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Removal of Potentially Toxic Metals from Soil by *para*-Sulphonato-thiacalix[4]arene:

Competitive Extraction and Selectivity Sequence

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Abstract

para-Sulphonato-thiacalix[4]arene (STC[4]A) is an emerging supramolecular receptor for enhancing the extraction of potentially toxic metals (PTMs) from soil. Batch extraction experiments were conducted to evaluate the competitive extraction of cadmium (Cd), copper (Cu), and lead (Pb) by STC[4]A from single- and multi-metal contaminated soils. The extraction capacity and selectivity mechanism were investigated by determination of the conditional stability constants ($\log K$) of the STC[4]A-M complex via spectrophotometric titration and the metal speciation using sequential extraction. Under STC[4]A deficiency, the order of metal extraction efficiencies was Cd > Cu > Pb for single-metal contaminated soils, while the selectivity sequence of metal extraction was Cu > Cd > Pb for multi-metal contaminated soils. Spectrophotometric titration indicated that the $\log K$ values of the STC[4]A-M complex were in the order of STC[4]A-Cu > STC[4]A-Cd > STC[4]A-Pb and that the values governed the metal extraction selectivity of STC[4]A in multi-metal contaminated soils. Although the $\log K$ values for STC[4]A-Cd were intermediate, STC[4]A showed the largest extraction yield for Cd from single-metal contaminated soil due to its larger proportion of exchangeable fraction in soil. The effectiveness of STC[4]A washing appeared to be highly dependent on the Metal-STC[4]A formation constants and the metal distribution in soil.

Key words: Potentially toxic metals; Competitive extraction; *para*-Sulphonato-thiacalix[4]arene; Conditional stability constant; Sequential extraction.

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1 Introduction

Soil contamination has become a major environmental problem throughout the world. Potentially toxic metals (PTMs) are one of the main causes of concern because they are persistent in soils and difficult to remove^{1,2}. The Agency for Toxic Substances and Disease Registry 2013 Substance Priority List ranked Cd #7, Cu #118, and Pb #2 as priority hazardous substances based on their frequency, toxicity, and potential for human exposure at the US National Priority List (NPL) site³. In China, the area of PTM-contaminated soils associated with mining activities reached approximately 3.2 Mha by the end of 2004, and this figure was increasing at an alarming rate of 46,700 ha per year⁴. Therefore, it is necessary to introduce proper methods for the remediation of PTM-contaminated soils.

Immobilisation⁵, phytoremediation⁶, and soil washing⁷ are frequently listed among the best demonstrated available technologies for remediation of PTM-contaminated soils. Immobilisation is fast, cost-effective, and applicable; however, the stored waste requires permanent control because the immobilised contaminants could still be released to the environment when its physicochemical condition is changed⁸. Phytoremediation is perceived as a

cost-effective, eco-friendly, and solar-driven technology with good public acceptance, but it also suffers from some limitations, such as long-term commitment and patience, difficulty in mobilisation of the more tightly bound fraction of metal ions from soil, and complicated post-treatment⁹. Among the number of available techniques, soil washing has gained world-wide attention as a permanent, rapid, and potentially cost-effective treatment alternative to remove PTMs from soil.

Soil washing is an *ex situ* treatment for separating contaminants (particularly metals) from soils/sediments via chemical, physical, biochemical, or physicochemical methods⁷. Its effectiveness is closely related to the ability of the extracting solution to dissolve contaminants in soils. Different extractants, such as acids, chelating agents, Chemo/Bio surfactants, and organic metabolites, have been used to enhance the desorption of contaminants from soil^{7, 10-13}. Most of these extractants could effectively desorb either PTMs or hydrophobic organic compounds (HOCs) from solids into aqueous phases. In recent years, the extraction reagents that could simultaneously remove HOCs and PTMs have become increasingly attractive for the remediation of soils that contained multiple contaminants¹⁴⁻¹⁸.

Recently, we reported a novel supramolecular

receptor, *para*-Sulphonato-thiacalix[4]arene (STC[4]A) for the remediation of metal-contaminated soils¹⁹. STC[4]A could selectively complex soft metal ions (e.g., Cd, Cu, and Pb) and encapsulate HOCs into its aromatic cavity²⁰, which has the potential for simultaneously removing both PTMs and HOCs from soils. Our previous study demonstrated that STC[4]A could effectively enhance the dissolution of single PTM, i.e., Cd, from contaminated soil and efficiently prevent co-dissolution of soil minerals¹⁹. Thus, STC[4]A is an attractive alternative in washing-based remediation of soil contaminated by Cd. However, the metal-contaminated sites are often affected by several PTMs rather than a specific PTM. The competitive effect among the metals could influence the transport behaviour of the metals in soils²¹. The competition between metals for the available chelating agents is particularly important at a low chelant-to-metal molar ratio (MR) or under chelant deficiency²².

In this study, therefore, batch experiments were conducted to investigate the removal efficiency and competition of different PTMs (i.e., Cd, Cu, and Pb) present in the soil under extraction by STC[4]A. The competitive extraction and selectivity sequence were elucidated based on determination of the conditional stability constants of the STC[4]A-M

complexes via spectrophotometric titration and the metal speciation in the soils using a sequential extraction procedure.

2 Materials and methods

2.1 Materials

STC[4]A used in this research was synthesised according to a previously described method²³, and other chemicals used in the experiments were analytically pure. Pure water obtained using a Milli-Q system was used for the preparation of all solutions.

The soil sample for the experiments was collected from a non-contaminated area located in Shenyang, China. The pH of the soil in distilled water (1:2.5 ratio, w/v) was measured with a pH meter, and the soil organic content was determined by the $K_2Cr_2O_7$ digestion method²⁴. The soil has a pH of 6.01 and an organic matter content of 16.01 g kg⁻¹.

