

Effects of surfactants on low-molecular-weight organic acids to wash soil zinc

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Abstract Soil washing is an effective approach to the removal of heavy metals from contaminated soil. In this study, the effects of the surfactants sodium dodecyl sulfate, Triton X-100, and non-ionic polyacrylamide (NPAM) on oxalic acid, tartaric acid, and citric acid used to remove zinc from contaminated soils were investigated. The Zn removal efficiencies of all washing solutions showed a logarithmic increase with acid concentrations from 0.5 to 10.0 g/L, while they decreased as pH increased from 4 to 9. Increasing the reaction time enhanced the effects of surfactants on Zn removal efficiencies by the acids during washing and significantly ($P < 0.05$) improved the removal under some mixed cases. Oxalic acid suffered antagonistic effects from the three surfactants and seriously damaged soil nutrients during the removal of soil Zn. Notably, the three surfactants caused synergistic effects on tartaric and citric acid during washing, with NPAM leading to an increase in Zn removal by 5.0 g/L citric acid of 10.60 % ($P < 0.05$) within 2 h. NPAM also alleviated the loss of cation exchange capacity of washed soils and obviously improved soil nitrogen concentrations. Overall, combining citric acid with NPAM offers a promising approach to the removal of zinc from contaminated soil.

Keywords Soil washing · Low-molecular-weight organic acid · Sodium dodecyl sulfate · Triton X-100 · Non-ionic polyacrylamide · Zinc

Introduction

Soil heavy metal pollution is one of the main environmental issues worldwide as heavy metals are widespread and non-biodegradable (Zhang et al. 2010a, b, c; Soleimani et al. 2010; Gusiati and Klimiuk 2012). Zinc (Zn) is an essential trace nutrient element required by many organisms (Marichali et al. 2014). However, excess Zn in soil, especially in agricultural areas, poses a potential threat to humans and the environment (Rossato et al. 2011; Dziubanek et al. 2015). Soil Zn contents have dramatically increased in recent decades as a result of anthropogenic activities such as mining, smelting, transportation, and the abuse of certain pesticides and fertilizers (Zaccone et al. 2010; Torres et al. 2012; Liu et al. 2013). Consequently, it is essential to remediate Zn-contaminated soils.

Many approaches such as electrokinetic remediation, soil replacement or filling, stabilization, and bioremediation have been widely applied to repair heavy-metal-contaminated soils (Maturi et al. 2006; Dellisanti et al. 2009; Vargas-García et al. 2012; Ali et al. 2013). Although these approaches can efficiently restore metal-contaminated soils to some extent (Zhang et al. 2010a, b, c), they usually show low efficiency for high contamination levels (Dermont et al. 2008) or require long periods of time. In contrast, soil washing, which consists of a series of physical or chemical techniques to remove heavy metals from contaminated soils, can remove high levels of heavy metals in a short period of time (Bolan et al. 2014; Kulikowska et al. 2015).

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Chemical leaching, which is the major soil washing technology, requires selection of an appropriate washing reagent. To date, many types of reagents, including acid/alkali, salt, chelating agents, and surfactants, have been shown to have the ability to remove target metals from soils (Moon et al. 2012; Torres et al. 2012) via ion exchange, adsorption, and chelating reactions (Dermont et al. 2008; Pocięcha et al. 2010). However, strong acids leach soil nutrients and other non-contaminant elements heavily, while inorganic salts cause soil salinization and destroy the basic nature of the soil (Makino et al. 2006; Torres et al. 2012). Although synthetic chelating agents such as ethylenediaminetetraacetic acid (EDTA), Na₂-EDTA, and nitrilotriacetic acid (NTA) have been shown to be effective at removing soil heavy metals (Giannis et al. 2009; Yang et al. 2012; Lo et al. 2012), they have also caused secondary pollution problems because of poor biodegradability (Di Palma et al. 2005; Tsang et al. 2007; Zhang et al. 2010a, b, c; Begum et al. 2012). Consequently, the selection of an appropriate reagent is essential to the removal of target metals by soil washing (Moutsatsou et al. 2006).

In contrast, low-molecular-weight organic acids (LMWOAs) are more biodegradable and have less secondary ecological risks (Wen et al. 2009) because they can be produced by plant roots or microorganisms (Schwab et al. 2008). Some LMWOAs such as oxalic acid, tartaric acid, citric acid, and acetic acid have been applied during soil washing in recent years (Makino et al. 2006; Moon et al. 2012), and these compounds are gradually replacing synthetic chelating agents as the major soil leaching reagents (Bolan et al. 2014). However, their abilities to remove soil heavy metals are not as effective as those of inorganic acids or chelating agents. Hence, it is necessary to identify new approaches to improve the efficiency of heavy metal removal from contaminated soils by LMWOAs.

Surfactants are amphiphilic molecules (Chang et al. 2005; Gupta et al. 2010) that can affect the adsorption and desorption of soil colloids through adsorption onto surfaces or interfaces with them (Ehsan et al. 2006; Zhang et al. 2008; Aşçı et al. 2008), which results in dispersion of soil colloids and improved solubility and mobility of heavy metals ions (Giannis et al. 2007). Two common surfactants, sodium dodecyl sulfate (SDS) and Triton X-100 (TX-100), have been applied to enhance removal of soil contaminants (Torres et al. 2012), including heavy metals (Song et al. 2008; Gupta et al. 2010). Indeed, addition of these compounds into EDTA resulted in increased Cu removal efficiencies (Ramamurthy et al. 2008). Yuan et al. (2010) reported that EDTA mixed with TX-100 could enhance the Zn removal efficiencies in sediments. However, information regarding the interactions of LMWOA and surfactants during removal of heavy metals from soil is scarce, especially for Zn. In addition, non-ionic polyacrylamide (NPAM) is a common non-ionic flocculant

for wastewater disposal and soil improvement owing to its large surface (Dai et al. 2014; Prats et al. 2014), which results in its surfactant characteristics. Moreover, almost no research has been conducted to investigate the use of NPAM during washing of heavy-metal-contaminated soil. In addition, few studies have been conducted to improve the washing of soil heavy metals with LMWOAs. Therefore, this study was conducted to investigate whether the use of surfactants would be an effective approach to enhance the capacity of LMWOAs to remove soil Zn.

The specific objectives of the present study were (1) to compare the abilities of the three LMWOAs, oxalic acid, tartaric acid, and citric acid, to remediate zinc contaminated soil; (2) to assess the effects of concentration, time, and pH on Zn removal; (3) to confirm whether SDS, NPAM, and TX-100 could enhance or weaken the removal of soil Zn by LMWOAs; and (4) to compare soil properties before and after washing.

