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Original Research

Simultaneous Washing Removal of Copper and Phenanthrene from Contaminated Soil with Sodium N-Lauroyl Ethylenediamine Triacetate

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Abstract

This study investigated the effectiveness of using a novel chelating surfactant, sodium *N*-lauroyl ethylenediamine triacetate (LED3A), on the removal of copper (Cu) and phenanthrene (Phe) simultaneously from artificially contaminated soil. The effects of operating conditions, such as the contact time, initial LED3A concentration, solution pH value and Cu/Phe combination of contaminated soil on the removal efficiencies were extensively examined by a series of batch tests. The results indicated that the equilibrium time (12 h) for Cu desorption was consistent with that of Phe, and the desorption processes of Cu and Phe could be well described by the Elovich and two-constant rate equations. Increasing the LED3A concentration improved effectively both Cu and Phe removal efficiencies, and at the optimum concentration of 18 g/L LED3A, the removal percentages of Cu and Phe were 60.40% and 52.27%, respectively. A wide pH value range from 5.0 to 9.0 was suitable for simultaneously removing of Cu and Phe from the co-contaminated soil. The removals of Cu and Phe were constrained each other in different degrees. The speciation analysis of contaminants in soil demonstrated that LED3A washing resulted in the decrease of the mobile fractions of Cu and Phe, and an increase in the fractions strongly bonded to the soil matrix, compared to their levels before washing. The use of LED3A as an extractant to enhance the removal of heavy metals and hydrophobic organic contaminants (HOCs) from co-contaminated soils appears as a promising remediation method.

Keywords: chelating surfactant, co-contaminated soil, desorption, copper, phenanthrene

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Introduction

The soil environment, an important compartment for global elemental cycling, is considered to be one of the most important natural resources for human beings. However, multiple inorganic and organic contaminants have been frequently found in soil as a result of industrial activities, sewage irrigation, agricultural practices, and atmospheric deposition, etc. [1, 2]. Polycyclic aromatic hydrocarbons (PAHs) contamination of soil is often associated with the presence of high levels of heavy metals [3, 4]. These contaminants are of great concern due to their persistence in the environment, and their potentially serious health consequences [5]. In general, the simultaneous removal of co-contaminants from polluted sites is more difficult than the removal of single one due to their different characteristics and the synergistic effects [6]. Therefore, the development of improved and effective remediation technologies for soils contaminated by heavy metals as well as PAHs has received great attention.

It has been reported that many methods are applied to practice on the remediation of heavy metals and PAHs, including physical, chemical and biological remediation technologies [7-9]. Soil washing and flushing technologies enhanced with chemical agents are widely used in the remediation practice for single type of pollutant (i.e., either heavy metals or organic contaminants) due to the features of short operation period and remarkable removal efficiency [10, 11]. Chelators or surfactants have received better focus among the extractants because of their minimal impact on the soil characteristics while removing contaminants [12, 13]. Aminopolycarboxylate chelators, such as ethylenediaminetetraacetic acid (EDTA) and S,S-ethylenediaminedisuccinic acid (EDDS) and nonionic surfactants, e.g. Tween 80 and Triton X-100, have been recognized as effective chemicals for removing heavy metals and hydrophobic organic compounds (HOCs) from soil, respectively [14, 15]. However, common surfactants were generally ineffective in mobilizing the heavy metals from soils and chelating agents also were unsuited for extracting HOCs from soils. Thus, a major challenge in remediation of co-contaminated soils is simultaneous removal of multiple contaminants by selecting suitable washing/flushing reagents.

The joint application of chelator and surfactant is often required to achieve effective performance on co-contaminated soil remediation. There are two approaches for simultaneous removal of heavy metals and HOCs, including sequential extracting with enhancing agents [16, 17] and combination of enhancing agents [18, 19]. However, the former approach would result in a protracted extraction period and high operational cost. In addition, there is a large amount of liquid and semiliquid waste when chemical agents are used as individuals through sequential washing [20]. The latter method would lead to the difficulties associated with simultaneously controlling the distribution of a chelating agent and a surfactant in soils because of their different properties, as well as the difficulties in separating contaminants and recycling washing agents [21, 22]. Furthermore, the residual content of synthetic surfactants or aminopolycarboxylate chelators in treated soils has been a concern because of the prolonged environmental persistence, resulting in secondary contamination [23].

An ideal washing solution should dramatically improve the solubility and mobility of heavy metal contaminants yet interact weakly with soil constituents and should be nontoxic and biodegradable [10]. EDTA is the most commonly used chelating agent, due to its ability to form stable complex species with several metals and its capacity of reaching high performances without affecting the original structure and composition of the soil [22, 24]. However, EDTA is quite persistent in the environment due to its poor biodegradability [25]. Therefore, in recent years, attention has been paid to chemical modification of the popular aminocarboxylic chelating agent. Despite EDTA or EDDS has been recognized as an effective component in combinational extraction agents for removing heavy metals from contaminated soils, it is common knowledge that they are invalid for removing PAHs from soils. Thus, introducing lipophilic hydrocarbon chain onto molecular structure of these ligands is deemed as a primary means for making them to possess solubilization property for organic compounds [26-29].

Currently, a novel biodegradable EDTA derivative (i.e. a chelating surfactant), sodium *N*-lauroyl ethylenediamine triacetate (LED3A), has received attention because its amphiphilic structure endues both surface activity (i.e., micellization) and chelation function for it to enable solubilizing organics and chelating metals, simultaneously. Our previous studies have shown that LED3A possesses the ability to form stable water-soluble chelates with copper (Cu), together with the capacity to increase the apparent aqueous solubility of phenanthrene (Phe) [21, 30]. The microbial degradation percentage for LED3A was 70.5 % within 30 days [31]. It seemed to be an attractive cleaning agent for soil washing because of its biodegradability. Although LED3A has been used in industry cleanliness (e.g. detergents, corrosion inhibitors), mining exploitation (e.g. mineral flotation, emulsion polymerization) and other fields (e.g. insecticide adjuvants) [31], the researches on employing it for remediating heavy metals and PAHs co-contaminated soils have not been reported previously.