Single- and multi-metal contaminated soils were prepared by mixing the soil with $Cd(NO_3)_2$, $Cu(NO_3)_2$, and $Pb(NO_3)_2$ solutions (pH 6.01) individually or simultaneously. The contaminated soils were then dried at room temperature and stored in plastic containers for 6 months with frequent and thorough mixing. The concentrations of metals were determined using an atomic absorption spectrometer (Varian

SpectrAA 220, Australia) after digestion with a HCl-HNO₃-HClO₄-HF solution. A standard reference soil (GBW 07401, obtained from the Institute of Geophysical and Geochemical Exploration, Langfang, Hebei Province, China) was included in the analytical process for quality assurance/quality control. Total Cd, Cu, and Pb concentrations in the artificially contaminated soils were 556-578, 312-329, and 1006-1043 mg kg⁻¹, respectively. The total concentration of each of the three contaminants was approximately 5 mmol·kg⁻¹. Next, the soils were passed through a 0.84-mm sieve for batch experiments.

2.2 Batch experiments

All batch experiments were conducted in acid-rinsed 50-mL plastic centrifuge tubes. Tubes containing 1 g of contaminated soil were prepared for each treatment, followed by addition of an STC[4]A solution. The tubes were then capped and continuously shaken using a shaker (180 rpm) at 25 °C for a given period of time.

Batch extraction experiments were performed at an STC[4]A:Cd molar ratio of 0.8:1, which was chosen to ensure a deficient amount of ligand was present. In the pH effect experiment,

0.2 mM STC[4]A (liquid:soil ratio of 20:1, i.e., 1 g of the soil with 20 mL of extracting solution, 48 h) was used at different pH values (4-12), adjusted with a diluted HNO₃ or NaOH solution.

In the kinetic study, the suspensions were shaken for different times from 10 to 1440 min (0.4 mM STC[4]A, pH 11, liquid:soil ratio of 10:1, i.e., 1 g of the soil with 10 mL of extracting solution).

After shaking was completed, the suspensions were centrifuged at 5000 rpm for 10 min, and then, the supernatants were filtered and acidified with diluted HNO₃ to pH 2 for metal analysis via flame atomic absorption spectrometry (FAAS, Varian SpectrAA 220, Australia). All of the tests were performed in triplicate, and the results are presented as the average of the triplicate measurements. The percentages of metals removed were calculated using the following equation:

$$\text{Percent metal removed}(\%) = \frac{C_1 V_1}{C_s m_s} \times 100 \quad (1)$$

where C_1 and C_s are the concentrations of metal in the supernatant (in mg L⁻¹) and soil (mg kg⁻¹), respectively; V_1 is the volume of the

supernatant (in L), and m_s is the dry mass of the soil (in kg).

2.3 Sequential extraction procedure

A sequential extraction procedure was selected to ascertain the distribution of the metals in the soil before and after treating the soil with a solution. The sequential extraction scheme, based on the procedures mentioned in the literature with a minor modification (Table 1)

Table 1 Sequential extraction procedure of metals from the soil and corresponding phases

Metal fraction	Abbreviation	Step	Extracting solution and condition
Exchangeable	EX	1	1 M MgCl ₂ , pH 7; 2h, 20°C
Weakly complexed and bound to carbonate	CA	2	1 M NaCH ₃ CO ₂ , pH 5; 5h, 20°C
Bound to Fe/Mn oxides of low crystallinity	OX	3	0.04 M NH ₂ OH-HCl in 25% (v/v) CH ₂ CO ₂ H; 6h, 96°C
Bound to organic matter	OM	4	30% H ₂ O ₂ + HNO ₃ (pH 2), 3.2 M CH ₃ CO ₂ NH ₄ in 20% (v/v) HNO ₃ ; 5h, 85°C
Residual	RE	5	Total minus sum of the extractable

2.4 Determination of the conditional stability constants of the STC[4]A-M complex

A spectrophotometric titration method, detailed procedures of which have been reported in previous studies¹⁹, was employed to investigate the conditional stability constants of the STC[4]A-Cu and STC[4]A-Pb complexes. Mixed solutions of STC[4]A and metals were prepared. The STC[4]A:M molar ratios were varied as follows: 1:0, 1:0.1, 1:0.15, 1:0.2, 1:0.3, 1:0.5, 1:0.75, 1:1, 1:1.7, 1:2, 1:2.5, 1:3.8, 1:5.8, and 1:8. The total volume of each mixed solution

²⁵, was performed in 50-mL centrifugation tubes. Following each extraction, the samples were centrifuged at 5000 rpm for 10 min at room temperature, and the concentrations of Cd, Cu, and Pb in the supernatants were analysed using FAAS. The samples were then washed with 10 mL of pure water prior to the next extraction step. The extraction experiments were performed in triplicate.

was maintained at 25 mL, and the solution pH values were adjusted to 5.04, 7.09, 11.01, and 12.07. The samples were shaken (120 rpm) for 24 h on a shaker at 25 °C to allow the mixtures to reach equilibrium. The UV absorption spectra of the mixed solutions of STC[4]A and M were recorded from 200 nm to 400 nm using a Cary 50 UV-VIS spectrophotometer (Varian, USA). The conditional stability constants ($\log K$) of the STC[4]A-M complexes were calculated from spectrophotometric titration data using Target Testing Factor Analysis (TTFA)²⁶.

2.5 Statistical analysis

All statistical analyses were performed using a commercial software package (SPSS 17.0 for Windows, SPSS Inc., Chicago, IL, USA). One-way analysis of variance (ANOVA) was used to test whether the amounts of metal desorbed from the soils in the presence of ligands were significantly different from each other and from the control. A *p* value of < 0.05 was considered to be statistically significant.

3 Results and discussion

3.1 Effect of pH on the metal extraction efficiency

In a previous study, STC[4]A was confirmed to significantly enhance the dissolution of Cd from soil and the solution pH was found to have an important effect on the Cd-removal efficiency of STC[4]A extraction¹⁹. The influence of the solution pH on the desorption of metals was also examined in this study. The extraction efficiencies of Cd, Cu, and Pb from single- and multi-metal contaminated soils are shown in Fig. 1, Fig. 2, and Fig. 3, respectively. The results show that the desorption of either Cu or Pb from the single-metal contaminated soil increased

with increasing pH, reaching the maximum value at pH 11, followed by a decrease at pH 12, akin to the behaviour of Cd desorption by STC[4]A. The extraction efficiencies of Cd, Cu, and Pb from single-metal contaminated soil followed the descending order: Cd > Cu > Pb.