Materials and methods

Soil preparation

Paddy soil samples (0–20 cm) were collected from a farm near a lead and zinc mine in Wushihe, Sichuan (29° 15' N, 102° 53' E), that had been impacted by irrigation with mining and smelting wastewater. Samples were air-dried at room temperature, after which the non-soil parts were removed and the remaining soil material was homogenized and sieved through a 2-mm mesh for washing. The contaminated soils (1.0 g) were digested with 1:2:2 (v/v/v) HNO₃/HCl/HClO₄ to extract the total Zn (Wang et al. 2014).

Batch experiments

LMWOAs for soil Zn washing alone

Oxalic acid (OA), tartaric acid (TA), and citric acid (CA) (Guoyao Group Chemical Reagent Co. Ltd., Chengdu, China) were prepared in concentrations of 0.5, 1.0, 2.0, 5.0, or 10.0 g/L. Next, 20.00 mL of prepared washing liquid was pipetted into cleaned polycarbonate plastic bottles containing 2.00 g of soils to give a soil-to-liquid (S/L) ratio of 1:10 (w/v). The bottles were subsequently sealed and transferred into a shaker for oscillation (25 °C±0.5 °C, 200 rpm) for 1, 2, and 4 h, respectively, after which they were centrifuged for 10 min at 3000 rpm and the supernatants were passed through a 0.45-µm filter membrane. Finally, the concentrations of Zn in the filtrate were determined by atomic absorption spectrophotometry (WFX-110, Shanghai, China).

Mixing of surfactant solutions for soil Zn washing

SDS, NPAM (0.5 g each; Guoyao Group Chemical Reagent Co., Ltd, Chengdu, China), and 0.5 ml TX-100 (Amresco, Solon, Ohio, USA) were dispersed in 1.00 L of 0.5, 1.0, 2.0, 5.0, and 10.0 g/L OA, TA, and CA. The solutions were then stirred continuously using a glass stirring rod until they reached homogeneous. Next, the prepared mixtures were pipetted to wash the Zn soils under the same control conditions as LMWOA solutions alone (S/L, 1:10) and then oscillated for 1, 2, or 4 h (25 ± 0.5 °C, 200 rpm). The supernatants were subsequently centrifuged for 10 min (3000 rpm), after which they were passed through a 0.45- μ m filter membrane. Finally, the Zn concentrations of the filtrates were measured as described above.

Effect of pH on soil Zn removal

First, 20 mL of 5.0 g/L LMWOAs alone and their corresponding mixtures with 0.5 g/L SDS, NPAM, or 0.5 mL/L TX-100 solutions were added into 2.00 g of soils in bottles. The pH values of the reaction systems were subsequently adjusted to 4.0, 7.0, and 9.0 (± 0.05) with diluted HNO₃ or NaOH and then shaken for 1 h (25 ± 0.5 °C, 200 rpm). Finally, the suspensions were centrifuged (3000 rpm) and filtered in preparation for subsequent analysis as described above. Deionized water washing solution was used as a control, and all analyses were conducted in triplicate to ensure reproducibility and reliability. Zn removal efficiency was calculated by the following equation:

$$R = \left(M_{\text{diss}} / M_{\text{total}} \right) \times 100\%, \quad (1)$$

where R is the removal efficiency, M_{diss} is the heavy metal mass dissolved by extraction from soil, and M_{total} is the total heavy metal mass of the soil.

Soil properties before and after washing

The soils washed with deionized water, 5.0 g/L LMWOAs and 0.5 g/L SDS, NPAM, and 0.5 mL/L mixed solutions were collected after 2 h of reaction at 1:10 S/L and an initial pH 4 ± 0.05 . The residual heavy metals and soil properties were then analyzed as described by Bao (2005). Additionally, soil pH was measured in a 1:2.5 soil/water mixture (w/v). Soil cation exchange capacity (CEC) was determined using the ammonium acetate method, while organic carbon and total nitrogen (N) were analyzed by Walkley–Black titration and the Kjeldahl method, respectively. Soil available N was measured by the alkaline hydrolysis diffusion method. Total phosphorus (P) was calcined and extracted with NaOH, after which the available P was extracted with 0.5 M NaHCO₃ (pH = 8.5) and analyzed by the molybdenum blue method. Total potassium

(K) and available K were determined using a flame photometer after being calcined and extracted with NaOH and 1 M NH₄OAc, respectively.

Statistical analysis

Statistical Product and Service Solutions (SPSS) Version 20.0 (IBM Inc., Armonk, NY) was used to analyze the data. Differences in Zn removal efficiencies among groups were identified by one-way analysis of variance, with a P value < 0.05 considered to indicate significance.

Results and discussion

Effect of LMWOAs on removal of soil Zn

The concentration of washing reagent is essential to soil washing, as it determines the amount of substance that will participate in the reaction. In this study, the Zn removal efficiencies were all approximately 3.00 % after 1, 2, and 4 h of reaction with deionized water, while they all increased logarithmically following the addition of OA, TA, and CA (Table 1). The Zn removal efficiencies increased significantly ($P < 0.05$) as the LMWOA concentrations increased from 0.5 to 5.0 g/L and then slightly increased from 5.0 to 10.0 g/L (Fig. 1). This trend was similar to the change in phenanthrene removal reported in response to increasing OA, TA, and CA concentrations in previous studies (An et al. 2011).

The different molecular structures of LMWOAs might lead to differences in the strength of their interactions with soil metals during chelating or ion exchange reactions (Wen et al. 2009; An et al. 2011). In this study, the Zn removal efficiencies of OA were greater than those of TA and CA at most concentrations, with the highest removals of 96.99, 88.65, and 82.05 % being observed in response to 10.0 g/L OA, TA, and CA, respectively (Fig. 1). These findings likely reflect the simpler molecular structure of OA relative to TA and CA, which makes it easier to transfer in the reaction. In addition, OA can provide more carboxyls than the other compounds, which play important roles in leaching of soil metals (Hernández-Soriano et al. 2010; Yip et al. 2010) under the equal mass concentration.