In this paper, LED3A is used as a washing reagent for treatment of Cu and Phe co-contaminated soils via batch equilibrium experiments. The objectives of this study are: (i) to evaluate the performance of LED3A for simultaneous removal of Cu and Phe from co-contaminated soil; (ii) to explore the synchronous desorption mechanisms of Cu and Phe by LED3A-enhanced washing; (iii) to ascertain the speciation of Cu and Phe in soils before and after washing by using sequential extraction. Results obtained from this investigation are expected to provide insight into LED3A as an enhancing agent for soil remediation technologies and provide valuable information for the selection of effective and safe agent on the remediation of the co-contaminated soils.

Materials and Methods

Chemicals

Sodium *N*-lauroyl ethylenediamine triacetate ($C_{20}H_{33}N_2O_7Na_3$, 482 g/mol) with purity>95% was purchased from Hangzhou Biotechnology Co. China. Phenanthrene ($C_{14}H_{10}$, 178 g/mol) with a purity of 98% was obtained from Aldrich Chemical Co. USA. $Cu(NO_3)_2$, $NaNO_3$, NaN_3, NaOH, HAc, $NH_2OH{\cdot}HCl$ and NH_4Ac were of analytical grade (Shanghai Biological Technology Co. Ltd, China). Organic solvents (methanol, acetone, *n*-butanol and dichloromethane) were of HPLC grade (Tianjin Tianzheng Fine Chemical Reagent Factory, China). Deionized water was used throughout the experiment.

Soils

The soil collected (0-20 cm depth) from Lanzhou is Calcisols [32], which is one of the most commonly found soils in northwest China [33]. The physicochemical properties of the soil were: pH 8.35; organic matter content 0.96%; cation exchange capacities (CEC) 5.40 cmol/kg; and soil texture: sand 19%, silt 53%, and clay 28%. Soil type: silty clay loam. The soil was air-dried, ground and passed through a 0.25-mm sieve [7, 34]. Cu-contaminated soil was prepared by adding an appropriate amount of $Cu(NO_3)_2$ solution to a known weight of soil, and the slurry was stirred thoroughly. Phe-contaminated soil was prepared by dissolving an appropriate quantity of Phe in acetone and a measured amount of soil was added slowly, with continuous mixing. The motivation for mechanical blending was to ensure that the spiked contaminant would be evenly distributed throughout the soil. Combining the above methods, Cu-Phe contaminated soil was prepared through three sequential steps as described by Saeedi et al. [7]. Firstly, the clean soil was spiked with $Cu(NO_3)_2$ solution. Secondly, Cu-spiked soil was left for a week to reach equilibrium, and then the dried soil was grinded gently. Thirdly, the acetone-Phe mixture was added to the soil to obtain co-contaminated soil. The above three types of mixtures were ventilated for a week, ground and sieved again to ensure homogeneity, then stored in brown containers and aged in the dark for a month [35]. The final content levels of Cu and Phe in single contaminated soil (S-Cu and S-Phe) and series of combined contaminated soils (C-Cu/C-Phe) were listed in Table 1.

Soil Washing Procedure

Batch washing experiments were conducted to investigate the desorption of Cu and/or Phe from Cu-, Phe- and Cu-Phe contaminated soils with LED3A solution. To probe the influence of contact time on contaminant removal in the washed soil, 0.5 g of single (S-Cu, S-Phe) or combined contaminated soil ($C\text{-}Cu_{500}/C\text{-}Phe_{300}$) was mixed with 20 mL LED3A solution (18 g/L) in a series of conical flasks (50 mL). All aqueous solutions for batch experiments contained $NaNO_3$ (0.01 M) to keep a constant ionic strength, and 0.1 mL of 100.0 mg/L NaN_3 to inhibit microbial growth. The flasks were agitated using reciprocating shaker (SHZ-82A, Jiangsu Danyang Experimental Instrument Plant, China) at 200 rpm and 25±2ºC for a desired interval from 0.083 h to 20 h. Then, the suspensions were centrifuged for 20 min in a centrifuge (TD6, Changsha Instrument Co., Ltd., China) at 3000 rpm and the supernatants were carefully decanted. After filtering through a 0.22 μm membrane, liquid samples were stored in amber vials at 4ºC prior to the analysis.

Other three sets of batch equilibrium experiments were conducted to investigate the influences of LED3A concentration, solution pH value, and Cu/Phe spiking levels on extracting efficiencies of contaminants by LED3A. In the first set, S-Cu, S-Phe and

Table 1. Cu and Phe concentration levels in spiked soils.

Combination	Cu content in soil (mg/kg)	Phe content in soil (mg/kg)	Combination	Phe content in soil (mg/kg)	Cu content in soil (mg/kg)
S-Cu	500	0	S-Phe	300	0
$C\text{-}Cu_{500}/C\text{-}Phe_{50}$		50	$C\text{-}Cu_{100}/C\text{-}Phe_{300}$		100
$C\text{-}Cu_{500}/C\text{-}Phe_{100}$		100	$C\text{-}Cu_{300}/C\text{-}Phe_{300}$		300
$C\text{-}Cu_{500}/C\text{-}Phe_{150}$		150	$C\text{-}Cu_{500}/C\text{-}Phe_{300}$		500
$C\text{-}Cu_{500}/C\text{-}Phe_{200}$		200	$C\text{-}Cu_{700}/C\text{-}Phe_{300}$		700
$C\text{-}Cu_{500}/C\text{-}Phe_{300}$		300	$C\text{-}Cu_{900}/C\text{-}Phe_{300}$		900
$C\text{-}Cu_{500}/C\text{-}Phe_{400}$		400	$C\text{-}Cu_{1200}/C\text{-}Phe_{300}$		1200