The variation of Cd or Cu extraction from the multi-metal contaminated soil under the impact of pH change followed the same trend as that from the single-metal contaminated soil. However, the Pb extraction efficiency increased from pH 4 to pH 10, after which its extraction efficiency decreased with increasing pH. The metal extraction from the multi-metal contaminated soils was less than that from the single-metal contaminated soils, especially for Pb and Cd. Compared to the single-metal contaminated soils, the equilibrium extraction efficiency of Pb at pH 11.0 was 28.2%, 37.1% and 43.9% lower when the soil was co-contaminated with Cd and Pb, Cu and Pb, and Cd, Cu and Pb, respectively, and the equilibrium extraction efficiency of Cd was 3.4%, 37.7% and 43.6% lower when the soil was co-contaminated with Cd and Pb, Cd and Cu, and Cd, Cu and Pb, respectively. Cu desorption was not greatly affected by competition from Pb and Cd desorption in the multi-metal contaminated soil. When the soil was

co-contaminated with Cd and Cu, or Cd, Cu and Pd, the Cu equilibrium extraction efficiency was only 10.1% and 10.4% lower than that in the single-metal contaminated soils at pH 11.0, respectively. Overall, the extraction efficiencies of Cd, Cu and Pb from the multi-metal contaminated soil followed the descending order: $Cu > Cd > Pb$.

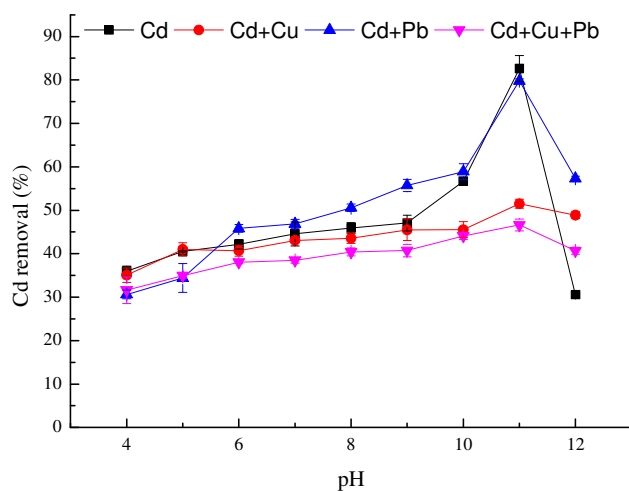


Fig 1 Cd removal efficiencies from single- and multi-metal contaminated soils as a function of pH with 0.2 mM STC[4]A (liquid:soil ratio of 20:1, 48 h). Error bars represent the standard deviations ($n = 3$). (Cd) Cd contaminated soil. (Cd+Cu) Cd and Cu multi-metal contaminated soil, (Cd+Pb) Cd and Pb multi-metal contaminated soil, (Cd+Cu+Pb) Cd, Cu, and Pb multi-metal contaminated soil.

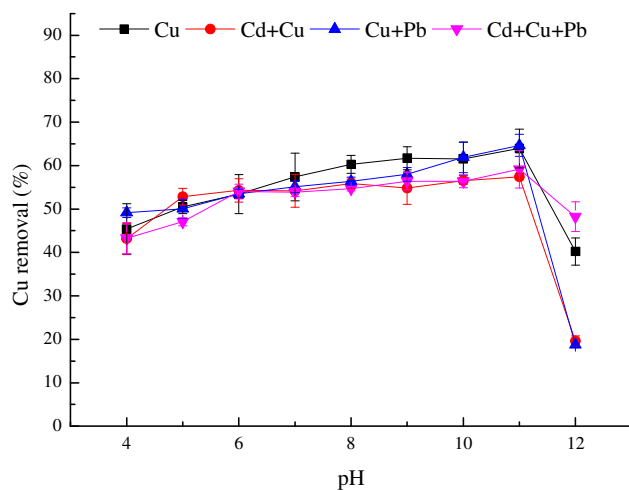


Fig 2 Cu removal efficiencies from single- and multi-metal contaminated soils as a function of pH with 0.2 mM STC[4]A (liquid:soil ratio of 20:1, 48 h). Error bars represent the standard deviations ($n = 3$). (Cu) Cu contaminated soil. (Cd+Cu) Cd and Cu multi-metal contaminated soil, (Cu+Pb) Cu and Pb

multi-metal contaminated soil, (Cd+Cu+Pb) Cd, Cu, and Pb multi-metal contaminated soil.

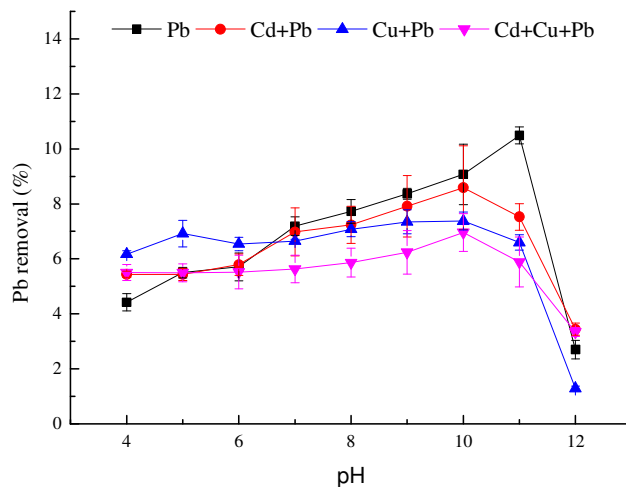


Fig 3 Pb removal efficiencies from single- and multi-metal contaminated soils as a function of pH with 0.2 mM STC[4]A (liquid:soil ratio of 20:1, 48 h). Error bars represent the standard deviations ($n = 3$).

(Pb) Pb contaminated soil, (Cd+Pb) Cd and Pb multi-metal contaminated soil, (Cu+Pb) Cu and Pb multi-metal contaminated soil, (Cd+Cu+Pb) Cd, Cu, and Pb multi-metal contaminated soil.

