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RESEARCH ARTICLE

Extractive and oxidative removal of copper bound to humic acid in soil

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Abstract Copper (Cu) is often found strongly bound to natural organic matter (NOM) in soil through the formation of strong Cu-NOM complexes. Therefore, in order to successfully remediate Cu-contaminated soils, effective removal of Cu bound to soil organic matter should be considered. In this study, we investigated soil washing methods for Cu removal from a synthetic Cu-contaminated model silica soil coated with humic acid (HA) and from field contaminated soil. Various reagents were studied to extract Cu bound to NOM, which included oxidant (H_2O_2), base (NaOH), and chelating agents (citric acid and ethylenediaminetetraacetic acid (EDTA)). Among the wash reagents, EDTA extracted Cu most effectively since EDTA formed very strong complexes with Cu, and Cu-HA complexes were transformed into Cu-EDTA complexes. NaOH extracted slightly less Cu compared to EDTA. HA was effectively extracted from the model soil under strongly alkaline conditions with NaOH, which seemed to concurrently release Cu bound to HA. However, chemical oxidation with H_2O_2 was not effective at destroying Cu-HA complexes. Fourier transform infrared spectroscopy and elemental analysis revealed that chelating agents such as citrate and EDTA were adsorbed onto the model soil via possible complexation between HA and extraction agents. The extraction of Cu from a field contaminated soil sample was effective with chelating agents, while oxidative removal with H_2O_2 and extractive removal with NaOH separated negligible amounts of Cu from the soil. Based on these results, Cu bound to organic matter in soil could be effectively removed by chelating agents, although remnant agents may remain in the soil.

Keywords Copper · Extraction · Humic acid · Organic matter · Remediation · Soil washing

Introduction

Copper (Cu) is an essential structural component of the environment and is an important trace element in biogeochemical cycles in soils and sediments (Komy et al. 2014). However, accumulation of Cu can adversely affect crop growth and threaten human health through the food chain (Zhou et al. 2013). Cu ingestion causes acute effects such as gastrointestinal symptoms including nausea, abdominal pain, and vomiting (Seeley et al. 2013). Cu can be introduced into soil environments via swine manure, sewage and municipal compost, mining waste, and fungicides (Uchimiya et al. 2011).

Soil washing is the most popular process for removing heavy metals from soil. Because of the unique physicochemical properties of each heavy metal in soil and the interaction between metals and soil constituents, the selection of washing agents is a key parameter for successful application of soil washing. Among various cationic metals, Cu has a unique physicochemical characteristic in soil, which is a high affinity for soil organic matter (SOM) or humic substances (HS) (Wang et al. 2001). SOM contributes to soil properties such as water retention capacity, biological activity, cation exchange capacity, and interactions with contaminants (Zhang

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et al. 2011). In addition, HA influences metal transport and controls metal uptake into plants through various functional groups including carboxyl, hydroxyl, and phenol and amino groups (Pandey et al. 2000), which can form complexes with metal cations (Wu et al. 2002). HS has a strong influence on the mobility of Cu in soil (Liu and Wang 2004). Furthermore, complexes between Cu and HS have been a hurdle in the removal of Cu in soil using washing processes, because such complexes are very stable (Pandey et al. 2000). The stability constant (log K) of Cu-HA is in the range of 4.06 to 5.73. The stability constant of a metal-HS complex influences various factors and is dependent on the age and depth of the HA (Dudare and Klavins 2013; Soler-Rovira et al. 2010). The stability constants of EDTA-Cu and citric acid-Cu are 18.8 and between 6.1 and 18, respectively. Based on these stability constants, EDTA and citric acid would presumably be able to break the Cu-HA complex (Yuan et al. 2007). The most effective and common method of SOM treatment has been oxidation by hydrogen peroxide (Plante et al. 2004). For successful application of soil washing for Cu-contaminated soil, the removal of Cu bound to HS in soil should be considered. Although Cu-HS complexes are important forms of Cu in soils, soil washing removal methods have received limited attention.

In this study, we investigated the removal of Cu from soil by oxidative release and extractive mechanisms (Fig. 1). We hypothesized that Cu could be released by oxidation of HS, since the oxidation process could degrade functional groups in HS (oxidative release mechanism). Second, extraction of HS from soil could also remove Cu because the main fraction of Cu in soil would presumably be Cu-HS complexes (HS extractive removal mechanism). Finally, strong chelating agents could extract Cu from soil because these agents have a higher affinity for Cu compared with HS (Cu extractive removal mechanism). The aim of this study was to investigate the effectiveness of these three protocols for removing Cu from soil.