C-Cu_{500}/C-Phe_{300} soil samples were washed with a series of concentration gradients of LED3A solutions (1~22 g/L). In the second set, the pH value of 18 g/L LED3A solution was adjusted from 4.0 to 12.0 using NaOH or HNO_3 to wash the co-contaminated soil of C-Cu_{500}/C-Phe_{300}. In the third set, two initial LED3A concentrations of 8 g/L and 14 g/L were selected for the washing process, and the study was conducted on all co-contaminated combinations as illustrated in Table 1. The levels of artificial contaminant in soils were designed as follows: (i) total content of Cu was kept constant as 500 mg/kg, while Phe content was increased from 50 to 400 mg/kg: (ii) A consistent content of Phe was 300 mg/kg, while Cu level was varied from 100 to 1200 mg/kg. All tests were performed in triplicate.

Fraction of Cu or Phe in Soils

Cu or Phe species in combined contaminated soil (C-Cu_{500}/C-Phe_{300}) before and after washing with LED3A (18 g/L) were fractionated by sequential extraction method. The optimized BCR scheme was chosen for fractionating of Cu in soils as the acid extractable, reducible, oxidizable, and residual fractions [36]. The three-step sequential extraction method described by Liu et al. [37] with some modifications was used to analyze Phe in soils as the bioaccessible, associated and bound residual fractions. Measurements were made in triplicate in each experiment to reduce errors.

The procedures for fractionating of Cu in soil were described as follows. (i) Acid extractable fraction: 20 mL CH_3COOH solution (0.11 M) was added to 0.5 g soil in a 50 mL centrifuge tube. The sample was shaken (16 h, 25°C), centrifuged (3000 rpm, 20 min) and the extract was separated for analysis. The residue was washed and centrifuged to discard the washings. (ii) Reducible fraction: 20 mL $NH_2OH{\cdot}HCl$ solution (0.5 M, pH 2) was added to the residue from step 1. The following extraction process was then performed as described above. (iii) Oxidizable fraction: 5 mL H_2O_2 solution (8.8 M, pH 2~3) was added to the residue from step 2. The mixture was digested for 1 h at room temperature with occasional hand shaking. Digestion was then continued at 85ºC for 1 h and the volume was reduced to near dryness by further heating. A second 5 mL of H_2O_2 was added and the digestion procedure was repeated. Afterward, 25 mL of NH_4Ac solution (1 M, pH 2) was added to the cooled residue, followed by the same procedure as in step 1. (iv) Residual fraction: the solid residue after step 3 was transferred into a Teflon crucible and digested with a total volume of 10 mL aqua regia and HF (HNO_3:HCl:HF = 6:2:2) on a hotplate.

The extraction of different forms of Phe in soil was divided into three steps. (i) Bioaccessible fraction: 0.5 g soil was extracted with 5 mL of butanol by shaking for 12 h, centrifuged and the supernatant rotary evaporated. The concentrated Phe was then reconstituted in 1 mL of methanol. (ii) Associated fraction: the remaining soil of step 1 was ultrasonically extracted with 10 mL dichloromethane for 30 min, which was repeated for three times. After centrifugation, the combined extracts were evaporated and dissolved in 1 mL of methanol. (iii) Bound residual fraction: the residual soil from step 2 was extracted with 10 mL of NaOH solution (2 M) at 100ºC for 2 h. After centrifugation and acidification (pH<2), liquid-liquid extraction was performed using 10 mL of dichloromethane. The organic phase was rotary evaporated and then exchanged to 1 mL methanol [37].

Analytical Methods

Cu concentration was quantified with an atomic absorption spectrophotometry (Varian Spectrum AAS110/220, USA). The detection wavelength was 324.7 nm. Phe concentration was determined by a high performance liquid chromatography (Thermo Scientific LCQ Advantage 4000 HPLC, USA) fitted with UV detector and XDB-C18 column (4.6 mm×250 mm, 5 μm). The mobile phase was combined solution of methanol and water (80:20, v/v) at a flow rate of 1 mL/min. The injection volume was set at 10 μL, and the UV wavelength was set at 250.4 nm. Cu or Phe extracts of each fraction were analyzed by AAS or HPLC, respectively, as described above.

Data Processing

All data were plotted using Origin 2018. The presented results were mean values of triplicate samples. The percentage of removal efficiency is expressed as the ratio of the mass of contaminant extracted from soil to the initial mass of contaminant in soil after spiking, and the decimal value is multiplied by 100 to convert to percentage.

Results and Discussion

Desorption Kinetics

The effect of contact time on Cu and Phe desorption by LED3A from single (S-Cu, S-Phe) and combined (C-Cu_{500}/C-Phe_{300}) contaminated soils are shown in Fig. 1. The curves indicate that Cu and Phe were removed with a rapid rate during the first 2 h and then were followed by a slower rate during the next stage. The desorption equilibrium for contaminated soil was attained within approximately 12 h, and the residual amounts of Cu and Phe in the solid phase finally remained constant. Therefore 12 h was considered a reasonably optimal contact time for the LED3A-enhanced washing process in the rest of the studies. The patterns of kinetic curves for the same contaminant exhibited the similar trend for both single and combined contaminated soils (Fig. 1 a vs b), yet the former had greater rates of Cu and Phe desorption than the latter. The equilibrium desorbed amount (i.e. q_e) of S-Cu and S-Phe contaminated soils were 320.18 and 193.60 mg/kg. The calculated removal percentages for Cu and Phe were 64.04% and 64.53%. As for the C-Cu_{500}/C-Phe_{300} co-contaminated soil, the q_e values for Cu and Phe were shown to be 279.34 and 145.83 mg/kg. Compared with the corresponding single contaminated soil, the interaction of coexisting contaminants reduced the removal rates with 8.17% for Cu and 15.92% for Phe, respectively. The results implied that the physicochemical interactions among the LED3A, contaminant and soil were more complex in combined contaminated soil washing system than those of single contaminated soil washing systems.

