Decontamination of metal-contaminated waste foundry sands using an EDTA-NaOH-NH3 washing solution

Decontamination of Metal-Contaminated Waste Foundry Sands Using an EDTA-NaOH-NH₃ Washing Solution

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Abstract

Waste foundry sand (WFS), which is a hazardous byproduct from the foundry industry, is often contaminated with potentially toxic elements (PTEs), such as Cu, Pb and Zn, and widely re-utilized as a construction material. Therefore, the depollution of WFS has been suggested due to its environment friendly reprocessing to avoid potential long-term hazardous impacts. In the current study, a unique chemically induced technique has been proposed for the removal of PTEs from WFS. EDTA, NaOH and NH_3 were used as extractants in combination or in succession. The optimum removal of PTEs was accomplished using a solid (WFS) to solution (50 mmol L^{-1} EDTA) ratio of 10 under strongly basic pH conditions, which was achieved with NaOH addition. The washing efficiency was further enhanced with the addition of NH_3 to the solution. The complete process cycle duration was adjusted to 9 h with a washing sequence that was repeated three times for 3 h each. The ultimate efficiencies (%) for the removal of PTEs were as follows: Cu, 98; Pb, 81; Sn, 83; and Zn, 50. The leaching of residual PTEs (%) from the decontaminated WFS was also in compliance with the regulatory levels that are defined by the monitoring authorities.

Keywords

1.0 Introduction

High-quality size-specific silica sands are blended with clay or organic chemical binders and used in molding and casting processes of ferrous and non-ferrous (e.g., copper, aluminum and brass) metal products in foundries [1]. The clay-bonded molding sands, which are also known as green sand, have been predominantly used in foundries and consist of a combination of silica sand (85–95%), bentonite (4–10%) and carbonaceous additive (2–10%) [2]. The other category of molding sand is identified as chemically bonded sand, and this material is produced by mixing 93–99% silica with 1–3% chemical binders (e.g., phenolic urethane, epoxy resins, furfuryl alcohol and sodium silicate) [2, 3]. The molding sands are reused in the process approximately 8 to 10 times depending on the molding utilities and mechanical properties [4], and the end-of-life molding sands are referred to as waste foundry sand (WFS) [5].

The foundries in the United States produce approximately 9 million metric ton of WFS per annum [3], and this amount is more than 30 million tons in China [6]. In 2011, 1.5 million tons of mixed waste, which includes WFS, slag and waste bricks, were produced by foundries in Japan, and this amount increases each year [7]. Rather than disposal in landfills, WFS has been employed as an alternative material for soil-reinforcement [2], roadbed construction [8], and concrete manufacturing [4]. This utilization of WFS is considered beneficial for both to the foundries and the construction industries. However, the consumption of WFS for soil-reinforcement and roadbed construction might have a hazardous impact on the soil environment including groundwater resources due to the presence of potentially toxic elements (PTEs) (e.g., Zn, Mg, Mn, Fe, Pb and Cu) in WFS [9], which is important with respect to the public health [10]. Therefore, the removal of PTEs in WFS has been proposed to ensure safer disposal or environmentally friendly recycling of waste materials.

The removal of PTEs from the waste solid has been achieved by leaching treatments using inorganic and/or organic acids (e.g., sulfuric [11], hydrochloric [12], nitric, oxalic and citric

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[13] acids). However, according to a preliminary estimate, approximately 0.5 metric tons of acid would be required for the removal of PTEs from each dry metric ton of waste solids [14]. In addition to the high costs, the use of acids for solid-waste treatment is also disadvantageous due to the negative environmental impacts and corrosion of the washing plant. The washing remediation of waste solids using chelants has been recommended to overcome the challenges related to acid-induced leaching of harmful elements [15, 16]. Chelant-assisted washing can transfer the PTEs from the solid phase to the aqueous solution at a significant rate due to the complexation reaction [16, 17].

In this study, a unique combination of ethylenediaminetetraacetic acid (EDTA; Table 1), sodium hydroxide (NaOH) and ammonia (NH_3) has been proposed for the quantitative decontamination of PTE-laden WFS from a copper foundry. The effects of the reagent concentrations, component doses and treatment time were studied to determine the optimized blending ratio of the washing solution. To the best of our knowledge, this study is the first report that focuses on the removal of PTEs from WFS to minimize hazardous impacts due to the untreated disposal or recycling of WFS.