Materials and methods

Preparation of HA-coated silica (HACS)

In this study, humic acid (HA) was used as a model humic substance even though HA is one constituent of HS. HA-coated silica was prepared as a model soil. Figure 2 shows the procedure for preparing Cu-bound HA-coated silica (Cu-HACS). To obtain Cu-HACS, modification of the previous synthetic method for the preparation of aminopropyl silica-immobilized HA was used (Kara et al. 2008).

First, to purify HA, 10 g of HA (Sigma-Aldrich Co. Ltd., St. Louis, MO, USA) was added to 1 M NaOH solution (1 L). The solution pH was adjusted to 11 using 1 M NaOH, stirred for 8 h, and centrifuged. In order to precipitate dissolved HA, the supernatant solution was adjusted to pH 2 with 1 M HCl and stirred for 24 h. Next, the mixture was centrifuged at 8000 rpm for 20 min, and the precipitate (purified HA, PHA) was rinsed twice with 0.01 M HCl and dried in an oven (60 °C) for 24 h.

To obtain the model soil (Cu-HACS), PHA (0.3 g) and aminopropyl silica (1 g, Sigma-Aldrich) were combined in 0.03 L of 0.1 M NaOH. The mixture was stirred for 20 h, then rinsed with 0.2 M NaCl (pH 7.5), and filtered. The residue was dried to give HA-coated silica (HACS). To obtain Cu-bound HACS, 50 mL of 0.01 M $Cu(NO_3)_2$ solution was added to 50 mL of HACS at a concentration of 10 g/L, and the mixture was stirred for 24 h. Upon adjusting the solution pH to 2, Cu-bound HACS (Cu-HACS) precipitated. The solution was filtered, and the precipitate was dried. The dried solid, Cu-HACS, was used as the Cu-contaminated model soil. To remove weakly bound Cu from Cu-HACS, the dried precipitate was rinsed several times with deionized water. Finally, the precipitate was dried and used for Cu removal experiments.

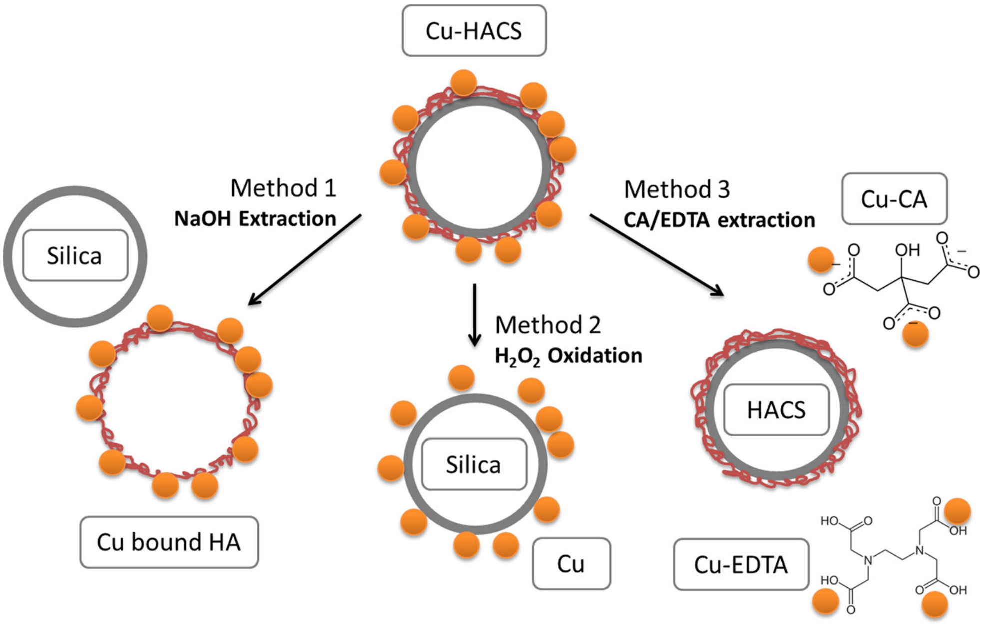
Characterization of HACS and Cu-bound HACS

The functional groups of the solids (PHA, HACS, and Cu-bound HACS) were analyzed using Fourier transform infrared spectroscopy (FT-IR, Spectrum GX, PerkinElmer, USA). The elemental composition including C, H, N, and S of the organic fraction was determined by elemental analyzer (EA, Vario EL, Elementar GmbH, Germany). The change of surface morphology was identified using a scanning electron microscope (SEM, JSM-5900, JEOL Ltd., Japan) equipped with energy dispersive X-ray spectroscopy (EDX).