The pseudo-first-order, pseudo-second-order, Elovich and two-constant rate models were used to describe Cu and Phe desorption kinetics from contaminated soils [38, 39]. The equations are expressed as Eqs (1)-(4).

$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{2}$$

$$q_t = a + b \ln t \tag{3}$$

$$q_t = a t^b \tag{4}$$

where q_e and q_t are the desorbed quantity of contaminant (mg/kg) from soil at the equilibrium state and at time t; t (h) is the contact time; k_1 (h^{-1}) and k_2 (kg/(mg·h)) are the desorption rate constants of pseudo-first-order and pseudo-second-order equations; a and b are constants.

The fitting parameters of the desorption kinetics models are summarized in Table 2. The goodness of fit was determined by comparison of coefficients of determinations (r^2). Referring to Table 2, the pseudo-first-order and pseudo-second-order equations poorly described the observed desorption kinetics. The values of coefficient r^2 from different models indicated that both the Elovich and two-constant rate equations predict accurately the desorption amount of Cu and Phe by LED3A. However, the desorption kinetics curves were correlated better with Elovich equation for it showed the higher r^2 (i.e. 0.9773, 0.9348, 0.9614 and 0.9861) than two-constant rate equation (i.e. 0.9646, 0.8941, 0.9461 and 0.9524).

The overall desorption process can be controlled by reaction kinetics or by one or more diffusion processes,

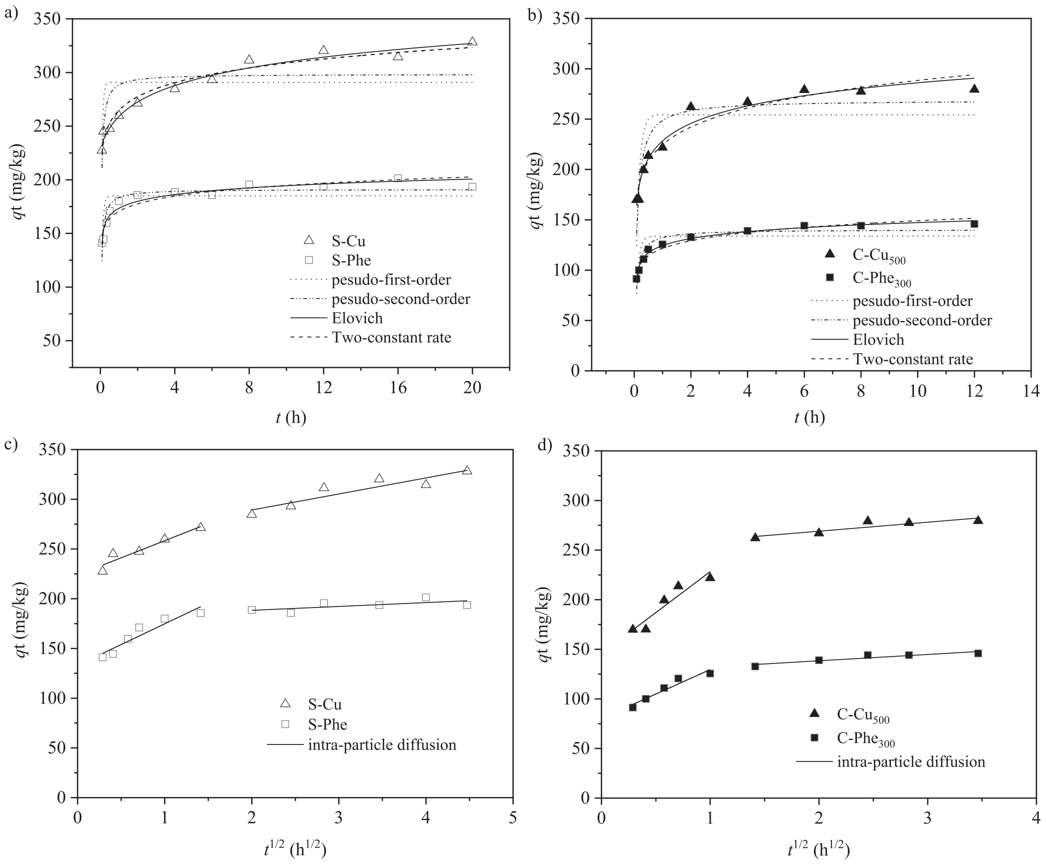

Fig. 1. Kinetics data and modeling of Cu and/or Phe desorption by LED3A (a, c: Cu or Phe single (S-) contaminated soil; b, d: Cu_{500}/Phe_{300} combined (C-) contaminated soil).

Table 2. Kinetics parameters of desorption of Phe and/or Cu from soils.

LED3A (g/L) 18	Pseudo-first-order			Pseudo-second-order			Elovich		
	q_e	k_1	r^2	q_e	k_2	r^2	a	b	r^2
S-Cu	290.79	15.931	0.3782	298.37	0.0971	0.6064	249.22	25.79	0.9773
S-Phe	185.04	13.299	0.5495	191.07	0.1271	0.8679	174.06	8.894	0.9348
C-Cu$_{500}$	254.34	8.016	0.5428	268.90	0.0456	0.8286	288.45	25.04	0.9614
C-Phe$_{300}$	133.71	10.185	0.6326	140.28	0.1134	0.9004	124.94	9.701	0.9861
Two-constant rate				Intra-particle diffusion					
	a	b	r^2	k_{d1}	c_1	r^2	k_{d2}	c_2	r^2
S-Cu	264.89	0.0666	0.9646	34.456	233.90	0.9106	16.124	256.00	0.8439
S-Phe	170.64	0.0575	0.8941	41.712	133.06	0.8853	3.889	180.58	0.4544
C-Cu$_{500}$	224.59	0.1087	0.9461	82.561	145.71	0.8907	9.076	250.90	0.7956
C-Phe$_{300}$	121.58	0.0884	0.9524	49.338	80.217	0.9236	6.377	125.66	0.8591

e.g. surface diffusion, external diffusion, pore diffusion and film diffusion [40]. To gain insight into the rate-controlling steps and desorption mechanism of Cu and Phe, the intra-particle diffusion model [40] was further used to fit the desorption data.