The reaction time is also an important factor that must be considered during washing of heavy metals from contaminated soil owing to the kinetic equilibrium of the adsorption and desorption process (Wang et al. 2014). Zn removal efficiencies showed no obvious differences ($P > 0.05$) among 1-, 2-, and 4-h reaction times, despite a slight decline with the extension of reaction time for most cases. These findings indicate that 1 h or less may be sufficient for the full effects of LMWOAs to manifest. Furthermore, because soil is a

Table 1 Optimal model of relationship between removal efficiencies (Y) and LMWOA concentrations (X)

Washing solutions	Time (h)	Formula: $Y=a+b\ln X$		R^2	P
		a	b		
OA	1	101.58	17.79	0.97	0.003
	2	95.064	17.01	0.94	0.009
	4	81.942	12.60	0.98	0.003
TA	1	95.90	15.27	0.93	0.006
	2	94.52	16.95	0.93	0.008
	4	81.83	12.73	0.99	0.009
CA	1	97.50	15.20	0.96	0.001
	2	95.71	18.13	0.93	0.001
	4	83.91	13.21	0.98	0.001
OA+SDS	1	86.800	15.85	0.96	0.004
	2	83.48	14.29	0.95	0.001
	4	87.245	16.43	0.96	0.003
TA+SDS	1	91.18	17.48	0.94	0.006
	2	90.88	15.39	0.92	0.010
	4	100.21	17.02	0.95	0.003
CA+SDS	1	75.62	13.09	0.98	0.002
	2	78.52	13.24	0.98	0.004
	4	100.03	14.07	0.94	0.001
OA+TX-100	1	84.35	14.18	0.99	0.001
	2	82.19	13.45	0.99	0.000
	4	90.72	15.29	0.98	0.002
TA+TX-100	1	89.76	13.80	0.99	0.001
	2	88.37	11.84	0.99	0.000
	4	94.83	14.80	0.96	0.004
CA+TX-100	1	86.91	13.87	0.99	0.001
	2	85.30	11.93	0.99	0.000
	4	97.08	14.17	0.98	0.001
OA+NPAM	1	87.05	13.63	0.95	0.005
	2	88.33	14.00	0.95	0.005
	4	90.31	14.84	0.91	0.012
TA+NPAM	1	92.213	14.79	0.94	0.007
	2	96.459	16.41	0.92	0.010
	4	91.800	13.73	0.91	0.013
CA+NPAM	1	89.224	14.10	0.94	0.006
	2	91.876	13.88	0.97	0.002
	4	92.908	12.96	0.95	0.005

Logarithmic function is the best fitting model for all solutions (a lower P and higher R^2 value compared with other simple equations)

LMWOAs low-molecular-weight organic acids, OA oxalic acid, TA tartaric acid, CA citric acid, SDS sodium dodecyl sulfate, TX-100 Triton X-100, NPAM non-ionic polyacrylamide

complex matrix (Conte et al. 2005), metal ions probably precipitate with other soil substances with increasing washing time.

Removal efficiency of surfactant alone

The soil Zn removal efficiencies of SDS, TX-100, and NPAM alone were only 4.50, 6.50, and 5.00 %, respectively, and there were no significant differences among reaction times ($P>0.05$). These findings are similar to those of previous studies that showed that SDS and TX-100 had little effect on the removal soil Zn alone (Yuan et al. 2010; Torres et al. 2012). These findings suggest that the potential for use of surfactant ligand washing agents alone has not been fully exploited.

Effect of mixed solutions on the removal of soil Zn

As shown in Fig. 2, Zn removal efficiencies of all mixed solutions showed a logarithmic increase with increasing LMWOA concentrations from 0.5 to 5.0 g/L (Table 1) and were similar to those of the LMWOAs. From 5.0 to 10.0 g/L, Zn removal increased only slightly. Unlike LMWOAs alone, the Zn removal efficiencies of some mixtures showed a significant increase ($P<0.05$) with increasing reaction time, which may indicate that LMWOAs and surfactants interact with each other within a certain period.

After the addition of SDS, the efficiency of Zn removal by TA became greater than that of the other two LMWOAs, with the highest removal of 95.55 % being observed for treatment with 10.0 g/L TA mixed with SDS for 4 h. Similarly, CA exceeded OA when the reaction time increased to 4 h (Fig. 2a–c). After combination with TX-100, the Zn removal efficiencies of OA were always lower than those of the other two LMWOAs, and CA surpassed TA as the most effective treatment at 4 h. When mixed with TX-100, the Zn removal efficiency of CA was notably enhanced, with the highest removal reaching 93.87 %. Moreover, 90.19 % of soil Zn was removed at 5.0 g/L CA, resulting in the concentration of Zn remaining in the soil being below the standard for Zn pollution in China (Fig. 2d–f). When combined with NPAM, the Zn removal efficiency of TA was slightly higher than that of OA and TA at the first two reaction times, while the efficiency of CA slightly exceeded that of TA at the longest reaction time. The removal by 5.0 g/L CA and TA reached 92.92 and 92.96 %, respectively, after only 2 h (Fig. 2g–i). Although the three surfactants only accounted for a small part of the mixed solutions, they had strong impacts on various LMWOAs when applied for the removal of soil Zn.

Effect of SDS on LMWOAs applied for soil Zn removal

SDS impeded the Zn removal efficiencies of LMWOAs in most cases (Table 2), especially that of OA. All treatments showed significant reductions in Zn ($P<0.05$), with a maximum decrease of 14.87 %, and no obvious regular change was summarized for the effects of SDS on OA along with the change of concentrations and reaction times. Nevertheless,

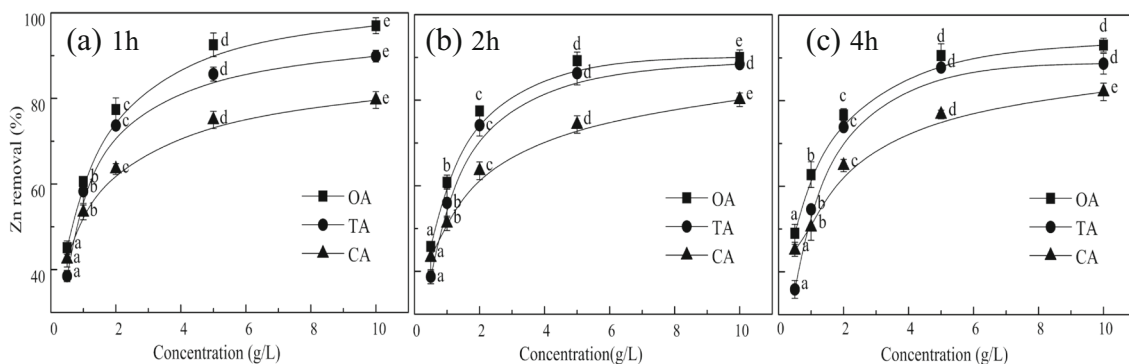


Fig. 1 Effect of concentrations and reaction times of different LMWOAs on the Zn removal efficiencies. OA, oxalic acid; TA, tartaric acid; CA, citric acid. The same letters in the same line of each rotation indicate no significant difference ($p>0.05$)

the effects of SDS on TA and CA shifted from negative to positive as the reaction time increased from 1 to 4 h, with the largest increases being 8.73 and 5.23 % ($P<0.05$), respectively.