2.0 Materials and methods

2.1 Samples

The WFS sample used in this study was supplied by a copper foundry located in Hakusan-Shi, Ishikawa, Japan that is owned by the Akashi Gohdoh Inc. According to the sample provider, the foundry sand used in the production process contained silicate (85%), bentonite (7%), cornstarch (5%) and moisture (3%).

2.2 Instruments

A microwave-assisted digestion apparatus (Multiwave 3000; Anton Paar GmbH, Graz, Austria) equipped with an 8-position rotor and hydraulic pressurized sensing system for all of the vessels was used for elemental characterization of the solids. The XF100 vessels of the digestion apparatus support 6 MPa of controlled pressure and 12 MPa of maximum operating pressure, and the maximum temperature can be 240 °C. A field-emission scanning electron

microscope (FE-SEM; JSM-7100F, JEOL Co., Tokyo, Japan) equipped with a dispersive X-ray spectrometer (EDX; INCA energy Oxford Instruments, Oxfordshire, UK) was used for the non-destructive detection of elements in the solid samples.

An inductively coupled plasma optical emission spectrometer (ICP-OES; iCAP 6300, Thermo Fisher Scientific, Waltham, MA) was used to determine the concentration of metals in the solution. The ratio frequency power used at the EMT duo quartz torch of the ICP-OES instrument was 1.15 kW, the gas flows in the plasma, auxiliary and nebulizer were 12, 1 and 0.5 L min^{-1}, respectively, and the integration time was 30 s.

A Digiprep Jr block heater (SCP Science, Quebec, Canada) and an oven (DX 600, Yamato Scientific, Tokyo, Japan) were employed during the heating or drying steps in the experiments. A Kokusan centrifuge (H-701FR, Kokusan Corporation, Tokyo, Japan) and a filtration assembly that consisted of a suction system (MAS-1, AS ONE, Osaka, Japan) and an acetate-mixed-ester membrane filter (pore size: 0.45 μm) were used in the separation steps. A water purification system (Arium Pro UV, Sartorius Stedim Biotech GmbH, Göttingen, Germany) was used to prepare the purified water (resistivity > 18.2 MΩ·cm). A pH meter (Navi F-52, Horiba Instruments, Kyoto, Japan) was used to determine the pH of the solutions.

2.3 Chemicals

All of the chemicals used during the experimental steps were of analytical reagent grade. EDTA, NaOH, NH$_3$, HF, HNO$_3$, HCl and H$_3$BO$_3$, which were used for the decomposition, extraction and other processes, were obtained from Kanto Chemical (Tokyo, Japan). The solution pH adjustments were performed using HNO$_3$ and/or NaOH solutions (1 mol L^{-1}). The buffer reagents used to maintain the solution pH consisted of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (Nacalai Tesque, Kyoto, Japan), N-tris(hydroxymethyl)-3-aminopropanesulfonate, 3-cyclohexhylaminopropane sulfonate (MP Biomedicals, Santa Ana, CA), and sodium acetate/acetic acid (Kanto Chemical, Tokyo, Japan).

A standard solution of tin (Sn) in 2.5 mol L^{-1} HCl (Kanto Chemical, Tokyo, Japan) and ICP multi-element standard solution IV that consisted of 23 elements (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl and Zn) in diluted nitric acid (Merck KgaA, Darmstadt, Germany) were used during metal analysis. The dilutions of the stock solutions of the standards and other reagents were conducted using purified water (resistivity > 18.2 MΩ·cm) to prepare working solutions.

2.4 Laboratory wares

Low-density polyethylene bottles (Nalge Nunc, Rochester, NY), polypropylene test tubes (Digi TUBEs, SCP science, Quebec, Canada), and micropipette tips (Nichiryo, Tokyo, Japan) were used during the experiments. All of the laboratory wares were soaked overnight in a 5% alkaline detergent solution (Scat 20X-PF, Nacalai Tesque, Kyoto, Japan) followed by a dipping in HCl solution (3 mol L^{-1}) overnight with pre-washing using purified water prior to each step.