Removal of Cu from Cu-HACS

To find an optimum method for removal of Cu from soil, three methods to desorb Cu from Cu-HACS were tried: base extraction, oxidation, and chelating extraction. The first approach to remove Cu from soil caused extraction of HA. Since HA can dissolve in basic solution, Cu-bound HA might be simultaneously removed. The second approach was oxidation of HA. If Cu were bound to HA, Cu could be dissolved by oxidation of HA. The last approach was extraction with chelating agents such as disodium ethylenediaminetetraacetic acid (EDTA) and citric acid (CA). Chelating agents can form complexes with Cu, which can dissolve in aqueous solution. Cu removal experiments were conducted with 1 g of Cu-bound HACS and 20 mL of 0.1 M extractant (NaOH, Na_2EDTA, or CA) or oxidant (H_2O_2). Deionized water was used as a control. The mixture of soil and extractant in a 50 mL tube was agitated for 24 h followed by filtration with a 5B filter (Advantec Co., Japan). The Cu concentration in the

Fig. 1 Proposed scheme of the removal methods for Cu-contaminated model soil



filtrate was analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, 720-ES, Agilent Co. Ltd., USA). All chemical reagents, purchased from Sigma-Aldrich Co. Ltd. (St. Louis, MO, USA), were of reagent grade or better and were used without further purification.

Removal of Cu from contaminated soil

To compare the removal of Cu from model soil and field soil, the extraction and oxidation methods were applied to a Cu-contaminated soil obtained from an industrial site in Seoul, Korea. The soil was dried in air and sieved using a 2.0-mm mesh sieve. Using soil of smaller than 2 mm, the three treatment methods, NaOH extraction, H_2O_2 oxidation, and chelate extraction, were applied in the same manner as with the model soil.

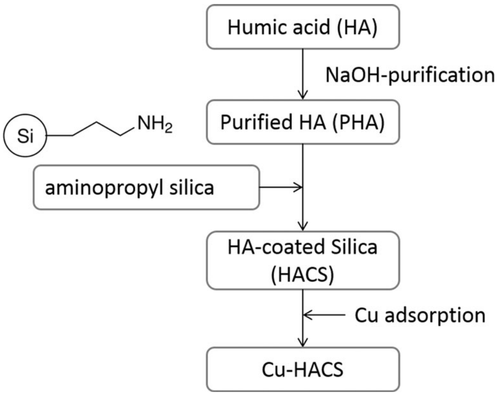


Fig. 2 Preparation of PHA, HACS, and Cu-HACS

The soil characteristics are presented in Table 1. The soil pH was measured using a pH meter for a mixture of 5 g of soil and 25 mL of deionized water after a 1 h equilibration. The organic matter content was measured by the ASTM D2974 method, and the soil texture was analyzed by the ASTM D421 method. The cation exchange capacity of the soil was measured using the sodium acetate method (US EPA SW-846 Method 9081) (Bianchi et al. 2008). The concentration of metals in the soil was measured by ICP-OES after *aqua regia* extraction. The concentrations of Cu, Pb, and Zn exceeded the Korean regulation level ('worrisome' level for 1 region) for soil: 150 mg/kg for Cu, 200 mg/kg for Pb, and 300 mg/kg for Zn.

To understand the change in metal fractionation, the Standard Materials and Testing (SM&T, former BCR) sequential extraction procedure (SEP) was applied (Rauret et al. 1999;

Table 1 Characteristics of the field soil used in this study

Soil characteristic		Values
Soil texture (%)	0.500–2.000 mm	33.6
	0.150–0.500 mm	36.1
	0.075–0.150 mm	20.8
	< 0.075 mm	9.5
Metal Concentration (mg/kg)	Cu	285.1
	Pb	615.6
	Zn	227.2
CEC (meq/100 g)		7.3
Soil pH		8.5
Organic matter content (%)		2.8

Sutherland 2010). There were three operationally defined fractions: (F1) soluble and exchangeable, (F2) bound to Fe-Mn oxides, and (F3) bound to organics and sulfides. An additional fraction, (F4) residual, was also used to compare the total content of metals. The SM&T SEP is summarized in Table 2.

Results and discussion

Removal of Cu from Cu-contaminated model soil

To characterize the model soil, Cu-HACS, the carbon content and FT-IR spectra of the model soil were analyzed. The initial carbon content from HA was approximately 40 %, which decreased to 7.5 % in the model soil. It indicates that the adsorbed amount of HA in the model soil was ca. 18.8 %. HA has various functional groups (Sutton and Sposito 2005) as shown in the FT-IR spectra of Fig. 3. As seen in Fig. 3a, the HA spectrum exhibits the presence of aromatic and aliphatic fractions and various oxygen-rich functional groups including carboxyl and hydroxyl groups (Han et al. 2011; Ribeiro et al. 2001). The absorption peak at 3423 cm is attributed to stretching of –OH groups, N-H stretching, and physical adsorption of water molecules (Ribeiro et al. 2001). These functional groups can serve as binding sites for Cu. The Cu concentration in the Cu-HACS was ca. 900 mg/kg.