$$q_t = k_d t^{1/2} + c \tag{5}$$

where q_t is the amount of contaminant desorption at time t (h), k_d is the intra-particle diffusion rate constant (mg/(kg·h$^{1/2}$)), and c is constant.

The relationships between $t^{1/2}$ and q_t are shown in Fig. 1c) and d). The dots represent the experimental data, and the lines are the fitted ones for the data. The intra-particle diffusion model parameters are listed in Table 2. From Fig. 1c) and d) it is obvious that the desorption process of Cu or Phe present two straight lines for both single and combined contaminated soils. This fitting result indicates that two stages occur in the desorption processes including initial boundary layer diffusion and gradual intra-particle diffusion [40]. Based on the kinetics parameters of Table 2, the decrease in the k_{di} value of Cu or Phe reveals that the second stage of the multi-linear plot is the rate-limiting step. The increase in the c_i value reflects the expanding in the thickness of the boundary layer surrounding the particle, which decreases the change in the external mass diffusion and increases the change of the internal mass transfer [41]. Such a multi-linearity curve with nonzero intercept demonstrated that intra-particle diffusion was not the only rate controlling step for the system [40, 42]. The complex desorption process maybe involved some other desorption mechanisms along with intra-particle diffusion [43]. It is possible that a predominantly reaction-controlled mechanism was a reasonable assumption. The carboxyl groups complexation for metals outside the micelle and solubilization for organics inside the micelle should be the significant evidence to confirm this assumption [21, 30]. The mechanism was similar to the views expounded previously in the studies on saponin or carboxymethyl-β-cyclodextrin for simultaneous removal of PAH and heavy metal from co-contaminated soils [44, 45].

Effect of LED3A Concentration

The removal efficiencies of Cu and/or Phe with different initial concentrations of LED3A in the single (S-Cu and S-Phe) and combined (C-Cu$_{500}$/C-Phe$_{300}$) contaminated soils are described in Fig. 2. These curves reflect three distinct successive stages of desorption process. In stage I, the removal efficiencies of S-Cu, S-Phe, C-Cu$_{500}$ and C-Phe$_{300}$ were all below 15%. The removal efficiency of S-Cu was highest among

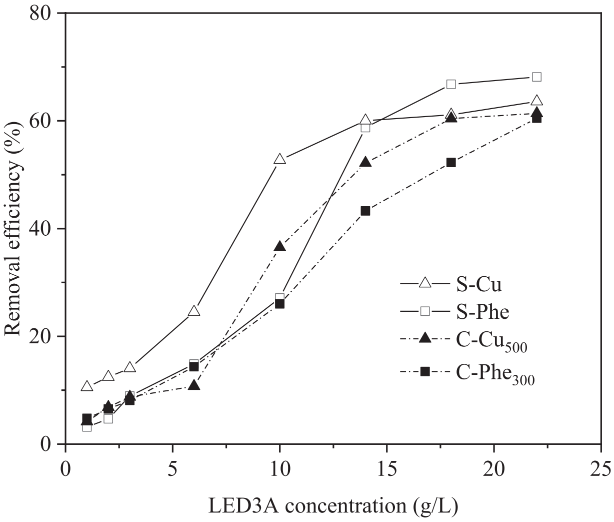

Fig. 2. Effect of LED3A concentration on desorption of Cu and/or Phe. The solid and dashed lines denoted Cu or Phe single (S-) and Cu$_{500}$/Phe$_{300}$ combined (C-) contaminated soil, respectively.

the four desorption curves and those of S-Phe, C-Cu_{500} and C-Phe_{300} were similar to other investigated soils. The removal efficiency of both Cu and Phe showed small change (≤6%) at a low initial LED3A concentration (≤3 g/L). The extracting capacities of LED3A for Cu and Phe were weakened and the removal efficiency of each contaminant appears to be trivial compared to the next stage. In stage II, the amount of contaminant desorption showed a rapid growth relationship with LED3A initial concentration ranged between 5 and 18 g/L. For instance, the removal efficiency of S-Cu and S-Phe increased from 24.53 to 61.11% and 14.84 to 66.77%, respectively. In the case of C-Cu_{500}/C-Phe_{300} co-contaminated soil, the removal efficiency increased from 10.74 to 60.40% for Cu and 14.35 to 52.27% for Phe. Substantial micellization enhanced the competitive ability of LED3A for chelating Cu due to the more ligand groups outside of the micelle. The solubilization capability of LED3A for Phe was also improved accompanying by the formation of larger hydrophobic phase inside of the micelles. The driving force for mass transfer was sharply improved when the LED3A concentration increased. In stage III, further increasing LED3A concentration virtually did not enhance the removal efficiency of S-Cu and S-Phe contaminated soils. Similarly, for C-Cu_{500}/C-Phe_{300} contaminated soil, the variation in the removal of Cu was also negligible. However, the removal efficiency of Phe in the co-contaminated soil was still increased to 60.48% with LED3A being up to 22 g/L. Accordingly, a plateau was reached corresponding to an approximate maximum removal efficiency of Cu or Phe (except the Phe of C-Cu_{500}/C-Phe_{300}) with the surfactant concentration around 18 g/L.