2.5 Methods

2.5.1 Characterization of WFS

A sieve analysis using a standardized mesh series was performed to assess the particle size distribution of the WFS. Elemental mapping of the PTEs in the solid WFS sample was performed using FE-SEM and EDX techniques. The microwave-assisted digestion of the WFS solids was performed to determine the total concentration of elements.

The PTFE vessels of the digestion system were loaded with 0.05 g of the WFS solid, HNO$_3$ (13.2 mol L^{-1}; 1 mL), HCl (12 mol L^{-1}; 3 mL) and HF (27 mol L^{-1}; 1 mL). The operating conditions were as follows: microwave power (max) – 1400 W; ramp time – 15 min; heating time at the maximum temperature – 120 min; and vent time – 30 min. Then, a 5% solution of H$_3$BO$_3$ (10 mL) was added to the digestion product to convert the residual HF to BF$_4^-$. The mixture was further treated in the digestion system under conditions similar to those in the previous step, except a shorter heating time of 30 min was employed at the maximum temperature. Then, the dissolved products from the PTFE vessels were transferred to 50 mL

polypropylene tubes and diluted to 50 mL using purified water. A blank run (digestion without WFS) was also performed to investigate the magnitude of the error from the solvents used during the microwave-assisted digestion. The concentration of elements in the WFS (C_{WFS}) was measured using ICP-OES and calculated using the following equation:

$$C_{WFS}\ [\text{mg kg}^{-1}] = \frac{C_{sol}[\text{mg L}^{-1}] \times v\ [\text{L}]}{m_{WFS}[\text{kg}]} \tag{1}$$

In Eq (1), C_{sol}, v and m_{WFS} were the concentration of elements in the digested solution, total volume of the digested solution, and weight of the WFS, respectively.

2.5.2 *Chemically assisted washing treatment of WFS*

For decontamination, EDTA, NaOH and NH_3 were employed as chemical extractants in the washing treatment of the WFS. The extractants were added to the WFS (~0.5 g) either individually or as a mixture at a pre-determined ratio. Then, the WFS-extractant mixture was agitated continuously for 24 h at 180 rpm and 25 °C in an end-over-end shaker. The shaking process was followed by centrifugation of the mixture at 1820 ×g for 30 min, and the aqueous supernatant was separated using a filtration assembly containing a glass-fiber filter. The supernatant was diluted to 10 times its original volume with purified water and stored at 25 °C prior to the ICP-OES analysis. The reported data was obtained from a representative triplicate experiment and is presented as a mean value ± SD. The removal efficiency (%RE) of the elements by the extractant (either individual or mixture) from the WFS was defined using the following equation:

$$\%RE = \frac{C_{sol}[\text{mg L}^{-1}] \times v\ [\text{L}]}{C_{WFS}\ [\text{mg kg}^{-1}] \times m_{WFS}[\text{kg}]} \times 100 \tag{2}$$

In Eq (2), C_{sol}, v, m_{WFS} and C_{WFS} are the concentration of elements in the washing solution, total volume of the washing solution, weight of the WFS, and concentration of the elements in the WFS, respectively.

2.5.3 *Rinsing treatment of the chemically treated WFS*

The chemically treated WFS was rinsed 5 times to remove the residual extractant using acidic (pH 3), neutral (pH 7) or basic (pH 11) purified water. The pH of the rinsing

water was adjusted using HNO_3 or NaOH (0.1 M). 10 g of chemically treated WFS was treated with 100 mL of the pH-adjusted rinsing solution for 10 min with continuous agitation at 180 rpm. The rinsed WFS solid was separated from the suspension by centrifugation (1820 ×g, 30 min).