3.2 Kinetics of metal extraction by STC[4]A

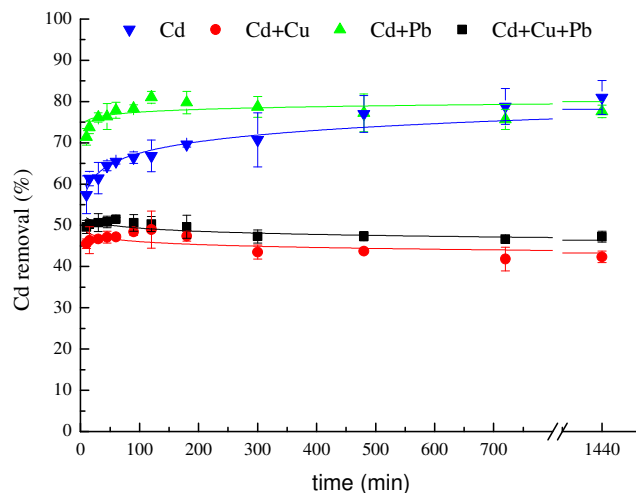


Fig. 4 Extraction kinetics of Cd with 0.4 mM STC[4]A (liquid:soil ratio of 10:1, pH 11). Error bars represent the standard deviations ($n = 3$). (Cd) Cd contaminated soil, (Cd+Cu) Cd and Cu multi-metal contaminated soil, (Cd+Pb) Cd and Pb multi-metal contaminated soil, (Cd+Cu+Pb) Cd, Cu, and Pb multi-metal contaminated soil.

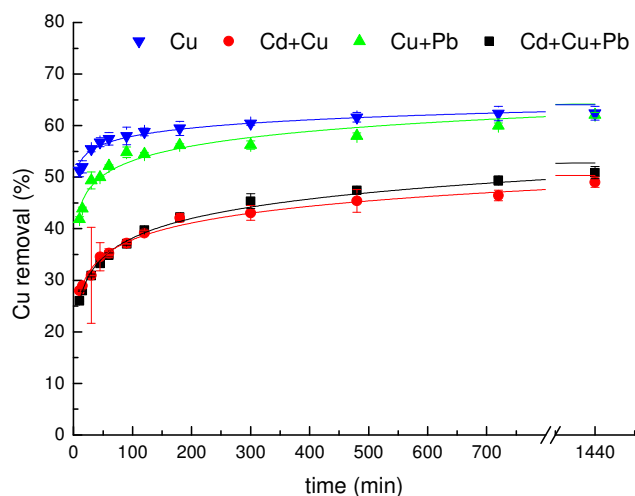


Fig. 5 Extraction kinetics of Cu with 0.4 mM STC[4]A (liquid:soil ratio of 10:1, pH 11). Error bars represent the standard deviations ($n = 3$). (Cu) Cu contaminated soil, (Cd+Cu) Cd and Cu multi-metal contaminated soil, (Cu+Pb) Cu and Pb multi-metal contaminated soil, (Cd+Cu+Pb) Cd, Cu, and Pb multi-metal contaminated soil.

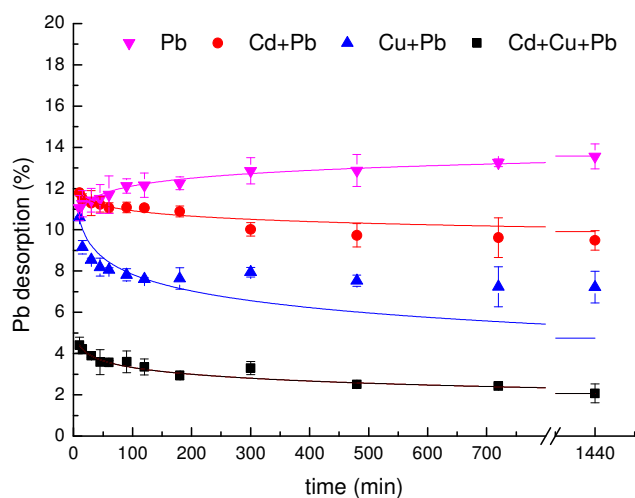


Fig. 6 Extraction kinetics of Pb with 0.4 mM STC[4]A (liquid:soil ratio of 10:1, pH 11). Error bars represent the standard deviations ($n = 3$). (Pb) Pb contaminated soil, (Cd+Pb) Cd and Pb multi-metal contaminated soil, (Cu+Pb) Cu and Pb multi-metal contaminated soil, (Cd+Cu+Pb) Cd, Cu, and Pb multi-metal contaminated soil.

Most of the previous metal extraction studies larger than 1, i.e., chelant excess. However, the demonstrated the effectiveness of chelant competitive effects of metals in the extraction application at chelant-to-metal molar ratios process could be elucidated exhaustively under

chelant deficiency. In this study, batch extraction experiments were conducted at an STC[4]A:M molar ratio of 0.8:1, which was chosen to ensure a deficient amount of ligand in the soil.

Kinetic data of Cd, Cu, and Pb extraction from the single- and multi-metal contaminated soils are shown in Fig. 4 to Fig. 6. For the single-metal contaminated soils, approximately 57% of Cd, 51% of Cu, and 11% of Pb were extracted in the first 10 min, and then the extraction efficiencies increased to 66% for Cd, 58% for Cu, and 12% for Pb in 90 min. Subsequently, the metal extraction considerably slowed down and reached equilibrium at approximately 77% for Cd, 62% for Cu, and 13% for Pb after 8 h. The kinetic data of metal extraction from the single-metal contaminated soils indicated that STC[4]A induced a rapid desorption of metals within the first 90 min, which was followed by a gradual release that occurred over the following hours. The longer the contact time, the more metals were removed from the soil.

Under the condition of STC[4]A deficiency, the desorption kinetic patterns of PTMs varied with the difference in the combination of PTMs. The desorption of Cd from the soil contaminated with Cd and Pb increased from 71.4% to 81% in the first 2 h and then slightly decreased and

reached equilibrium in the following several hours. The desorption of Cd from the soil contaminated with Cd and Cu reached 45.6% in the first 10 min and continuously increased to 49% during the first 2 h, then decreased to 43% and approached equilibrium in the following 22 h. The desorption kinetics of Cu from the multi-metal contaminated soils were similar to that from the single-metal contaminated soil, except that the amount of Cu in equilibrium solution decreased with the co-presence of Cd. The extraction efficiencies of Pb, in contrast, continuously decreased with increasing contact time.