The EDTA extractive removal of Cu from Cu-contaminated model soil showed the best removal efficiency among the three methods (Fig. 4 and Table 3). Using 0.1 M NaOH solution (Method 1), the Cu removal efficiency was 51 %. Because HA can dissolve in high pH solution, NaOH solution can extract HA adsorbed on silica. Presumably, NaOH solution extracted HA from the HACS, and Cu was released into the solution phase in the form of HA-Cu complexes. The oxidative removal of Cu with H_2O_2 (Method 2) removed only 10 % of the initial Cu content, which was similar to the extraction efficiency of deionized water. Oxidation by H_2O_2 was not productive since humic substances are residual matter that has been subjected to thorough oxidative processes in nature. In addition, oxidation with H_2O_2 might require an initiator for radical production, and there was no initiator such as Fe(II) in the model soil sample. However, there are plenty of iron oxides in the field soil, which could act as an initiator for radical production (Bissey et al. 2006; De Laat and Gallard 1999; Lin and Gurol 1998; Lipczynska-Kochany and Kochany 2008; Wang et al. 2001). Therefore, H_2O_2 oxidation could be applied to the removal of soil organic matter in field soil. By contrast, EDTA was a superior agent for extracting Cu bound to HA. EDTA is a very effective chelating agent for the extraction of heavy metals because of its great affinity for most metals (Bianchi et al. 2008; Di Palma et al. 2007; Di Palma and Mecozzi 2007; Tsang et al. 2007), and EDTA was able to extract 74 % of the Cu from the Cu-HACS (Method 3). Citric acid extracted 40 % of the Cu (Method 3), which was lower than that of EDTA because the binding affinity of citrate-Cu is lower than that of EDTA-Cu (Di Palma and Mecozzi 2007).

In order to analyze the HA removal mechanisms, the change in carbon content was investigated (Table 3). The oxidation using hydrogen peroxide did not significantly change the carbon content (7.2 %), which indicated that HA was not oxidized by hydrogen peroxide. Extraction using NaOH decreased the carbon content by up to 50 % of the model soil, which shows that HA was effectively extracted or

Table 2 Brief optimized SM&T SEP modified from Sutherland (2010) used in this study

Fraction	Operational definition	Chemical reagents and conditions
F1 (Step 1)	Soluble and exchangeable	0.5 g aliquot, 20 mL 0.11 M acetic acid, end-over-end shaking (30 rpm) for 16 h at 20 °C. Separate extract from the solid residue by centrifugation at 3000×g for 20 min, decant supernatant and analyze. Wash residue with 10 mL distilled water, shake for 15 min, and centrifuge. Decant supernatant and discard, taking care not to discard any solid residue
F2 (Step 2)	Bound to Fe-Mn oxides	To Step 1 residue add 20 mL 0.5 M $NH_2OH \cdot HCl$ from a 1 L solution containing 25 mL 2 M HNO_3, shake for 16 h at 20 °C. Centrifuge extract as per Step 1. Wash, shake and centrifuge as per Step 1.
F3 (Step 3)	Bound to organic and sulfides	To Step 2 residue add small aliquots of 5 mL H_2O_2. Cover and digest for 1 h at room temperature (occasional manual shaking), heat to 85 °C for 1 h in a water bath and reduce volume to <1.5 mL (uncovered); add a further 5 mL H_2O_2 and heat to 85 °C for 1 h; add 25 mL 1 M NH_4OAc (pH 2) and shake for 16 h at 20 °C. Separate the extract from the solid residue by centrifugation and decantation as per Step 1.
F4 (Step 4)	Residual	To Step 3 residue add 2 mL concentration HNO_3 and 6 mL HCl and leave to room temperature for 2 h; heat to 65 °C for 1 h. Centrifuge extract as per Step 1.