2.5.4 *Leaching test to evaluate the hazardous impact*

The rinsed samples were dried at 105 °C for 3 h and then subjected to the leaching test according to the method recommended by the Ministry of the Environment, Japan. The water-assisted leaching test of the WFS (0.5 g) was performed using purified water (5 mL) with a pH of 5.8~6.3 that was adjusted using either a NaOH or HCl solution. The acid-assisted leaching test of the WFS (0.5 g) required 16.7 mL of 1 mol L^{-1} HCl. The WFS-liquid mixtures for the water or acid-assisted leaching test were continuously agitated for 6 h at 180 rpm and 25 °C in an end-over-end shaker. Then, the aqueous phase of the mixture was separated from the suspension by centrifugation (1820 ×g, 30 min) followed by filtration using an acetate-mixed-ester membrane filter (pore size: 0.45 μm). The total content of elements in the water-leached (L_{water}) or acid-leached (L_{HCl}) solution was determined using ICP-OES. The reported values represent the mean of a triplicate experiment ± SD.

3.0 Results and discussion

3.1 Characterization of WFS

The WFS samples consisted of black sand particles of various sizes with median and mode sizes of 151 and 113 μm, respectively (Figure 1).

The content of major PTEs (%) that were determined in the WFS using the microwave-assisted digestion and ICP-OES analysis was as follows: Zn (3.01 ± 0.04), Cu (2.17 ± 0.06), Pb (0.410 ± 0.005) and Sn (0.120 ± 0.004). A higher content (%) of Al (2.13 ± 0.01) was detected, which is due to the component mineral in the sand (i.e., aluminosilicate). The contents (%) of Fe (0.840 ± 0.003), Mg (0.286 ± 0.004), Na (0.231 ± 0.009), Ca (0.20 ± 0.02), K (0.121 ± 0.009), and Mn (0.022 ± 0.002) were considerable, but the concentrations of the

other elements were either below 0.01% (Ba, Cd, Cr, Li, Ni, and Sr) or below the detectable limits (Ag, Bi, Co, Ga, In, Tl). A list of various metal contents in the WFS sample is provided in Table 2. A typical chemical composition (%) of the WFS, as reported by Siddique *et al.* [1], may be as follows: SiO_2: 87.91, Al_2O_3: 4.70, Fe_2O_3: 0.94, CaO: 0.14, MgO; 0.30, SO_3: 0.09, Na_2O: 0.19, K_2O: 0.25, TiO_2: 0.15, Mn_2O_3: 0.02, and SrO: 0.03. The concentration of PTEs (%) in a WFS sample, as reported by Guney *et al.* [8], was as follows: Ni: 0.004, Cr: 0.003, Cu: 0.002, Pb: 0.003, Zn: 0.003, and Cd: 0.001. In comparison to the other WFS samples reported in the literature, the samples used in the current study have a higher concentration of PTEs. Therefore, the WFS samples from each molding operation will vary and be representative of the type of metal molded in a specific foundry.

The FE-SEM and EDX images of the WFS indicated the existence of Cu and Sn as comparatively larger-sized independent particles (> 10 μm) than silicate (Figure 2a), and Pb and Zn existed as fine particles that were homogeneously adhered to the surfaces of the silica or copper particles (Figure 2b). Therefore, the distribution of PTEs in the WFS was heterogeneous among the sand particles. However, the relative standard deviation in the concentration of PTEs remained in a lower range (e.g., Cu: 2.17±0.06%), and the WFS samples were analyzed using microwave-assisted digestion followed by ICP-OES as bulk specimens (~0.05 g). Moreover, the differences in the distribution patterns of the PTEs indicate that the origins of the contaminants may not be the same even though the WFS was presumed to be contaminated with the PTEs during the copper molding activities.

3.2 Decontamination treatment of WFS

3.2.1 Effect of ethylenediaminetetraacetate-assisted washing

The washing treatment using a chelant (e.g., EDTA) was expected to remove metal ions from the solid phase due to the complexation reaction between the metal (M) and EDTA (L) (see Eq 3).

$$M^{2+} + EDTA^{4-} \leftrightarrow M - EDTA^{2-} \tag{3}$$

The changes in the solution/solid ratio (EDTA/WFS; 2~10 mL g^{-1}; EDTA concentration = 50 mmol L^{-1}; solution pH = 7) affected the %RE of PTEs from the WFS (Figure 3a). A similar trend was also observed as the EDTA concentration in the solution increased (10~50 mmol L^{-1}; EDTA/WFS ratio = 10 mL g^{-1}; solution pH = 7), and the %RE reached a constant value within 50 mmol L^{-1} (Figure 3b). The %RE of Cu (78%) or Pb (61%) was notable with 50 mmol L^{-1} EDTA in the solution but the dissolution was only 28 and 11% for Zn and Sn, respectively. The calculated results confirmed that 0.5 g of the WFS contained 0.18, 0.14, and 0.01 mmol of Zn, Cu and Pb, respectively, in the solid phase. However, the content of EDTA in the solution was 0.5 mmol. Therefore, the %RE was not quantitative even in the presence of excess chelant in the solution, which is due to the lack of complexation between EDTA and the metal species or the speciation variability of the elements in the solid phases [16].