In this study, SDS did not exert a synergistic effect on LMWOAs, as expected. This differed from the results of previous studies that showed that the addition of SDS to EDTA could enhance Zn and Pb removal (Ramamurthy et al. 2008; Zhang et al. 2008). Moreover, SDS was shown to significantly increase Cd and Cu removal by Lauroyl-ED3ANa2 (LED3A) (Chang et al. 2005). Such differences may be ascribed to the distinctive characteristics of metal ions and chelating agents themselves. Moreover, SDS, a type of anionic surfactant with

strong emulsification, usually reacts with the surface of soil colloids first because of its hydrophobicity (Zhang et al. 2008; Conte et al. 2005), after which it reacts with heavy metals via ion exchange, electrostatic interaction, and solubilization (Zhang et al. 2008; Gupta et al. 2010). In addition, SDS was likely precipitated by alkaline metal ions such as Ca^{2+} and Mg^{2+} in the soils (Torres et al. 2012). Taken together, these characteristics might have weakened the motilities of LMWOAs and reduced their chances of interacting with soil Zn^{2+} upon initial treatment. As a result, the negative effects of TA and CA eased slowly with increasing reaction time. However, lengthening the reaction time did not improve the effects of OA; maybe its molecule was fettered very seriously.

Fig. 2 Effect of different LMWOA concentrations and reaction times of various combined solutions on Zn removal efficiencies. OA, oxalic acid; TA, tartaric acid; CA, citric acid; SDS, sodium dodecyl sulfate; TX-100, Triton X-100; NPAM, non-ionic polyacrylamide. Different letters in the same line of each rotation indicate no significant difference ($p>0.05$)

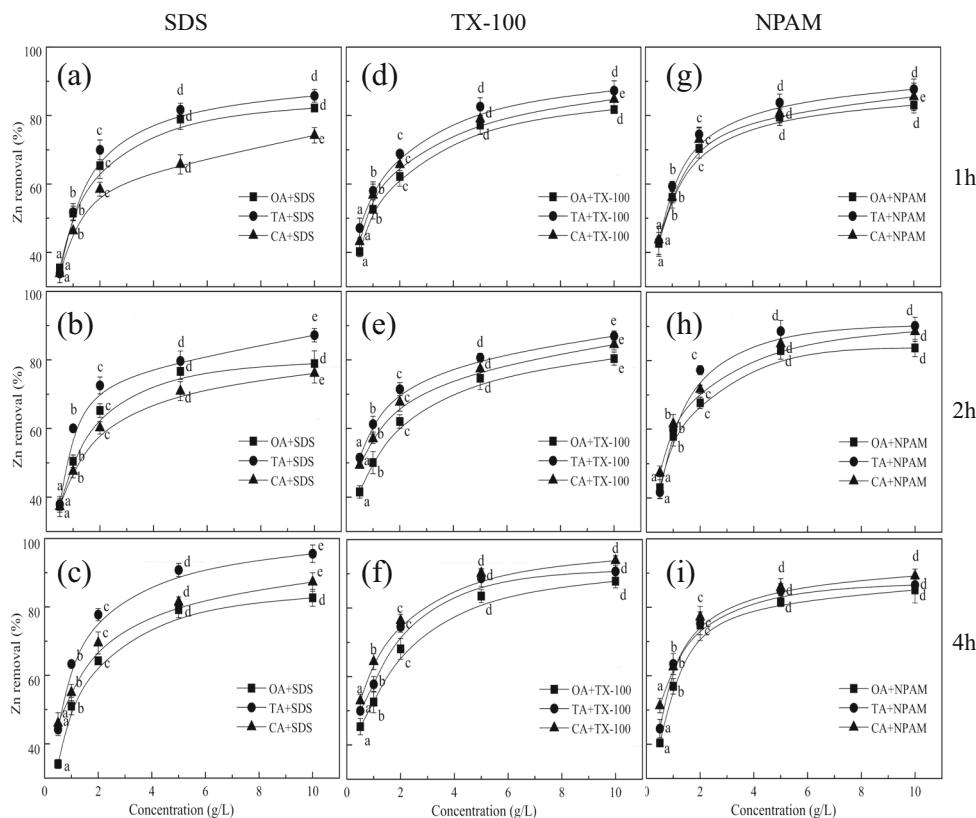


Table 2 Comparison of the effects of surfactants on LMWOA washing alone

Surfactants	LMWOA concentrations (g/L)	OA			TA			CA		
		1 h	2 h	4 h	1 h	2 h	4 h	1 h	2 h	4 h
SDS	0.5	-9.66 ^a	-8.38 ^a	-14.87 ^a	-4.62 ^a	-0.85	+8.33 ^a	-8.59 ^a	-5.94 ^a	+0.96
	1.0	-9.12 ^a	-10.36 ^a	-11.68 ^a	-6.60 ^a	+4.00 ^a	+8.73 ^a	-7.09 ^a	-3.66	+4.53 ^a
	2.0	-12.05 ^a	-12.27 ^a	-12.40 ^a	-3.72	-1.64	+3.92	-5.02 ^a	-3.35	+4.67 ^a
	5.0	-13.56 ^a	-12.60 ^a	-11.32 ^a	-4.00	-6.63 ^a	+3.05	-9.23 ^a	-3.44	+4.64 ^a
	10.0	-14.78 ^a	-11.07 ^a	-10.32 ^a	-4.10 ^a	-1.21	+6.91 ^a	-5.40 ^a	-4.04 ^a	+5.23 ^a
TX-100	0.5	-4.91 ^a	-4.27 ^a	-3.66	+8.63 ^a	+12.78 ^a	+14.05 ^a	+0.74	+6.05 ^a	+7.86 ^a
	1.0	-8.02 ^a	-10.74 ^a	-10.19 ^a	-0.28	+5.22 ^a	+3.14	+3.36	+5.76 ^a	+13.92 ^a
	2.0	-15.22 ^a	-15.48 ^a	-8.60 ^a	-4.82 ^a	-2.74	+0.71	+2.17	+4.12 ^a	+11.55 ^a
	5.0	-15.32 ^a	-14.60 ^a	-7.04 ^a	-3.09	-5.66 ^a	+0.96	+4.05	+3.05	+13.41 ^a
	10.0	-15.22 ^a	-9.61 ^a	-5.11 ^a	-2.58	-1.47	+2.07	+5.09 ^a	+4.38 ^a	+11.81 ^a
NPAM	0.5	-2.50	-2.83	-8.65 ^a	+4.76 ^a	+2.94	+8.68 ^a	+1.27	+4.12	+6.24 ^a
	1.0	-4.53 ^a	-2.97	-5.78 ^a	+1.10	+3.79	+8.85 ^a	+2.78	+10.31 ^a	+12.15 ^a
	2.0	-7.03 ^a	-9.83 ^a	-1.87	+0.82	+3.07	+5.48 ^a	+9.53 ^a	+8.10 ^a	+12.36 ^a
	5.0	-13.00 ^a	-6.30 ^a	-9.03 ^a	-1.92	+2.28	-0.96	+5.59 ^a	+10.60 ^a	+9.08 ^a
	10.0	-13.95 ^a	-6.27 ^a	-7.92 ^a	-2.17	+1.71	-1.88	+5.87 ^a	+8.37 ^a	+7.11 ^a

Positive sign “+” indicates that the addition of surfactant enhanced the ability of LMWOAs to remove Zn, while negative sign “-” indicates that the addition of surfactant decreased the ability of LMWOAs to remove Zn.