For the soil contaminated with Cd, Cu, and Pb, the extraction efficiency of Cu increased continuously from 26.0% to 50.9% from 10 min to 24 h. The extraction efficiency of Cd was 49.6% initially, rose to its peak of 50.3% at 2 h, and then started to decline steadily to approximately 47.2% at 24 h. The extraction percentage of Pb decreased continuously from 4.4% at 10 min to approximately 2.1% at 24 h. In other words, while the extraction of Cu from the multi-metal contaminated soil increased to reach equilibrium, the extraction of Cd decreased after 2 h, and the extraction of Pb decreased immediately after 10 min. These results showed that STC[4]A-extracted Cd and

Pb were subsequently re-sorbed in the soil. Tsang et al. and Yip et al. also found that desorption and re-adsorption of metals occurred simultaneously with the addition of chelating agents for chemical extraction^{27, 28}. Yip et al. documented that EDDS-extracted Zn and Pb were re-sorbed due to adsorption and metal exchange of newly formed ZnEDDS²⁻ and PbEDDS²⁻ on the soil surfaces under EDDS deficiency²⁹. EDDS preferentially complexed with Cu, and the newly formed Pb-EDDS might be exchanged with Cu sorbed on the soil surfaces because the stability of Cu-EDDS was higher than that of Pb-EDDS²⁸.

The extraction efficiency of Cd or Cu in the soil co-contaminated with Cd and Cu was significantly less than that of the soil

contaminated with only Cd or Cu. Such a strong suppression of desorption of Cd/Cu by the presence of Cu/Cd suggested that the complexation ability of STC[4]A toward Cd and Cu may be quite similar. However, the presence of Pb did not significantly influence the extraction of Cd or Cu. Conversely, desorption of Pb was obviously affected by the co-presence of Cd and Cu. The molar amounts of metals removed from the contaminated soils by STC[4]A at 24 h are listed in Table 2; the data show that the metal extraction yields of STC[4]A varied in the order: Cd > Cu > Pb for the single-metal contaminated soils, whereas the selectivity sequence of metal desorption by STC[4]A was Cu > Cd > Pb for the multi-metal contaminated soils.

Table 2 The metals and standard deviations (n=3) from contaminated soils extracted by 0.4 mM STC[4]A (liquid:soil ratio of 10:1, pH 11, 25 °C, 24 h)

Contaminated soil	Cd (mmol kg ⁻¹)	Cu (mmol kg ⁻¹)	Pb (mmol kg ⁻¹)
Cd	4.05(±0.20)		
Cu		3.12(±0.07)	
Pb			0.68(±0.03)
Cd+Cu	2.12(±0.07)	2.45(±0.05)	
Cd+Pb	3.88(±0.08)		0.64(±0.02)
Cu+Pb		3.10(±0.03)	0.51(±0.04)
Cd+Cu+Pb	2.36(±0.06)	2.54(±0.06)	0.10(±0.02)

3.3 Conditional stability constants of the STC[4]A-M complex

The metal extraction capacity of a chelant is directly dependent on its ability to form stable complexes with metal elements and is usually

characterised by the conditional stability constant (log *K*). Tandy et al. found that the extraction of Pb at a low chelant:metal ratio depends mainly on the log *K* values of the Pb-complexes²². Yuan et al. reported that the

log K values for citric acid with Cu and Cd are smaller than those for EDTA with Cu and Cd, which was responsible for their less efficient desorption for citric acid than for EDTA³⁰. In a previous work, the extraction mechanism of metal extraction from soil by STC[4]A was considered to be primarily related to three processes: deprotonation of STC[4]A, complexation of STC[4]A with metals, and dissolution of metals¹⁹.

In this study, the complexation abilities of STC[4]A toward Cu and Pb were investigated

using UV spectrophotometric titrations (Figs. 7 and 8). Upon addition of metal ions, the absorption bands were red-shifted with an increase in molar ratio of metal:STC[4]A, indicating the formation of the STC[4]A-metal complexes. However, the extent of the red shift was different between the two metals, indicating the different complexing abilities of STC[4]A to each metal. The extents of the red shift of both Cu and Pb at pH 11.01 were apparently larger than those at pH 5.04, 7.09, and 12.07, revealing stronger complex abilities of STC[4]A to metals at pH 11.01, akin to Cd¹⁹.

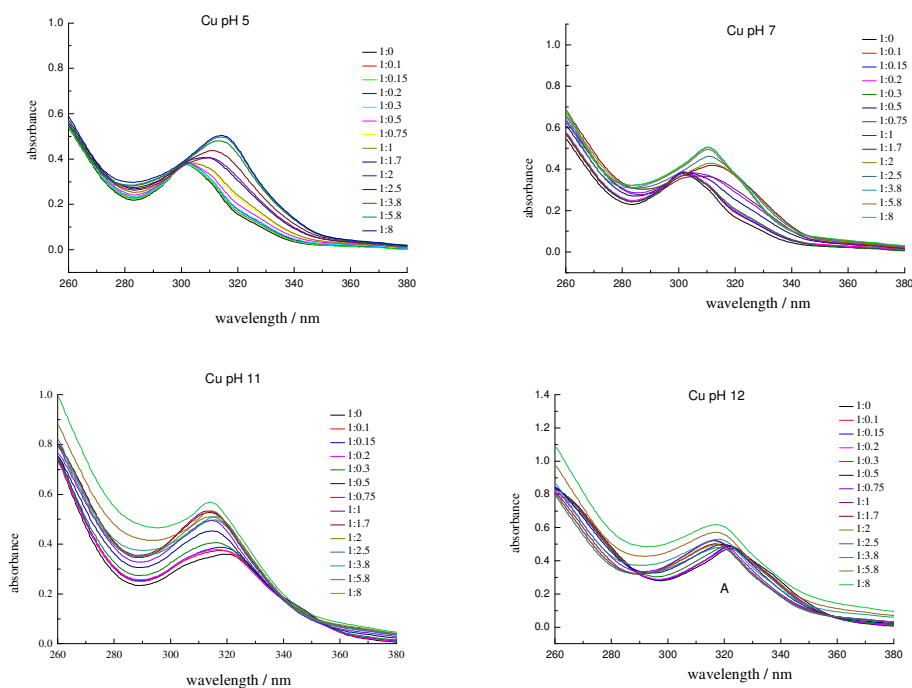


Fig. 7. UV absorption spectra of STC[4]A-Cu mixed solutions with different STC[4]A:Cu molar concentration ratios at pH 5.04, 7.09, 11.01, and 12.07.