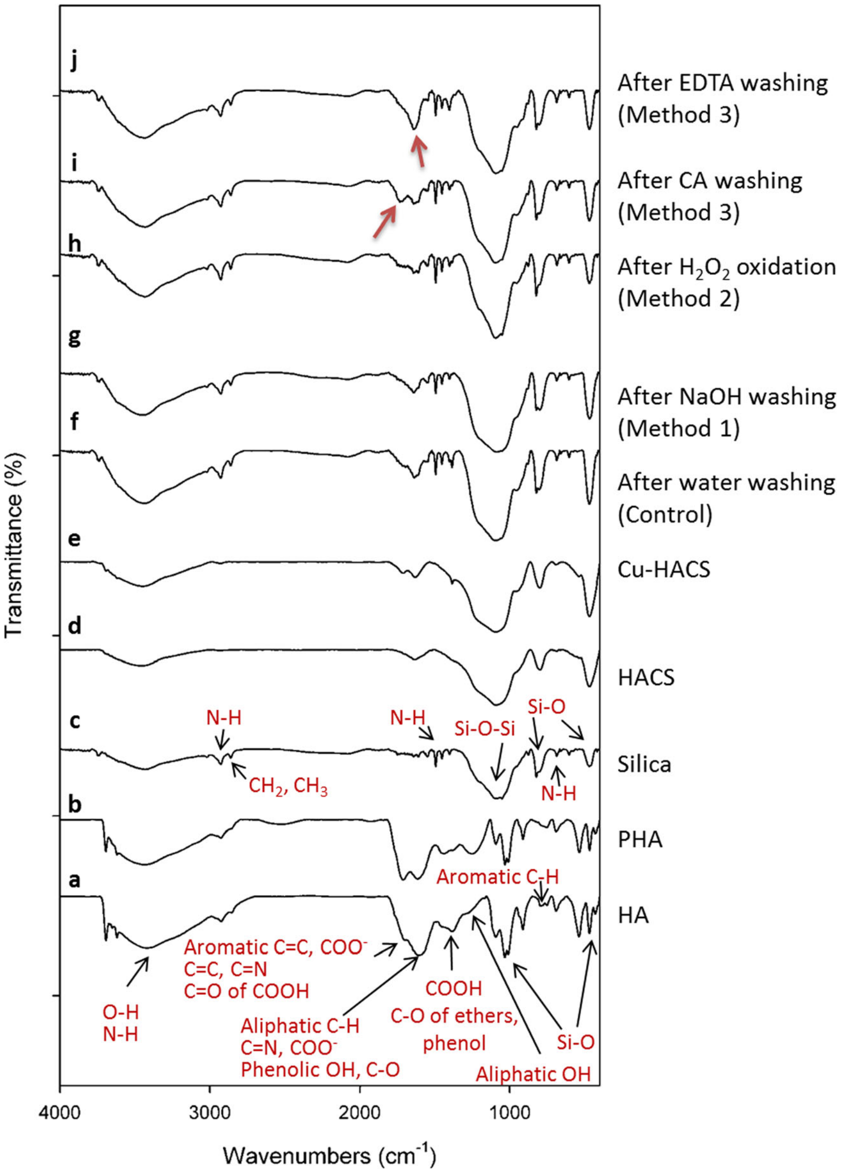


Fig. 3 FT-IR spectra of **a** HA, **b** PHA, **c** silica, **d** HACS, and **e** Cu-HACS, Cu-HACS after **f** water washing (control), **g** NaOH washing (Method 1), **h** H_2O_2 oxidation (Method 2), **i** CA washing (Method 3), and **j** EDTA washing (Method 3). The notation of functional group of HA was adapted from Han et al. (2011) and Ribeiro et al. (2001). The *arrows* at (**i**) and (**j**) imply the adsorption of citrate and EDTA onto HACS, respectively

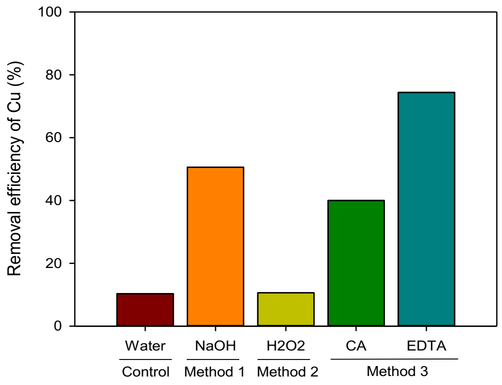


Fig. 4 Removal efficiency of Cu using three methods for Cu-contaminated model soil

removed from the model soil by the extraction process. However, extraction using EDTA and citric acid increased the carbon content of the model soil. This increase might be the result of adsorption of EDTA and CA onto the model soil. Based on the calculation of carbon content, the adsorbed amounts of EDTA and citric acid in Cu-HACS were approximately 15 and 8 %, respectively.

The change of functional groups of the model soil during the oxidation and extraction procedures was investigated by FT-IR spectra (Fig. 3). In silica-based materials, typical Si–O–Si bands of IR spectra are observed around 1080, 802, and 464 cm (Fig. 3c–j) (Sun et al. 2014). Also, there exist inherent absorption peaks for Si–O of silicate in HA, which indicate that PHA and HA combine with the silicate material making them difficult to separate though the applied purification

Table 3 Removal efficiency of metals after treatment with three methods for Cu-contaminated model and field soils