LMWOA low-molecular-weight organic acid, OA oxalic acid, TA tartaric acid, CA citric acid, SDS sodium dodecyl sulfate, TX100 Triton X-100, NPAM non-ionic polyacrylamide

^a Indicates that the mixed solutions caused significant diversity relative to LMWOAs alone

Effect of TX-100 for LMWOAs on soil Zn removal

TX-100 is a non-ionic surfactant that may disperse soil or change the solubility and mobility of heavy metal ions via adsorption onto soil colloids (Giannis et al. 2007; Gupta et al. 2010) because of its hydrophobicity (Conte et al. 2005; Zhang et al. 2008). Therefore, it could affect the soil Zn removal by LMWOAs with increased reaction time. In this study, TX-100 did not improve the Zn removal by OA, and the maximum reduction of the removal efficiency was 15.48 % ($P < 0.05$). The negative effect was seemingly alleviated when the reaction time increased to 4 h. However, the effects of TX-100 on TA shifted from negative to positive as the reaction time increased from 1 to 4 h, and the efficacy of 0.5 g/L TA increased significantly (14.05 %, $P < 0.05$). The Zn removal efficiencies of all CA solutions were enhanced with increasing reaction time after the addition of TX-100 (Table 2).

The various effects of TX-100 on Zn removal by different LMWOAs may be the result of the various degrees and orders of interactions among TX-100, LMWOAs, and soil colloids. TX-100 likely filled the binding sites of soil colloids or interfered with the organo-functional groups of LMWOAs via lipophilic groups, which may have prevented the LMWOA molecules from contacting the Zn entrapped in the soil colloids upon

initial treatment. OA apparently showed the strongest binding with TX-100. This may have occurred because it was the simplest molecule; therefore, the degree of free mobility was greatly reduced relative to when OA was applied as a washing agent alone. In contrast, TA and CA showed fewer constraints; therefore, Zn removal efficiencies may have been impeded by OA and TA immediately upon addition of TX-100. However, as the reaction time increased, more soil Zn²⁺ was exposed and desorbed by LMWOAs, especially CA, possibly in response to the dispersal mechanism of TX-100. Moreover, the balance of the reaction moved toward the generation of Zn-LMWOAs, and the restrained LMWOA molecules might have been simultaneously released.

Previous studies indicated that TX-100 could enhance the removal of heavy metals from soil by EDTA (Ramamurthy et al. 2008; Yuan et al. 2010). Although the structures of the LMWOAs investigated in the present study are not as complex as EDTA, they all have multiple carboxyls. Consequently, TX-100 could enhance the soil Zn removal efficiency of LMWOAs to some extent through its dispersal mechanism (Yuan et al. 2010). Specifically, the lipophilic group of TX-100 may have been drawn by the soil colloid hydrophobic surface or soil organic matter through van der Waals attractions, resulting in dispersion of the soil colloid (Gupta et al. 2010).

Effect of NPAM for LMWOAs on soil Zn removal

As shown in Table 2, the effects of NPAM on LMWOAs were similar to those of TX-100, probably because they are both non-ionic surfactants. NPAM also had negative effects on OA for the removal of soil Zn. For TA, NPAM caused negative and positive effects under different treatments. Specifically, lower concentrations led to a greater increase in removal, with the highest removal being 8.85 % ($P<0.05$). When compared with TX-100, NPAM had an obviously synergistic effect on CA solutions for Zn removal under a short reaction time, notably, 5.0 g/L CA could remove 85.15 % ($P<0.05$) after increasing by 10.60 % within 2 h.

NPAM is a common non-ionic polymeric flocculant for wastewater disposal and soil structure improvement because it can form large flocs among particles (Chatterjee et al. 2009; Dai et al. 2014; Prats et al. 2014). To the best of our knowledge, little research has been conducted to investigate the combination of NPAM with LMWOAs to wash soil heavy metals. However, the functional mechanism of NPAM could be inferred based on its characteristics. On the one hand, NPAM can form gel at low concentrations because of its low solubility, which may reduce the tension of water accordingly. Therefore, it can affect the migration of the three LMWOAs in solutions. On the other hand, NPAM may be adsorbed onto the surface of soil organic or inorganic colloids via H-bonding between the C=O group on the amide and proton donors on the oxide surfaces (Al-Hashmi et al. 2012), which will likely increase the soil dispersive effects similar to TX-100 because they are both non-ionic surfactants. As the reaction time increased, the negative effects decreased and the positive effects were enhanced. It should be noted that NPAM could promote the Zn removal efficiencies of LMWOAs in a shorter time than TX-100. Moreover, NPAM showed obvious potential to enhance the removal of Zn from soil by CA. Overall, this is a novel process for enhancing soil Zn removal by LMWOAs; however, additional studies are needed to elucidate the mechanisms by which this occurs.

The different effects of surfactants on the removal of Zn by LMWOAs were mainly due to the different physicochemical

characteristics of reagents and further various interactions in the complex soil-liquid systems. Specifically, surfactants appeared to exert antagonistic effects on OA and synergistic effects on CA. Moreover, reaction time was an important factor influencing mixed solutions because there are sequences for the key functional groups of LMWOAs and surfactants to contact with the reaction binding sites of soil colloid.

Effect of pH on the removal of soil Zn

The pH during washing is essential to removal of Zn from soil as it can affect metal retention and desorption in soil colloids (Zou et al. 2009) and then influence soluble metal ion concentrations and the capabilities of reagents to extract metals from soil (Begum et al. 2013; Wang et al. 2014). As shown in Fig. 3, the removal of Zn by various solutions was high at pH 4 and then decreased sharply from pH 4 to 7 but showed little further reduction from pH 7 to 9. This trend was similar to the findings observed during extraction of Zn by nitrilotriacetic acid and 3-hydroxy-2, 2'-iminodisuccinic acid at pH 4–10 (Begum et al. 2012).

These results were consistent with the regularity of Zn adsorption by soil, in which pH influences the adsorption of cations onto the surface of oxide minerals (Bradl et al. 2004). Under acidic conditions, heavy metal cations competed with H^+ for adsorption of soil colloids, with more soluble carbonates providing easier access to carbonate-bound metals by washing reagents (Begum et al. 2012). Therefore, the highest Zn removal efficiency in this study was observed at pH 4. Under neutral or alkaline conditions, the solubility of the oxides and other solid phases was low because of the formation of metal hydroxy complexes or insoluble calcium zincate (Bradl et al. 2004; Begum et al. 2012), resulting in comparatively lower extraction abilities.