Fig. 2 reveals that compared to the removal percent values in single contaminated soil, there was a reduction trend of Cu desorption in combined contaminated soil for LED3A ranging from 1 g/L to 14 g/L, and the distinction in the removal efficiency of Cu disappeared with a further increase of LED3A concentrations. On the contrary, the similar results of Phe removal for single and combined contaminated soils were received within the range of applied LED3A (1~10 g/L). Interestingly, when the dosage of LED3A increased further, the efficiency of Phe desorption in combined contaminated soil decreased appreciably compared to that in single contaminated soils. A similar degree of reduction was observed for Cu and Phe removal efficiency, i.e. 5.31%-16.21% and 7.66%-15.47% respectively, between single and combined contaminated cases. In summary, LED3A is an effective agent in soil washing, not only for single heavy metal or PAH contamination but also for the combined contamination of them. Comparing the four curves in Fig. 2, the optimal removal efficiency of Phe or Cu from the combined contaminated soil was almost the same as that from the single contaminated soil, which was in close agreement with the findings by Song et al. [46]. For example, at 22 g/L LED3A, the removal efficiencies of Cu and Phe in single contaminated soil (S-Cu and S-Phe) were 63.54% and 68.14% respectively, and that in combined contaminated soil (C-Cu_{500}/C-Phe_{300}) were 61.39% and 60.48% respectively. In comparison, the eluting efficiencies of Cd (56.4%) and petroleum (50.8%) from co-contaminated soil was less efficient by washing with chelating surfactant [47]. Zhang et al. [29] have also reported that the removal efficiencies of Cu (55.3%-65.8%) and decabromodiphenyl ether (BDE209)(31.4%-46.4%) would be increased with the applied voltage gradient and concentration of chelating surfactant in the enhanced electrokinetic remediation for co-contaminated soil. Based on these results, LED3A could simultaneously and efficiently remove Cu and Phe from co-contaminated soils but the mutual constraint may be existed between the two different contaminants [47].

Effect of pH Value

As shown in Fig. 3, the lowest removal efficiency of each contaminant in combined contaminated soil (C-Cu_{500}/C-Phe_{300}) occurred at pH 4. When pH values increased from 5 to 9, LED3A solution (18 g/L) exhibited a high extraction capability for both contaminants. The removal efficiency within this period for Cu and Phe was 59.26%-66.67% and 44.34%-53.21%, respectively. However, the data gradually decreased as pH values increased from 10 to 12, especially for the removal of Cu. At pH 12, 27.75% of Cu and 41.51% of Phe was removed by LED3A. It is clear that the pH value is an important parameter that affects the desorption effectiveness, and the influence of pH variation is higher on Cu than on Phe.

LED3A was prone to protonation when the pH value was less than 5, which was not conducive to its chelation with metal elements and micelles formation

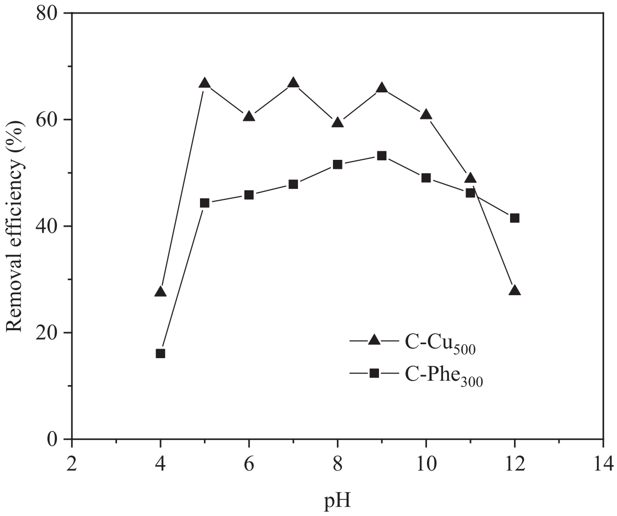

Fig. 3. Effect of pH on desorption of Cu and Phe from combined contaminated soil (C-Cu_{500}/C-Phe_{300}) using LED3A.

[21, 30]. Additionally, LED3A adsorption on soil increased with decreasing pH because the carboxylic groups of it became less negatively charged at low pH and the electrostatic repulsion between LED3A and soil decreased [48]. The effectiveness of LED3A for extracting of contaminants was limited due to its adsorption loss by soils at solution pH of 4. As the solution pH increased, the soil particle surface increasingly acquired negative charge and hence LED3A adsorption was inhibited by electrostatic repulsion. Therefore, at a higher pH (i.e. 5-9), less LED3A was adsorbed on the soil surface and more LED3A in solution could be available to form micelles enhance the removal efficiencies of Phe and Cu. Surfactant molecules accumulated at the soil-water and soil-contaminant interfaces, which could increase the contact angle between the hydrophobic contaminant and the soil to change the wettability of the system [49]. LED3A adsorbed on the surface of the Phe contaminant would cause the repulsion between the hydrophilic head groups of the LED3A molecules and the soil particles. Thus, the hydrophilic groups become oriented towards the aqueous phase to reduce the interfacial tension between Phe and solution, favorably enhancing the Phe removal [50]. Moreover, due to the strong coordinating capacity, the aggregated LED3A molecules on the solid-liquid interface could also directly contact with adsorbed Cu and then seized them from the soil to form soluble aminoxatyl complex, which would lead to distinct increase in the Cu desorption amount [30, 49]. Conversely, the hydrophobic chains might be driven towards the aqueous phase so as to reduce the mass transfer resistance under the circumstances. Since the dual function of micelle-partitioned Phe dissolution and complexation-promoted Cu dissolution was the predominant mechanisms for simultaneous removal of Phe and Cu from soils using LED3A. The optimal pH should be a compromise of the two contradictory effects mentioned above, and the maximum removal of Cu or Phe should take place at an intermediate pH value between 5 and 9. As pH is increased from 5 to 9, the removal efficiencies of Cu and Phe by LED3A were markedly higher than that of other pH values in Fig. 3, exhibiting a wide pH range suitable for treatment of co-contaminated soil. When pH increased within the range from 10 to 12, most of the LED3A might exists in free form due to the repulsion of negative soil surface charge, and the formation of micelle would be impeded meanwhile [29, 48]. Consequently, the effectiveness of removing Cu and Phe from contaminated soil continues to decrease. In addition, the speciation of Cu would also lead to a decrease in the elution efficiency of LED3A due to the increase in anionic forms of copper share (e.g. $CuOH_3^-$) at alkaline pH.

