transport of metal ions in mildly acidic groundwater, Environ. Pollut. 153 (2008) 44–52.

[25] P. Theodoratos, N. Papassiopi, T. Georgoudis, A. Kontopoulos, Selective removal of lead from calcareous polluted soils using the Ca–EDTA salt, Water Air Soil Pollut. 122 (2000) 351–368.

[26] T.A. Kirpichtchikova, A. Manceau, L. Spadini, F. Panfili, M.A. Marcus, T. Jacquet, Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence. EXAFS spectroscopy, chemical extraction, and thermodynamic modeling, Geochim. Cosmochim. Acta 70 (2006) 2163–2190.

[27] A. Polettini, R. Pomi, G. Calcagnoli, Assisted washing for heavy metal and metalloid removal from contaminated dredged materials, Water Air Soil Pollut. 196 (2009) 183–198.

[28] Z. Zou, R.L. Qiu, W. Zhang, H.Y. Dong, Z.H. Zhao, T. Zhang, X.G. Wei, X.D. Cai, The study of operating variables in soil washing with EDTA, Environ. Pollut. 157 (2009) 229–236.

[29] H. Grcman, D. Vodnik, S.V. Bolta, D. Lestan, Ethylenediaminedissuccinate as a new chelate for environmentally safe enhanced lead phytoextraction, J. Environ. Qual. 32 (2003) 500–506.

[30] S. Tandy, R. Schulin, B. Nowack, Uptake of metals during chelant-assisted phytoextraction with EDDS related to the solubilized metal concentration, Environ. Sci. Technol. 40 (2006) 2753–2758.

[31] M. Udovic, Z. Plavc, D. Lestan, The effect of earthworms on the fractionation, mobility and bioavailability of Pb, Zn and Cd before and after soil leaching with EDTA, Chemosphere 70 (2007) 126–134.

[32] N. Finzgar, D. Lestan, Multi-step leaching of Pb and Zn contaminated soil with EDTA, Chemosphere 66 (2007) 824–832.

[33] M. Pociecha, D. Lestan, EDTA leaching of Cu contaminated soil using electrochemical treatment of the washing solution, J. Hazard. Mater. 165 (2009) 533–539.

[34] B. Sun, F.J. Zhao, E. Lombi, S.P. McGrath, Leaching of heavy metals from contaminated soils using EDTA, Environ. Pollut. 113 (2001) 111–120.

[35] N. Finzgar, D. Lestan, The two-phase leaching of Pb, Zn and Cd contaminated soil using EDTA and electrochemical treatment of the washing solution, Chemosphere 73 (2008) 1484–1491.

[36] J.P. Gustafsson, Visual MINTEQ Version 2.53, Department of Land and Water Resources Engineering, Royal Institute of Technology, Stockholm, Sweden, 2008.

[37] A.E. Martell, R.M. Smith, R.J. Motekaitis, NIST Critically Selected Stability Constants of Metal Complexes, Version 8.0, National Institute of Standards and Technology, Gaithersburg, MD, 2004.

[38] C.J. Milne, D.G. Kinniburgh, W.H. van Riemsdijk, E. Tipping, Generic NICA-Donnan model parameters for metal-ion binding by humic substances, Environ. Sci. Technol. 37 (2003) 958–971.

[39] I.M.C. Lo, D.C.W. Tsang, T.C.M. Yip, F. Wang, W. Zhang, Significance of metal exchange in EDDS-flushing column experiments, Chemosphere 83 (2011) 7–13.

[40] W. Zhang, H. Huang, F. Tan, H. Wang, R. Qiu, Influence of EDTA washing on the species and mobility of heavy metals residual in soils, J. Hazard. Mater. 173 (2010) 369–376.