							Removal efficiency (%)	
							Model soil	Field soil
Method	Chemicals	Solution pH[a]	Equilibrium pH[b]	Total carbon (%)[c]	Cu	Cu	Pb	Zn
Control	Water	5.9	9.0	7.3	10.3	0.2	–[d]	0.3
1	NaOH	13.1	13.1	3.5	50.6	4.1	1.8	1.1
2	H_2O_2	5.6	8.2	7.2	10.6	0.2	–[d]	0.1
3	CA	1.5	2.5	9.4	40.0	50.6	17.5	45.2
	EDTA	4.6	4.7	9.7	74.4	55.0	36.5	35.7

[a] Solution pH of the each method applied to washing experiments

[b] Solution pH equilibrated with field soil after treatments

[c] Initial content of total carbon in model soil was 7.5 %. The values indicated the total carbon contents (%) in model soil after treatment with three methods

[d] It indicates the removal efficiency of Pb was less than 0.1 %

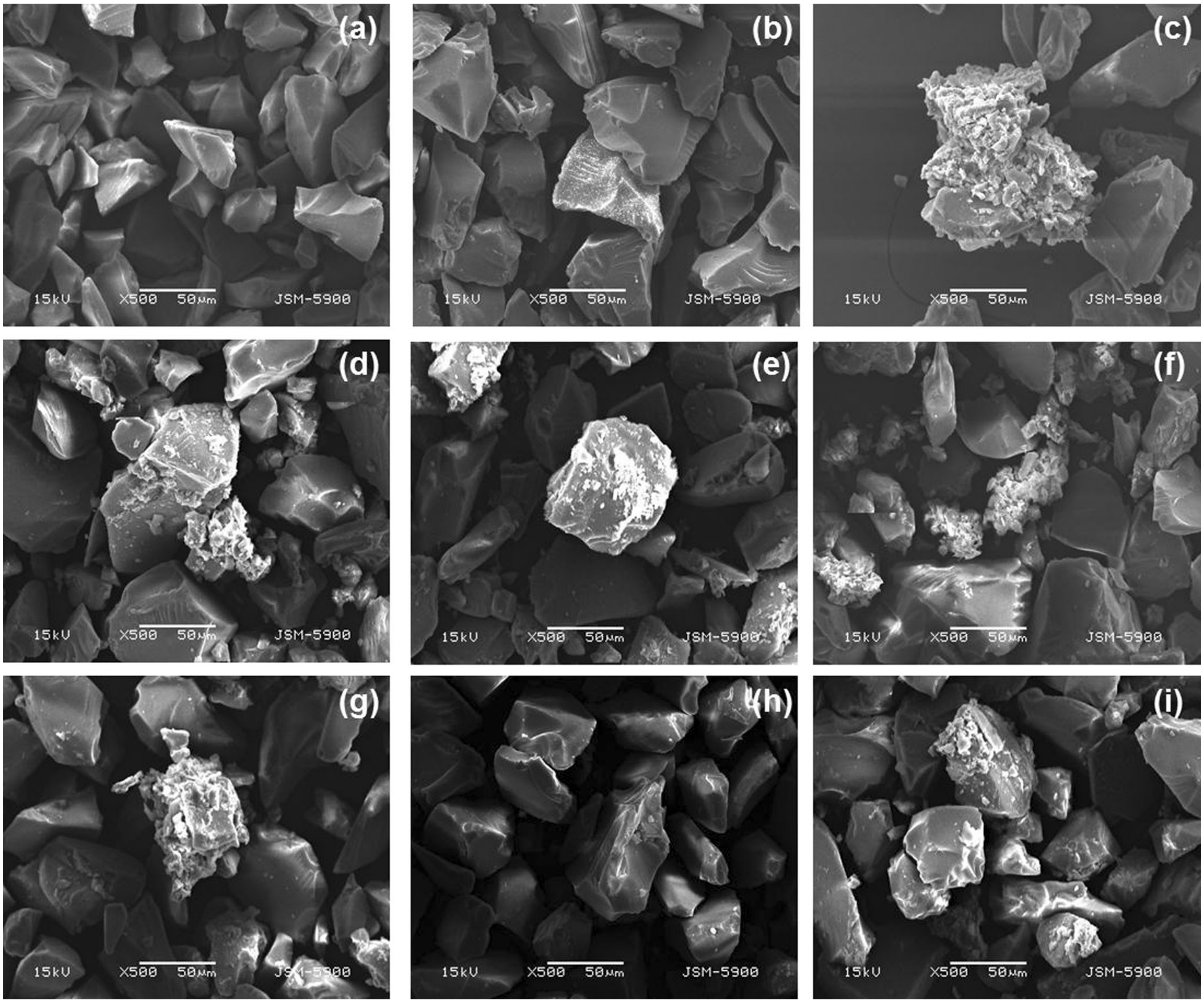


Fig. 5 SEM images of **a** silica, **b** HACS, **c** Cu-HACS, and **d** Cu-HACS before waster washing and after **e** water washing (control), **f** H_2O_2 oxidation (Method 2), **g** CA washing (Method 3), **h** NaOH washing (Method 1), and **i** EDTA washing (Method 3)

processes (Han et al. 2011). The IR spectra of HACS after extraction or oxidation processes (Fig. 3f–j) were similar to the raw silica spectra (Fig. 3c). Since most of the HACS fractions included silica, the IR spectra of HACS were dominated by silica peaks.