The Zn removal efficiencies of CA and its corresponding surfactants were relatively higher than those of other washing solutions at the same pH and showed better stability along with changes in acidity. This may indicate that CA has better buffer performance because of its more complicated molecular structure. Overall, these findings indicate that variations in

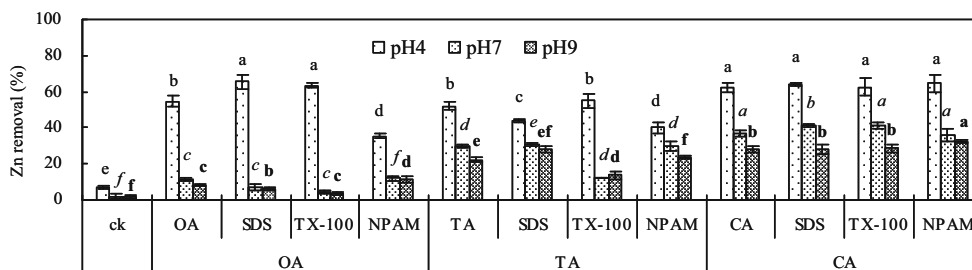


Fig. 3 Effect of pH of different washing solutions on Zn removal under 1 h. CK, deionized water; OA, oxalic acid; TA, tartaric acid; CA, citric acid; SDS, sodium dodecyl sulfate; TX-100, Triton X-100; NPAM, non-

ionic polyacrylamide. Different letters in the same histogram of each rotation indicate no significant difference ($p>0.05$)

Table 3 Soil properties before and after washing by various treatments

Treatments	pH	CEC (cmol kg ⁻¹)	OC (g kg ⁻¹)	TN (g kg ⁻¹)	TP (g kg ⁻¹)	TK (g kg ⁻¹)	AN (mg kg ⁻¹)	AP (mg kg ⁻¹)	AK (mg kg ⁻¹)	Zn (mg kg ⁻¹)
UW	6.29±0.05d	19.07±0.04d	18.78±0.06c	1.24±0.02c	1.78±0.01c	30.4±1.8c	75.9±1.3c	38.3±1.8a	145.5±3.1f	1037±9 g
DW	6.19±0.02de	18.91±0.17d	17.89±0.19b	1.22±0.05bc	1.71±0.21bc	25.1±2.3ab	82.8±2.4de	40.6±1.7ab	138.6±1.9e	960±5f
OA	5.02±0.09ab	17.12±0.12a	16.29±0.48a	1.14±0.04ab	1.59±0.01ab	23.6±1.0a	63.5±1.6a	53.7±2.0d	134.0±3.6de	428±6a
TA	5.09±0.06bc	17.43±0.37ab	19.08±0.28c	1.18±0.03bc	1.75±0.03bc	25.6±0.6ab	72.8±1.9bc	48.2±1.9c	119.0±1.6ab	449±8a
CA	5.07±0.10bc	17.46±0.06ab	19.27±0.85 cd	1.17±0.03b	1.74±0.04bc	25.8±1.2ab	69.8±0.5b	42.9±0.5b	127.3±2.5c	482±5c
OA+SDS	5.16±0.11c	17.68±0.02b	18.09±1.00bc	1.10±0.11a	1.51±0.09a	26.0±0.1b	85.5±1.4e	45.0±2.4bc	118.0±1.0ab	494±4d
OA+TX-100	5.14±0.05bc	17.72±0.18b	18.84±0.44c	1.16±0.01ab	1.59±0.02ab	25.6±1.6ab	89.2±2.0f	49.5±2.2c	120.6±3.1b	507±7e
OA+NPAM	5.09±0.03bc	18.04±0.21bc	19.28±0.46 cd	1.24±0.05bc	1.64±0.01b	24.4±1.8ab	102.1±2.0 g	58.9±1.1e	131.5±2.2d	492±4d
TA+SDS	5.10±0.03bc	17.48±0.53ab	20.85±0.19e	1.18±0.01bc	1.62±0.02ab	25.5±0.5ab	84.5±1.6de	47.7±2.7c	125.7±2.0c	480±3c
TA+TX-100	5.16±0.05c	17.45±0.31ab	20.99±0.57e	1.22±0.01bc	1.61±0.01ab	25.4±1.6ab	94.7±1.6 g	61.5±2.1e	136.2±1.1e	461±4b
TA+NPAM	5.05±0.05ab	17.97±0.07bc	21.04±0.31e	1.26±0.02 cd	1.57±0.01ab	24.5±0.7ab	113.8±2.7 h	64.4±0.7f	122.7±1.8bc	454±5b
CA+SDS	4.94±0.02a	17.52±0.07ab	19.36±0.08 cd	1.19±0.01bc	1.72±0.04bc	24.9±1.7ab	82.1±1.1d	52.6±1.9d	122.6±2.7bc	435±4a
CA+TX-100	4.99±0.05a	17.67±0.36b	19.06±0.42c	1.15±0.01ab	1.73±0.02bc	24.7±0.8ab	83.4±2.3de	63.9±1.1f	129.4±1.8 cd	427±6a
CA+NPAM	4.91±0.06a	18.34±0.16c	19.94±0.16d	1.32±0.02d	1.68±0.01bc	26.7±0.5b	120.9±2.3i	70.0±2.2 g	116.1±2.2a	431±9a

Data are mean values±SD ($n=3$). The same letters in the same column of each rotation indicate no significant difference ($p>0.05$)

UW unwashed, DW deionized water, OA oxalic acid, TA tartaric acid, CA citric acid, SDS sodium dodecyl sulfate, TX-100 NPAM non-ionic polyacrylamide, CEC cation exchange capacity, OM organic matter, TN total nitrogen, TP total phosphorus, TK total phosphorus, AN available nitrogen, AP available phosphorus, AK available potassium, Zn concentration in soils

pH could influence the removal of soil Zn in the presence of LMWOAs and surfactants.