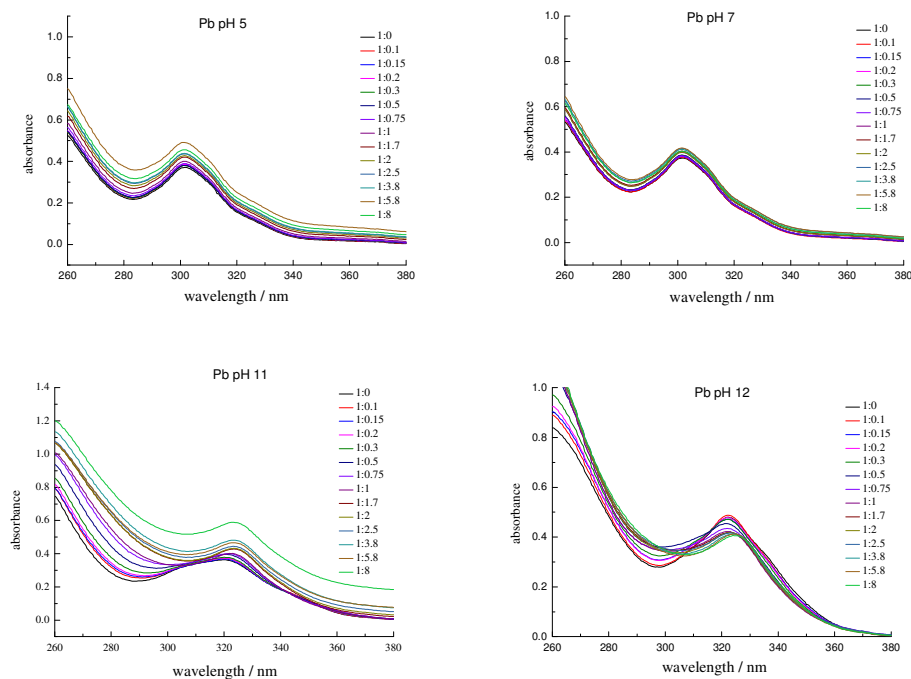


Fig. 8. UV absorption spectra of STC[4]A-Pb mixed solutions with different STC[4]A:Pb molar concentration ratios at pH 5.04, 7.09, 11.01, and 12.07.

The log K values of the STC[4]A-M complexes were calculated from the spectral data using TTFM and are summarised in Table 3. The log K values of the STC[4]A-Cu and STC[4]A-Pb complexes both increased with increasing pH, reaching the maximum value at pH 11 and then declining at higher pH values. This variation tendency was the same as that in the previous study of the STC[4]A-Cd complex¹⁹. The complexation capacities of STC[4]A varying with the solution pH contributed to its

complexation mechanisms to metals. The complexation of STC[4]A to metals is actualised through cooperative coordination of the bridging sulphur atom and two adjacent phenoxide O⁻ moieties³¹. STC[4]A exhibits four acid dissociations of the phenolic hydroxyl groups at pH 2.18, 8.45, 11.19, and 11.62²⁰. Therefore, four-step acid dissociations of the phenolic OH groups will occur in aqueous solution. The phenolic OH groups of STC[4]A remain protonated in acidic solution, which is

unfavourable for the cooperative coordination of the bridging sulphur atom and the two adjacent phenoxide O⁻ moieties, leading to a lower complexation capacity of STC[4]A to metals under acidic conditions. The increased solution pH enhanced deprotonation of the phenolic hydroxyl groups and intensified the complexation between STC[4]A and metals. However, when the solution pH value exceeded 11.62, the four phenolic OH groups of STC[4]A were all deprotonated, and the cone conformer can adopt a partial-cone, 1,2-alternate, or 1,3-alternate conformer²⁰. The complexation or recognition abilities of STC[4]A decreased³². Therefore, the complexation capacity of STC[4]A to metals decreased at pH > 11.62, leading to a reduction in the metal-removal efficiency at pH 12. Thus, changes in the metal-removal efficiency by STC[4]A extraction with the solution pH were consistent with variations in the complexing capacity of STC[4]A to metals and were caused by

transformations in the speciation and molecular conformation of STC[4]A. The log *K* value of STC[4]A to the three metals was in the order of STC[4]A-Cu > STC[4]A-Cd > STC[4]A-Pb at each pH, showing that the complexation abilities of STC[4]A toward the three metals decreased with the order of Cu > Cd > Pb.

STC[4]A is a polydentate ligand, which contains eight donor atoms (four oxygen atoms and four sulphur atoms). The complexation of STC[4]A to a metal ion is actualised through cooperative coordination of the bridging sulphur atom and two adjacent phenoxide O⁻ moieties³¹. Morohashi has demonstrated that the metal extraction selectivity of the sulphur bridged calix[4]arenes may be explained by 'the hard and soft acids and bases (HSAB) rule'³³. For example, thiacalix[4]arenes may bind to soft metal ions by the coordination of a lone pair of electrons of the sulphur atom besides two phenolic oxygen atoms. However, lacking the lone pair of electrons on S, thiacalix[4]arenes are unable to coordinate to soft metal ions. Therefore, the difference in the three stability constants should depend on the characteristics of these metal ions. The strongest bond between STC[4]A and metal ions is formed by the metal

ions with the greatest charge-to-radius ratio, resulting in the selectivity sequence of Cu > Cd > Pb. McBride also indicated that if chemisorption of metals depends only on the electrostatic force of attraction, then the strongest bond follows the selectivity sequence of Cu > Cd > Pb³⁴. This selectivity sequence is the same as the selectivity sequence of metal desorption by STC[4]A from the multi-metal contaminated soils. These results showed that the competition among the target pollutant metals for the available STC[4]A appeared to depend mainly on the stability constants of the STC[4]A-metal complexes. Wuana et al. also found that the order of the metal extraction

yields of organic chelants obeyed the order of their formation constants³⁵. STC[4]A could preferentially complex with Cu and the newly formed Cd-STC[4]A, or Pb-STC[4]A might be exchanged with Cu sorbed on the soil surfaces because the conditional stability constant of Cu-STC[4]A was higher than that of either Cd-STC[4]A or Pb-STC[4]A. Therefore, it was not surprising to obtain higher efficient extraction of Cu under STC[4]A deficiency at MR 0.8. Overall, the selectivity sequence of metal extraction from the multi-metal contaminated soils by STC[4]A obeyed the order of Metal-STC[4]A formation constants.