As described previously, NaOH extracted HA from soil samples, but there was no significant change in the FT-IR spectrum, which is indirect evidence of Cu being released in the form of Cu-HA complexes. In Fig. 3h, the intensity of the carboxyl group at 1620 cm was slightly weakened, which indicates that H_2O_2 reacted with HA; however, the oxidation of HA was limited. In contrast, extraction using EDTA and citric acid increased the bands at 1620 and 1720 cm, respectively. EDTA and citric acid contain carboxyl groups in their molecular structures, and the adsorption of EDTA and citric acid onto the soil surface increased the intensity of the carboxyl peak.

Both the carbon content and FT-IR spectral analysis indicate adsorption of EDTA and citric acid onto HACS. The SEM image also provided evidence of HA binding and extraction (Fig. 5). The surface of particles after NaOH washing was relatively smooth (Fig. 5h), which indicates a large amount of HA had been extracted. Other samples before and after chelation washing or oxidation had a rough surface (Fig. 5c–g, i), which shows that the HA bonded to silica was not extracted or oxidized. Thus, EDTA washing was the best Cu removal method for the Cu-contaminated model soil. NaOH extracted HA from HACS, while EDTA and citric acid were adsorbed onto HACS. H_2O_2 oxidation was not effective in removing Cu from the model soil because of the lack of a radical initiator. As these results were obtained from the Cu-contaminated model soil and actual metal contaminated soil consists of various minerals and organic materials, the three methods were applied to a field Cu-contaminated soil sample.

Removal of Cu from field contaminated soil

The EDTA and CA extractive removal of Cu from field Cu-contaminated soil showed the best removal efficiency of the three methods (Table 3). In addition, organic matter bound Cu and Zn was decreased after CA and EDTA washing in sequential extractions, while bound Pb increased (Fig. 6). The F1, F2, F3, and F4 for Cu in sequential extractions were 30.2 % (89.2 mg/kg), 44.6 % (131.8 mg/kg), 15.7 % (46.3 mg/kg), and 9.5 % (27.9 mg/kg), respectively. When CA and EDTA extractions were applied, the F1, F2, and F3 of Cu decreased, while F4 of Cu increased. The overall removal efficiencies of Cu were 50.6 and 55.0 % using CA and EDTA, respectively.

With method 1 (NaOH washing) and method 2 (H_2O_2 oxidation), there was almost no change in the Cu fractions, and the removal efficiency of Cu was also negligible. The organic matter bound Cu fraction (F3) decreased approximately 23.4 and 28.6 % using CA and EDTA, respectively.