Assessment of soils before and after washing

Soil washing may alter the soil properties through dissolution of indigenous oxides, carbonates, and organic matter (Tsang et al. 2007; Jelusic et al. 2013). As shown in Table 3, the properties of washed soils changed to some extent. Specifically, the pH values of all washed soils were higher than those of the initial of leachate (4 ± 0.05) and lower than those of un-washed and deionized water washed soils. These results indicate that the LMWOAs and surfactants underwent a series of chemical reactions with soil. When compared with un-washed soil, the cation exchange capacities (CECs) of different washed soils decreased to some extent; however, the addition of NPAM appeared to alleviate the loss of CECs. Soil total K, total P, and available K all decreased after washing (Table 3), which may have been due to the non-selective extraction of soil non-Zn cations by LMWOAs and surfactants. Organic carbon, total N, and available N of different washed soils increased or decreased relative to the un-washed soils. This may indicate that washing agents removed some of the nutrients, while partial residues of LMWOAs and surfactants resulted in the addition of carbon to soils. Moreover, NPAM containing elemental N improved the N concentrations of washed soils and significantly increased the available N ($P < 0.05$). A washing agent may dissolve a portion of soil minerals, resulting in the release of other N and P species, and therefore an appreciable increase in available P (Hu et al. 2014). Among the investigated washing solutions, OA removed the most soil nutrients; however, NPAM-containing solutions significantly improved the available N concentration of washed soils and alleviated the loss of CEC.

Conclusion

This study investigated the effects of SDS, TX-100, and NPAM on the LMWOAs OA, TA, and CA applied to remove Zn from contaminated soils. All washing solution removals showed logarithmic increases with increasing LMWOA concentrations, but decreases in response to changing the pH from 4 to 9. Increased reaction time enhanced Zn removal under some mixed cases significantly ($P < 0.05$) owing to the effects of surfactants on LMWOAs. The effects of the three surfactants alone on Zn removal were small, and they impeded the Zn removal efficiency of OA. Conversely, the three surfactants exerted synergistic effects on removal by TA and CA. Moreover, the Zn removal efficiency of CA was obviously enhanced by two non-ionic surfactants, and NPAM required a shorter reaction time for enhancement than TX-100. In

addition, OA led to a serious loss of soil nutrients, while the addition of NPAM improved the N concentrations of washed soils and alleviated the loss of CEC. Taken together, combining CA with NPAM offers a promising remediation approach to removal of Zn from contaminated soil. However, further studies are needed to optimize the conditions to enable large-scale application.

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References

- Al-Hashmi AR, Luckham PF, Al-Maamari RS, Zaitoun A, Al-Sharji HH (2012) The role of hydration degree of cations and anions on the adsorption of high-molecular-weight nonionic polyacrylamide on glass surfaces. *Colloids Surf A: Physicochem Eng Asp* 415:91–97
- Ali H, Khan E, Sajad MA (2013) Phytoremediation of heavy metals—concepts and applications. *Chemosphere* 91:869–881
- An C, Huang G, Wei J, Yu H (2011) Effect of short-chain organic acids on the enhanced desorption of phenanthrene by rhamnolipid biosurfactant in soil–water environment. *Water Res* 45:5501–5510
- Aşçı Y, Nurbaş M, Sağ Açıkel Y (2008) Removal of zinc ions from a soil component Na-feldspar by a rhamnolipid biosurfactant. *Desalination* 223:361–365
- Bao SD (2005) Soil agrochemical analysis. China Agriculture Press, Beijing (in Chinese)
- Begum ZA, Rahman IMM, Tate Y, Sawai H, Maki T, Hasegawa H (2012) Remediation of toxic metal contaminated soil by washing with biodegradable aminopolycarboxylate chelants. *Chemosphere* 87:1161–1170
- Begum ZA, Rahman IMM, Sawai H, Mizutani S, Maki T, Hasegawa H (2013) Effect of extraction variables on the biodegradable chelant-assisted removal of toxic metals from artificially contaminated European reference soils. *Water Air Soil Pollut* 1218:3–21
- Bolan N, Kunhikrishnan A, Thangarajan R, Kumpiene J, Park J, Makino T, Kirkham MB, Scheckel K (2014) Remediation of heavy metal (loid)s contaminated soils—to mobilize or to immobilize? *J Hazard Mater* 266:141–166
- Bradl HB (2004) Adsorption of heavy metal ions on soils and soils constituents. *J Colloid Interf Sci* 277:1–18
- Chang S, Wang K, Kuo C, Chang C, Chou C (2005) Remediation of metal-contaminated soil by an integrated soil washing-electrolysis process. *Soil Sediment Contam* 14:559–569
- Chatterjee T, Chatterjee S, Lee DS, Lee MW, Woo SH (2009) Coagulation of soil suspensions containing nonionic or anionic surfactants using chitosan, polyacrylamide, and polyaluminium chloride. *Chemosphere* 75:1307–1314
- Conte P, Agretto A, Spaccin R, Piccolo A (2005) Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils. *Environ Pollut* 135:515–522
- Dai X, Luo F, Yi J, He Q, Dong B (2014) Biodegradation of polyacrylamide by anaerobic digestion under mesophilic condition and its performance in actual dewatered sludge system. *Bioresour Technol* 153:55–61
- Dellisanti F, Rossi PL, Valdrè G (2009) In-field remediation of tons of heavy metal-rich waste by Joule heating vitrification. *Int J Miner Process* 93:239–245