The effect of the variation in the solution pH from 3 to 10 during the EDTA-assisted washing was investigated (Figure 3c). The washing solution pH was measured before and after treatment, and an increase in the solution pH by ~1.0 unit after the washing treatment was observed (e.g., the pH of the washing solution adjusted to a pH of 3 increased to 4.074 after the washing step). The changes in the solution pH after the washing treatment indicated the coexistence of unidentified alkali sources in the WFS, such as CaCO$_3$ and CaO. During the EDTA-assisted washing of the WFS, competitive complexation with EDTA occurred with Cu and Zn under the different pH conditions (Figure 4b). The Zn-EDTA species was dominant under acidic conditions even though the apparent stability constant of Cu-EDTA was greater than that of the corresponding Zn complex under the same pH conditions. Furthermore, an increase in the %RE of Pb was observed under acidic conditions. The higher %RE in the acidic region was primarily due to the dissolution reaction between the solid-phase components of the metals (e.g., metal-oxide; MO) and the protons (H^{+}) (Eq 4) [18]. The complexation reactions between M^{2+} and EDTA (Eq 3) are considered the main reactions that occur during washing with acidic solutions. However, the stability constants of metal-EDTA complexes are not the primary factors that affect the %RE of PTEs under acidic conditions.

$$MO + 2H^+ \leftrightarrow M^{2+} + H_2O \qquad\qquad (4)$$

The %RE of Cu and Sn were higher at a pH of 9 but a lower Cu solubility under alkaline conditions was most likely due to the possibility of hydroxide precipitation (i.e., Cu(OH)$_2$) [19]. However, the comparatively higher stability of the Cu-EDTA complexes in solution, which further increased due to deprotonation of EDTA (Eq 5; Figure 4a) in the weakly alkaline region (pH 9), may minimize this possibility. The Cu-EDTA complex was a more dominant species than the Zn-EDTA complex (Figure 4b) in the alkaline pH region, and the trend in the %RE of Cu and Zn confirmed the correlation between the stability constant and %RE in a specific pH region.

$$H_4EDTA \leftrightarrow 4H^+ + EDTA^{4-} \qquad\qquad (5)$$

The Sn removal behavior was similar to that of Cu. However, the %RE was significantly lower than those of the other PTEs (Zn, Cu and Pb) in the WFS, which was due to the co-existence of Sn species in the WFS solid phase. Sn(IV), which is the most predominant among the Sn species, exhibits poor solubility in weakly acidic or basic conditions, and Sn(II) can be dissolved in an alkaline aqueous medium as oxyanions (e.g., Sn(OH)$_3^-$) [20]. Therefore, the complexation reaction between Sn and EDTA in a pH range of 3 to 11 is unlikely, and the Sn content in the aqueous phase most likely consists of anionic species that were released during the dissolution of Cu. In fact, Sn(OH)$_3^-$ was observed as the more predominant species compare to Sn(II)-EDTA at higher pH values based on chemical equilibrium calculations (Figure 4b).