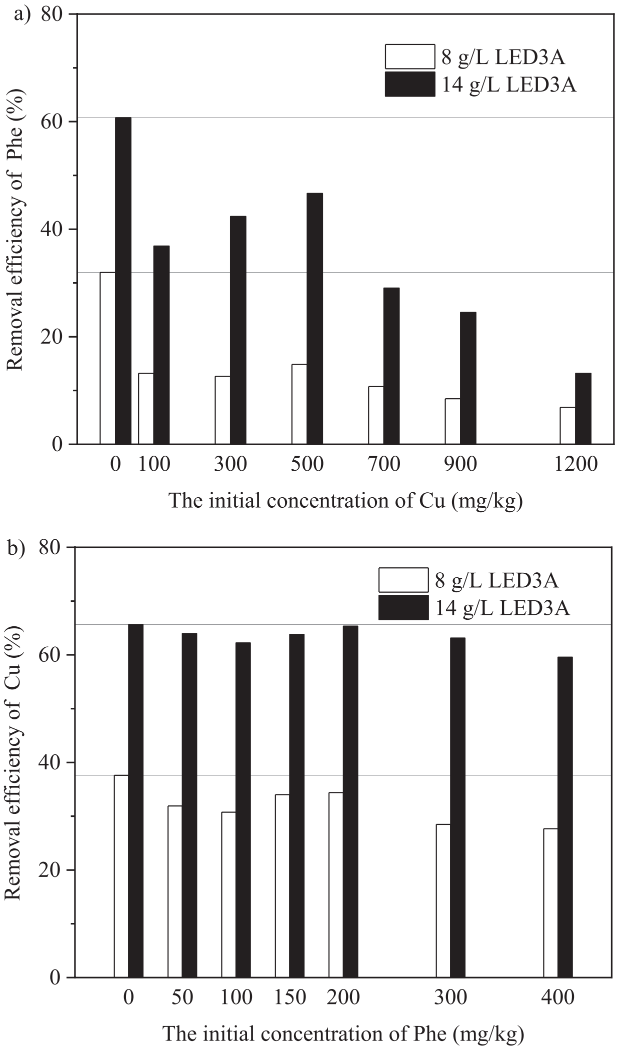

Fig. 4. Effect of Cu/Phe initial concentration on the removal efficiency of each other.

Interaction Mechanism between Cu and Phe

As shown in Fig. 4a), the results clearly indicate that the increasingly coexisting Cu (100~1200 mg/kg) reduced the Phe removal efficiency from 31.96% to 6.85% in 8 g/L LED3A, and from 60.74% to 13.20% in 14 g/L LED3A, respectively, indicating that the presence of Cu in soil significantly inhibited the effectiveness of Phe removal, especially at high level of Cu. There were two possible mechanisms involved. Firstly, the formation of LED3A-Cu ternary surface complex between strongly adsorbed Cu in soils and LED3A chelating hydrophilic head would decrease the effective amount of LED3A available in solution to form micelles that solubilize Phe [51]. Secondly, the LED3A hydrophobic monolayers at soil surface display their hydrophobic tails sticking out into aqueous phase, resulting in a stronger hydrophobic force that favors the retention of Phe on soil minerals [50, 52]. These two processes may contribute to the observed reduction in the effectiveness of LED3A in removing Phe under different levels of coexisting Cu. However, the results in Fig. 4b) indicate that the Cu removal efficiency both decreased less than 10% with the increase of soil coexistence of Phe (50~400 mg/kg) by washing with

Table 3. Content of Cu and Phe for each fraction in co-contaminated soil (C-Cu_{500}/C-Phe_{300}) before (b) and after (a) LED3A washing, and washing percentage of each fraction (*p*).

Fraction	Cu (mg/kg)			Fraction	Phe (mg/kg)		
	b	a	*p* (%)		b	a	*p* (%)
Acid extractable	266.7	56.6	78.8	Bioaccessible	181.8	73.7	59.5
Reducible	123.4	59.7	51.6	Associated	90.9	55.3	39.2
Oxidizable	61.0	41.2	32.5	Bound residue	2.82	2.60	7.8
Residual	45.2	35.5	21.5	/	/	/	/

8 g/L and 14 g/L LED3A. The probably reason for such a decrease was that a little free-phase Phe covering soil surface physically isolated the adsorbed Cu on soils, and thus limiting the interaction between LED3A and Cu [53]. These results indicated that the impediment in Cu removal induced by coexisting Phe was weak and could be ignored in LED3A washing, especially at high dosage of LED3A.

Effect of LED3A Washing on Cu and Phe Speciation

Fig. 5 illustrates the different fractions of Cu and Phe in co-contaminated soil (C-Cu_{500}/C-Phe_{300}) before (b) and after (a) washing by LED3A. Table 3 lists the contents and removal rates of Cu and Phe for their respective several fractions. In general, the bioavailability of contaminants (i.e., either heavy metals or organic contaminants) is closely correlated to easily extractable portion of them. The fractionation by extractability could therefore form a better basis for evaluating remediation performance than total contaminants content in soils [45, 54].