- Dermont G, Bergeron M, Mercier G, Richer-Lafleche M (2008) Soil washing for metal removal: a review of physical/chemical technologies and field applications. *J Hazard Mater* 152:1–31
- Di Palma L, Ferrantelli P (2005) Copper leaching from a sandy soil: mechanism and parameters affecting EDTA extraction. *J Hazard Mater* 122:85–90
- Dziubanek G, Piekut A, Rusin M, Baranowska R, Hajok I (2015) Contamination of food crops grown on soils with elevated heavy metals content. *Ecotoxicol Environ Saf* 118:183–189
- Ehsan S, Prasher SO, Marshall WD (2006) A washing procedure to mobilize mixed contaminants from soil: II. Heavy metals. *J Environ Qual* 35:2084–2091
- Giannis A, Gidaracos E, Skouta A (2007) Application of sodium dodecyl sulfate and humic acid as surfactants on electrokinetic remediation of cadmium-contaminated soil. *Desalination* 211:249–260
- Giannis A, Nikolaou A, Pentari D, Gidaracos E (2009) Chelating agent-assisted electrokinetic removal of cadmium, lead and copper from contaminated soils. *Environ Pollut* 157:3379–3386
- Gupta MK, Srivastava RK, Singh AK (2010) Bench scale treatability studies of contaminated soil using soil washing technique. *J Chem Theory Comput* 7:73–80
- Gusiatin ZM, Klimiuk E (2012) Metal (Cu, Cd and Zn) removal and stabilization during multiple soil washing by saponin. *Chemosphere* 86:383–391
- Hernández-Soriano MDC, Peña A, Mingorance MD (2010) Release of metals from metal-amended soil treated with a sulfosuccinamate surfactant: effects of surfactant concentration, soil/solution ratio, and pH. *J Environ Qual* 39:1298–1305
- Hu P, Yang B, Dong C, Chen L, Cao X, Zhao J, Wu L, Luo Y, Christie P (2014) Assessment of EDTA heap leaching of an agricultural soil highly contaminated with heavy metals. *Chemosphere* 117:532–537
- Jelusic M, Grcman H, Vodnik D, Suhadolc M, Lestan D (2013) Functioning of metal contaminated garden soil after remediation. *Environ Pollut* 174:63–70
- Kulikowska D, Gusiatin ZM, Bulowska K, Kierklo K (2015) Humic substances from sewage sludge compost as washing agent effectively remove Cu and Cd from soil. *Chemosphere* 136:42–49
- Liu G, Tao L, Liu X, Hou J, Wang A, Li R (2013) Heavy metal speciation and pollution of agricultural soils along Jishui River in non-ferrous metal mine area in Jiangxi Province, China. *J Geochem Explor* 132:156–163
- Lo IMC, Tanboonchuy V, Yan DYS, Grisdanurak N, Liao CH (2012) A hybrid approach for PAHs and metals removal from field-contaminated sediment using activated persulfate oxidation coupled with chemical-enhanced washing. *Water Air Soil Pollut* 223:4801–4811
- Makino T, Sugahara K, Sakurai Y, Takano H, Kamiya T, Sasaki K, Itou T, Sekiya N (2006) Remediation of cadmium contamination in paddy soils by washing with chemicals: selection of washing chemicals. *Environ Pollut* 144:2–10
- Marichali A, Dallali S, Ouerghemmi S, Sebei H, Hosni K (2014) Germination, morpho-physiological and biochemical responses of coriander (*Coriandrum sativum* L.) to zinc excess. *Ind Crop Prod* 55:248–257
- Maturi K, Reddy KR (2006) Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin. *Chemosphere* 63:1022–1031
- Moon DH, Lee J, Wazne M, Park J (2012) Assessment of soil washing for Zn contaminated soils using various washing solutions. *J Ind Eng Chem* 18:822–825
- Moutsatsou A, Gregou M, Matsas D, Protonotarios V (2006) Washing as a remediation technology applicable in soils heavily polluted by mining–metallurgical activities. *Chemosphere* 63:1632–1640
- Pociecha M, Lestan D (2010) Using electrocoagulation for metal and chelant separation from washing solution after EDTA leaching of Pb, Zn and Cd contaminated soil. *J Hazard Mater* 174:670–678
- Prats SA, Martins MADS, Malvar MC, Ben-Hur M, Keizer JJ (2014) Polyacrylamide application versus forest residue mulching for reducing post-fire runoff and soil erosion. *Sci Total Environ* 468–469:464–474
- Ramamurthy AS, Vo D, Li XJ, Qu J (2008) Surfactant-Enhanced removal of Cu (II) and Zn (II) from a contaminated sandy soil. *Water Air Soil Pollut* 190:197–207
- Rossato L, MacFarlane J, Whittaker M, Pudmenzky A, Doley D, Schmidt S, Monteiro MJ (2011) Metal-binding particles alleviate lead and zinc toxicity during seed germination of metallophyte grass *Astrebala lappacea*. *J Hazard Mater* 190:772–779
- Schwab AP, Zhu DS, Banks MK (2008) Influence of organic acids on the transport of heavy metals in soil. *Chemosphere* 72:986–994
- Soleimani M, Hajabbasi MA, Afyuni M, Akbar S, Jensen JK, Holm PE, Borggaard OK (2010) Comparison of natural humic substances and synthetic ethylenediaminetetraacetic acid and nitrilotriacetic acid as washing agents of a heavy metal-polluted soil. *J Environ Qual* 39:855
- Song S, Zhu L, Zhou W (2008) Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin, a plant-derived biosurfactant. *Environ Pollut* 156:1368–1370
- Torres LG, Lopez RB, Beltran M (2012) Removal of As, Cd, Cu, Ni, Pb, and Zn from a highly contaminated industrial soil using surfactant enhanced soil washing. *Phys Chem Earth Parts A/B/C* 37–39:30–36
- Tsang DCW, Zhang W, Lo IMC (2007) Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils. *Chemosphere* 68:234–243
- Vargas-García MDC, López MJ, Suárez-Estrella F, Moreno J (2012) Compost as a source of microbial isolates for the bioremediation of heavy metals: In vitro selection. *Sci Total Environ* 431:62–67
- Wang G, Zhang S, Xu X, Li T, Li Y, Deng O, Gong G (2014) Efficiency of nanoscale zero-valent iron on the enhanced low molecular weight organic acid removal Pb from contaminated soil. *Chemosphere* 117:617–624
- Wen J, Stacey SP, McLaughlin MJ, Kirby JK (2009) Biodegradation of rhamnolipid, EDTA and citric acid in cadmium and zinc contaminated soils. *Soil Biol Biochem* 41:2214–2221
- Yang Z, Zhang S, Liao Y, Li Q, Wu B, Wu R (2012) Remediation of heavy metal contamination in calcareous soil by washing with reagents: A column washing. *Procedia Environ Sci* 16:778–785
- Yip TCM, Yan DYS, Yui MMT, Tsang DCW, Lo IMC (2010) Heavy metal extraction from an artificially contaminated sandy soil under EDDS deficiency: Significance of humic acid and chelant mixture. *Chemosphere* 80:416–421
- Yuan S, Wu X, Wan J, Long H, Lu X, Wu X, Chen J (2010) Enhanced washing of HCB and Zn from aged sediments by TX-100 and EDTA mixed solutions. *Geoderma* 156:119–125
- Zaccone C, Di Caterina R, Rotunno T, Quinto M (2010) Soil – farming system – food – health: Effect of conventional and organic fertilizers on heavy metal (Cd, Cr, Cu, Ni, Pb, Zn) content in semolina samples. *Soil Tillage Res* 107:97–105
- Zhang W, Tsang DCW, Lo IMC (2008) Removal of Pb by EDTA-washing in the presence of hydrophobic organic contaminants or anionic surfactant. *J Hazard Mater* 155:433–439
- Zhang W, Huang H, Tan F, Wang H, Qiu R (2010a) Influence of EDTA washing on the species and mobility of heavy metals residual in soils. *J Hazard Mater* 173:369–376
- Zhang W, Tong L, Yuan Y, Liu Z, Huang H, Tan F, Qiu R (2010b) Influence of soil washing with a chelator on subsequent chemical immobilization of heavy metals in a contaminated soil. *J Hazard Mater* 178:578–587
- Zhang X, Zhang S, Xu X, Li T, Gong G, Jia Y, Li Y, Deng L (2010c) Tolerance and accumulation characteristics of cadmium in *Amaranthus hybridus* L. *J Hazard Mater* 180:303–308
- Zou Z, Qiu R, Zhang W, Dong H, Zhao Z, Zhang T, Wei X, Cai X (2009) The study of operating variables in soil washing with EDTA. *Environ Pollut* 157:229–236