Table 3. Conditional stability constants (log $K \pm$ RSD) for Cd, Cu, and Pb with STC[4]A

Metal	pH							
	5		7		11		12	
	Log K	RSD	Log K	RSD	Log K	RSD	Log K	RSD
Cu	9.79	0.0032	11.34	0.0038	18.23	0.0025	11.74	0.0021
Pb	5.00	0.0024	7.64	0.0026	10.66	0.0023	6.63	0.0032
Cd ^a	6.87	0.0039	9.68	0.0024	16.66	0.0029	7.01	0.0041

^a Data from Li et al¹⁹.

EDTA (Na₂EDTA) is recognised as the most effective synthetic chelator to remove metal trace elements (especially Cd, Pb, Cu, and Zn) from soils¹⁰. Conversely, the low selectivity of EDTA causes increased consumption of this reagent due to potential chelation of all of the exchangeable cations present in soil, such as Ca²⁺ and Mg²⁺³⁶. STC[4]A has outstanding

selective abilities to complex with soft metal ions (e.g., Cd, Cu, and Pb) by cooperative coordination of the bridging sulphur atom and two adjacent phenoxide O⁻ groups. In addition, STC[4]A does not interact with alkali or alkaline earth metal ions, such as Na⁺, K⁺, Ca²⁺, and Mg²⁺^{20,31}. In the previous study, the solubilisation of Ca from soil was determined by

different chemical extraction. The results showed that STC[4]A extraction not only perfectly decontaminated a soil polluted by Cd but also extensively prevented co-dissolution of Ca¹⁹, which could be ascribed to the selective complexing ability of STC[4]A to metal trace elements^{20,31}.

3.4 Metal redistribution in the soils before and after STC[4]A extraction

Metal speciation is essential to the stability and leachability of metals in soil, and sequential extraction techniques have been widely used for formal distribution analysis²⁵. Furthermore, some documents have indicated that the form of the metals can affect the extraction efficiency of the chelating agents. Moreover, different chelating agents could extract different metal forms. It has been shown that EDDS extracted metals are almost exclusively from the exchangeable, mobile and Mn-oxide fractions²². In addition to extraction from the weakly sorbed fractions, a large portion of Cu was extracted from oxide, organic matter and residual fractions by EDTA²⁵.

The effect of STC[4]A extraction on metal fractionation was evaluated using sequential extraction, of which the five fractions from exchangeable to residual (Table 1) are operationally defined. In terms of increasing the

metal binding strength, sorption on the first two fractions is weak and nonspecific, while sorption on the latter three fractions is of high binding strength and considered to be specific²¹. The distribution patterns of Cd, Cu and Pb fractionations in the single-metal contaminated soil before and after STC[4]A extraction are shown in Fig. 9. The figure shows that 81.5% of total Cd was present in EX form before STC[4]A extraction. In addition, Cd was also found in other forms but at very small amounts. This result suggests that the sorption of Cd in soils is governed mainly by nonspecific interactions. Tiller et al. reported that the non-specifically sorbed form of Cd usually exceeded the specifically sorbed form³⁷. Saha et al. also documented that at low metal concentrations, metals were mainly sorbed onto specific sorption sites, while at higher metal concentrations, soils lose some of their ability to bind metals as sorption overlapped, thus becoming less specific for a particular metal³⁸. The large proportion of Cd in the SE fraction suggested that Cd was a relatively soluble and mobile element in soil. The CA (28.1%), OX (22.7%), RE (21.6%) and EX (18.0%) fractions of Cu and the EX (45.3%), CA (22.8%), OX (18.6%), and RE (10.9%) fractions of Pb were relatively high. The larger OX and RE fractions for Cu and Pb compared with that for Cd reflected that Cu and Pb were

preferentially sorbed by high-energy binding sites. Regardless of when Pb is introduced to a soil, it should be less labile than Cd because Pb appears to more readily undergo inner-sphere surface complexation with soil surface functional groups than Cd³⁹.

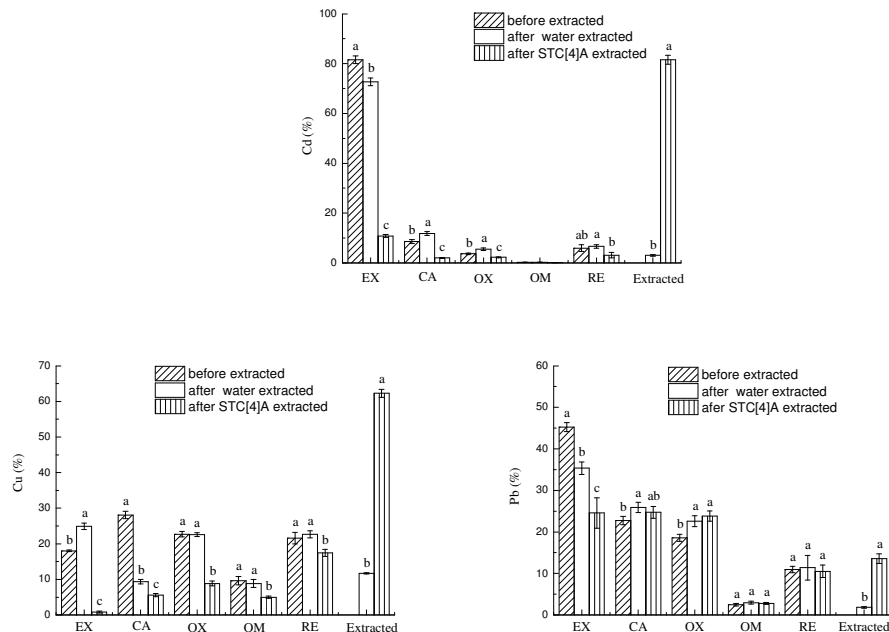


Fig. 9. Relative distribution of Cd, Cu, and Pb in unextracted soils and extracted soils: (A) relative distribution. Error bars represent the standard deviations ($n = 3$). Different letters above each column indicate significantly different means ($p < 0.05$; LSD test).