In Fig. 5, the largest amount of Cu in the untreated soil was found in the acid extractable fraction (53.7%), and much less in the reducible (24.9%), the oxidizable (12.3%) and the residual (9.1%) fraction. LED3A washing caused a significant decrease in the Cu content of the acid extractable fraction (29.3%) and increases in the reducible fraction (30.9%), oxidizable fraction (21.3%) and residual fraction (18.5%). The results illustrate that the percentage of Cu in the mobile fractions decreased and that in the immobile fractions increased, especially in the residual fraction. In Table 3, the corresponding Cu values (mg/kg) dropped from 266.7 to 56.6 in the acid extractable fraction, from 123.4 to 59.7 in the reducible fraction, from 61.0 to 41.2 in the oxidizable fraction, and from 45.2 to 35.5 in the residual fraction, respectively. With respect to Phe, the proportion of extractable Phe including bioaccessible and associated fractions, decreased from 65.9% and 56.1% in the unwashed soil to 32.9% and 42.0% in the washed soil, respectively (Fig. 5). The non-extractable soil bound residue Phe was both less than 2% of the total Phe in the soils before and after washing. The corresponding Phe values (mg/kg) of bioaccessible and associated fractions were reduced from 181.8 and 90.9 to 73.7 and 55.3, respectively (Table 3). The bound residue fraction as 2.82 mg/kg was much lower than those of the bioaccessible and associated fractions in soil. This was consistent with the result described previously that PAHs were more likely to be present in the extractable fractions [55, 56]. The results indicate that LED3A took an active part in improving the solubilization of Phe and releasing the labile and potentially bioavailable fraction remained in the soil solid phase.

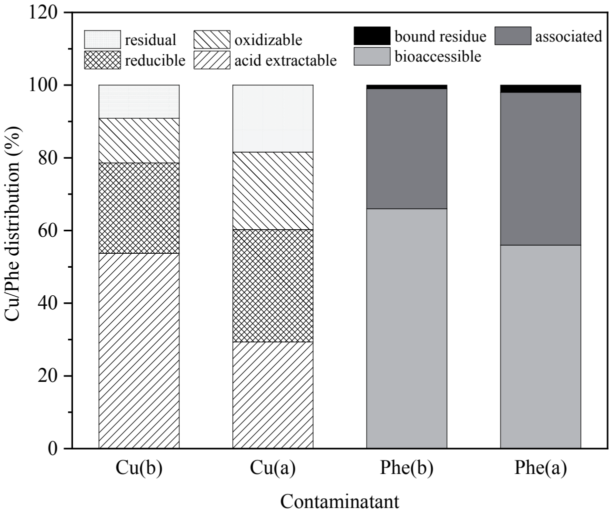

Fig. 5. Cu or Phe fractions in co-contaminated soil (C-Cu_{500}/C-Phe_{300}) before (b) and after (a) washing with LED3A.

LED3A washing resulted in reduction of each Cu speciation in soil (Table 3). Compared to the magnitude of these fractions in the unwashed soil, the four fractions were reduced by 78.8% (acid extractable fraction), 51.6% (reducible fraction), 32.5% (oxidizable fraction), and 21.5% (residual fraction). It was observed that LED3A readily extracted metal from the acid extractable fraction, and partially also from the reducible, the oxidizable and the residual one. Qiao et al. [41] also reported that LED3A had the ability to remove various forms of heavy metals in the soils. However, the difference in this study was that the proportion of Cu in the oxidizable fraction of washed soil decreased markedly, which possibly attribute to the enhanced solubilizing effect of surfactant on PAH in metal-PAH-soil bond [7].

As for Phe, higher washing percentages of Phe were found in the bioaccessible fraction (59.5%) and the associated fraction (39.2%). The washing percentage of the bound residue fraction was only 7.8%. Its released amount was even less than 0.2% relative to the total desorbed content of Phe in soil. The significant difference lied in elution amount between bound residue fraction and other fractions probably due to the limited biological activity in treatment soils. The significant elution amount difference between bound residue fraction and other fractions was probably due to the limited biological activity in treatment soils. Since microbial activity was shown to play an important role in the formation of bound PAH residue [54]. These results are approved by the previously reported result of that tea saponin washing pyrene-Cd contaminated soil showed a great advantage in improving solubilization capability and promoting the morphological transformation [55].

Conclusions

The chelating surfactant LED3A had been used as the washing agent for remediation of Cu-Phe co-contaminated calcareous soil in this study. The desorption processes fitted well with Elovich and two-constant rate kinetics models, and the desorption rates controlled by both the internal diffusion of particles and the external diffusion of liquid membrane. Chelation and solubilization by the LED3A micelle are the main mechanisms for Cu and Phe removal. With the LED3A concentration increasing, the removal rate of pollutants were significantly increased in succession, reaching 60.40% for Cu and 52.27% for Phe at the optimal washing concentration of 18 g/L. In the pH range 5-9, LED3A showed good extraction performance for both Cu and Phe from the co-contaminated soil, while strong acid and alkaline environments were unfavorable for desorption. Coexisting Cu was obviously detrimental to Phe removal, while the presence of Phe had little effect on Cu removal. The residual fraction analysis of contaminants in soil demonstrated that the proportion of bioavailable fractions of Cu and Phe was significantly decreased. Correspondingly, soil environmental hazards and ecological risk induced by co-contaminants could be effectively reduced by the LED3A-enhanced soil washing approach. The results implicated that treatment of heavy metals and PAHs co-contaminated soil by washing with the biodegradable LED3A could be a practical and eco-friendly ex-situ remediation pathway.

As a promising agent for the soil washing process, LED3A could also be used in column experiments to explore the effectiveness of in-situ soil flushing remediation systems. Moreover, further research directions for LED3A would be to apply it as a strengthening agent to assist phytoremediation or enhance electrokinetic remediation, thereby broadening its application in combined remediation technology for soils co-contaminated with heavy metals and HOCs.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

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