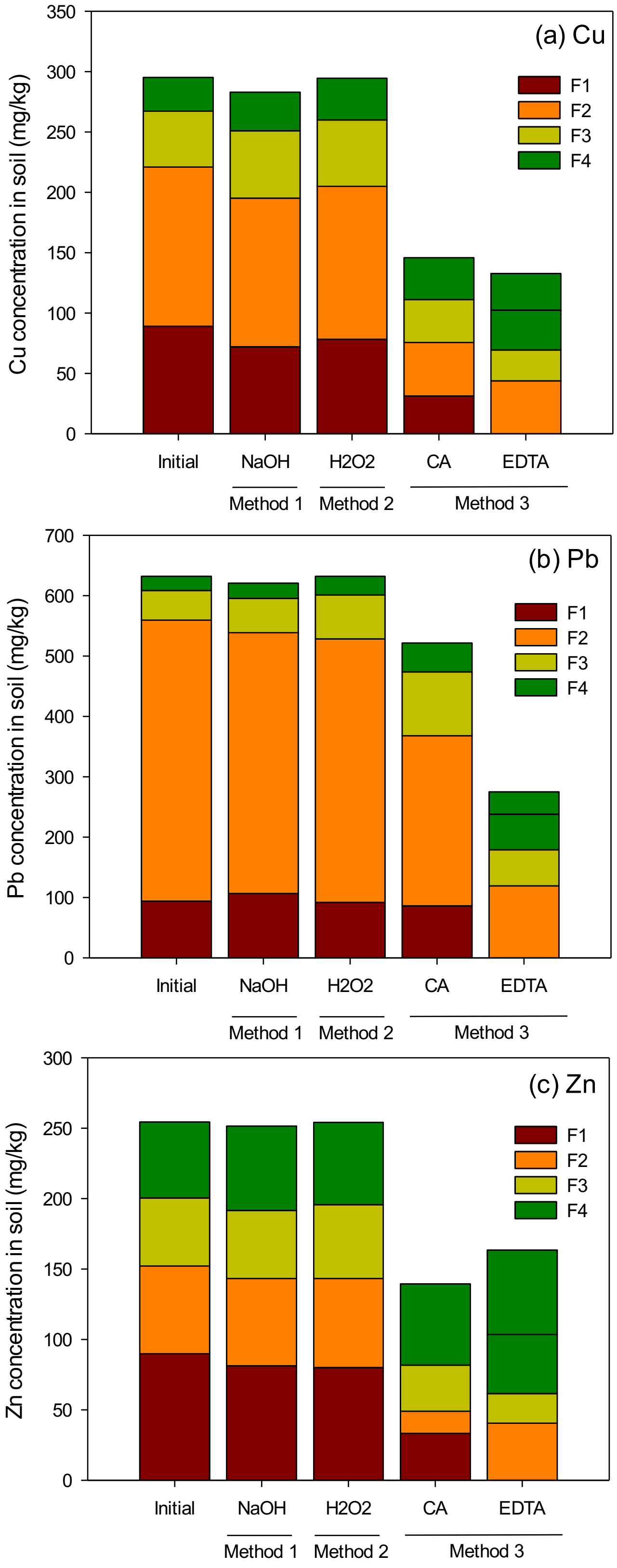


Fig. 6 Fractionation of metals (Cu, Pb, and Zn) before and after extraction or oxidation for the field soil

These results imply that the organic matter bound Cu (F3) can be extracted using CA and EDTA, while there was no effect from extraction of organic matter bound Cu using NaOH extraction and H_2O_2 oxidation.

There was little difference between the model soil and field soil in the removal of Cu bound to organic matter. Although NaOH extraction was effective in the removal of HA-Cu complex from the model soil, the removal of Cu bound to organic matter in field soil was negligible with the NaOH extraction method. When H_2O_2 oxidation was applied, the removal of Cu from both the model and field soils was negligible. As described previously, radicals from H_2O_2 could be produced in field soil by initiators such as Fe(II) and iron oxides, which could react with soil organic matter. However, with the field soil used in this study, the Cu removal was negligible, and the fractionation of Cu did not change, which suggests that radicals might not be produced in the field soil sample used in this study. Between CA and EDTA, EDTA was more effective in removing Cu bound to organic matter in both the model and field soil samples, although the amount of organic matter-bound Cu extracted from field soil was lower than from the model soil.

The different extraction behavior for Cu between model and field soils might be occurred by the complex composition of real soil compared with model soil. The model soil was just consisted with silica and HA while the field soil contains a lot of soil constituent such as carbonates, iron oxides, manganese oxides, sulfides, organic matters (HA, fulvic acid, humin, and etc.), silicates, and etc. Also, there are some limitations of SM&T SEP. When the composition of soil is very complex, the accurate fractionation of metals in soil could not be obtained by the SEP. For example, the Cu in the organic matter bound fraction (F3) could be bound to not only organic matter but also sulfides (Rauret et al. 1999). Therefore, the complexity of the field soil and the inaccuracy of SEP might derive the different extraction patterns of Cu between model and field soils.

Conclusion

Three proposed processes to remove Cu bound to organic matter in soil were investigated using silica and HA model soil, which resulted in the following conclusions. First, oxidation was not effective in breaking Cu-humic complexes in either the model soil or field contaminated soil, since humic substances are residual matter resulting from extensive oxidation in nature. In addition, oxidation with H_2O_2 might require an initiator or catalyst for OH radical production, and there were no such initiators such as Fe^{2+} present in the model soil. However, with the field soil, the removal of Cu was negligible and the fractionation of Cu did not change, which suggests that radicals might not be produced in the field soil used in this study. Second, NaOH was effective in extracting HA from the model soil, and Cu was simultaneously extracted from the soil as a complex with HA. However, extraction of Cu by NaOH from the field soil sample was not effective. Similar to H_2O_2, treatment with NaOH did not alter the Cu fraction, and the removal efficiency was negligible. Finally, EDTA and CA extracted Cu from the HA complex by chelation and ion-exchange with both the model and field soils, and they most effectively decreased the F3 of Cu in the field soil, even though the removal efficiency was lower than with the model soil. However, EDTA and CA were adsorbed onto the model soil, i.e., EDTA and CA could cause secondary pollution of the soil or groundwater. Generally, the removal rate was lower with the field soil as compared to the model soil, probably because field soil contains only limited amounts of organic matter and the amount of Cu bound to organic matter was relatively less than in the model soil.

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