In the control treatment with water extraction, the extracted Cd (3.1% of the total) and Pb (1.9% of the total) were from the EX fraction, whereas the extracted Cu (11.7%) was from the CA fraction. For the EX form of Cu, the amount was even higher than before extraction due to the changing of Cu from the other forms into this form. The form that can be changed with the highest possibility was also the CA fraction. However, STC[4]A was able to extract Cd and Cu from all fractions, as shown by the change in absolute concentration of each fraction. It was

revealed that Cd, Cu and Pb were extracted marginally by background solution (water) only, indicating that their extraction was primarily driven by complexation with STC[4]A. In fact, STC[4]A was able to extract Cu and Cd from all fractions, as shown by the change in absolute concentration of each fraction (Table 4), even though some fractions presented small amounts. STC[4]A extraction of strongly sorbed metals could be attributed to two probable reasons. First, thermodynamically favourable complexation between metals and STC[4]A can directly

disrupt some relatively less strong interactions between the metals and soils. Second, STC[4]A-promoted dissolution, which partially breaks down the soil structure, can indirectly release metals that are bound to carbonate and oxide or occluded in the soil interior. Metal extraction yields by STC[4]A varied approximately in the decreasing order of EX > CA > OX > OM > RE (Table 4). This result revealed that specific sorbed fractions were more resistant to STC[4]A extraction. Moreover, for each metal fraction, the extraction yield approximately obeyed the order of Cu > Cd > Pb, according to the order of their formation constants. In spite of the intermediate values of formation constants for Cd, STC[4]A showed the largest extraction yields for Cd from the single-metal contaminated soil, possibly due to its weak association with the soil. STC[4]A showed the lowest extraction yields for Pb, with the extracted Pb mainly from the SE fraction because of both the lowest values of formation constants for Pb and the preferential sorption by high-energy binding sites in the soil.

Table 4. Efficiencies (%) of the 0.4 mM STC[4]A solution in removing metals for different soil fractions. Experimental data are expressed as the mean \pm SD. Different letters followed by experimental data indicate significantly different means ($p < 0.05$; LSD test).

Metal	EX	CA	OX	OM	RE
Cd	86.68 \pm 0.67 ab	76.16 \pm 2.11 b	38.87 \pm 4.18 d	24.04 \pm 6.23 e	47.92 \pm 18.27 d
Cu	95.45 \pm 1.44 a	80.22 \pm 1.67 b	60.96 \pm 3.15 c	48.21 \pm 3.28 d	18.99 \pm 4.57 e
Pb	45.72 \pm 8.13 d	-8.66 \pm 6.25 fg	-28.14 \pm 6.56 h	-12.30 \pm 9.73 g	3.79 \pm 13.60 f

4 Conclusions

Extractive-decontamination of PTMs (Cd, Cu, and Pb) from single-metal and multi-metal contaminated soils using STC[4]A, a novel supramolecular receptor, was evaluated based on batch extraction. STC[4]A can significantly enhance the dissolution of the three PTMs from the contaminated soils, and competitive extraction was found. The order of metal desorption efficiencies was Cd > Cu > Pb for single-metal contaminated soils, while the selectivity sequence of metal desorption was Cu

> Cd > Pb for multi-metal contaminated soils.

The selectivity sequence of metal extraction from multi-metal contaminated soils by STC[4]A followed the order of the Metal-STC[4]A formation constants. In spite of the intermediate values of formation constants for Cd, STC[4]A showed the largest extraction yield for Cd from single-metal contaminated soil due to the large proportion of Cd in the SE fraction. Hence, the effectiveness of STC[4]A washing was highly dependent on the Metal-STC[4]A formation constants and the distribution of metals in the

soil.

STC[4]A appeared to possess great potential to decontaminate the soil through ex situ washing treatment in the study. However, the strategies for recycling chelating agents and process water from spent washing solution to achieve optimal efficiency must be improved. In the current work, we proposed a method for treating the spent washing solution obtained after STC[4]A washing of PTM-contaminated soil. The method combines the three approaches outlined above, with the proposed method as follows: first, most of the STC[4]A-PTM complexes were decomplexed in the spent washing solution at a high pH level ($\text{pH} > 12.0$); second, the released PTM ions are precipitated from the spent soil washing solutions as insoluble sulphides after the addition of Na_2S ; third, the process water is then filtered, acidised and recycled for PTM extraction. Preliminary results revealed that this method is a feasible proposal for recycling STC[4]A and process water from spent washing solution. However, only some basic work has been accomplished, and more experiments and further study are needed to improve the method and make it practical. Additional research is required to evaluate the cost effectiveness of this technology in field applications. A cost-effective strategy

would be a system where the contaminants are precipitated from the spent washing solution, while the agents and process water are reused for continuous washing. The development of more robust recycling methods in a closed process loop would greatly increase the economic value of STC[4]A-washing technologies because the main item of the treatment cost is the purchase or synthesis of STC[4]A.

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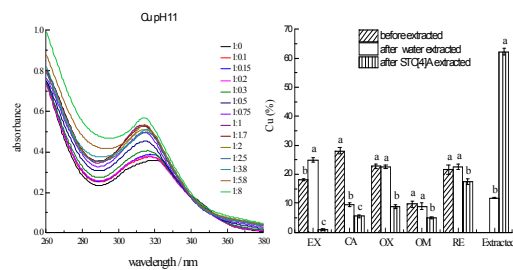
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PTMs extraction capacity and selectivity mechanism of STC[4]A were investigated by the determination of $\log K$ and the metal speciation.