The %RE of metal species was enhanced at high pH values due to the deprotonation of EDTA (Eq 5). In general, the weakly alkaline solution environment contributes to the precipitation of the metals (Eq 6) [19], and the solubility increases under stronger basic pH conditions due to the formation of soluble metal hydroxide species (Eq 7) [20].

$$M^{2+} + 2OH^- \leftrightarrow M(OH)_2 \downarrow \qquad\qquad (6)$$

$$M^{2+} + nOH^- \leftrightarrow M(OH)_n^{2-n} \qquad\qquad (7)$$

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Therefore, the effect of the strong alkaline environment on the dissolution of PTEs in the WFS was evaluated via spiking the solution with NaOH (Figure 3d). The NaOH concentration in the solution was varied from 0.2 to 1.0 mol L^{-1}, and the %RE of the PTEs in the WFS improved with 0.2 mol L^{-1} NaOH in the solution. The changes in %RE in the Zn were insignificant, and the increase in %RE of Cu or Pb was minor. However, a notable increase in the %RE for Sn was observed. The dissolution of Sn(IV) compounds (e.g., SnO_2) in the strongly basic solution via the generation of soluble oxyanion species may result in a high %RE for Sn. The %RE for all of the target elements remained constant even when the NaOH concentration increased to 1.0 mol L^{-1}, which indicated that the strongly alkaline conditions were favorable for the formation of soluble metal-hydroxide species with 0.2 mol L^{-1} NaOH in the solution.
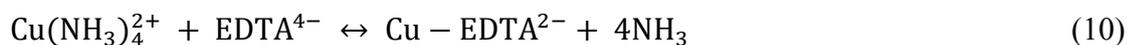
Based on these mentioned steps, the optimum washing combination was as follows: EDTA / WFS ratio, 10 mL g^{-1}; EDTA concentration, 50 mmol L^{-1}; and solution pH, strong basic (0.2 mol L^{-1} NaOH).

3.2.2   Effect of ammonia-assisted washing

Ammoniacal lixiviant has been utilized for Cu removal from Cu-rich gold ore [21] using the specific complexation reaction between Cu and NH_3 [22]. Therefore, the EDTA-NaOH solution (as optimized in the previous section) was dosed with NH_3 with a concentration ranging from 0.1 to 1.0 mol L^{-1} to facilitate the enhanced removal of elements from WFS. The evaluation results indicated that the %RE of Cu, Pb and Sn increased with a NH_3 dose as low as 0.3 mol L^{-1} (Figure 5a). The variations in the Cu-complex formation ratio in the EDTA-NaOH-NH_3 solution were calculated using the HySS2009 [23] computer simulation program for chemical equilibria, which indicated that the Cu-EDTA complex was the dominant species (Figure 5b).

The effect of NH_3 addition (0.3 mol L^{-1}) on the %RE of Cu at varying treatment times (h) was investigated, and rapid removal was achieved with NH_3 in the EDTA-NaOH solution

compared to that without NH_3 (Figure 5c). The reactions that may occur between NH_3 and Cu^{2+} in solution are shown in Eqs 8 to 10.

$$Cu_{(s)} \leftrightarrow Cu^{2+}{}_{(aq)}; Cu_{(s)} : Cu, CuO, Cu_2O \tag{8}$$

$$Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{2+} \tag{9}$$

$$Cu(NH_3)_4^{2+} + EDTA^{4-} \leftrightarrow Cu - EDTA^{2-} + 4NH_3 \tag{10}$$

In washing treatments without EDTA, ammonia only provides 15% Cu removal. However, the extraction equilibrium was achieved within 6 h when ammonia lixiviant was added, and more time was required when only EDTA was used. The reactions between NH_3 and Cu^{2+} occur more rapidly than those with EDTA (Eq 9), and therefore, the dissolution of Cu^{2+} from the solid phase increased (Eq 8). The stability constant of Cu-EDTA ($\log K = 18.80$) was higher than that of $Cu(NH_3)_4^{2+}$ ($\log \beta = 12.6$), which induced a chelant-exchange reaction (Eq 10) in the washing solution. Therefore, an increase in the reaction rate for metal dissolution occurred with the addition of NH_3 to the EDTA-NaOH solution. However, the addition of NH_3 did not affect the chemical species formation (Figure 5d). An optimum NH_3 dose of 0.3 mol L^{-1} was selected for addition to the EDTA-NaOH mixture to ensure the quantitative removal of Cu from the WFS.

3.2.3 *Effect of multiple washing treatments with the EDTA-NaOH-NH₃ solution*

The washing decontamination of WFS using the EDTA-NaOH-NH_3 solution under the optimum conditions will be more successful if the process is continued for 24 h. To minimize the process cycle duration and ease the handling process, a multi-stage washing treatment was evaluated. The WFS (10 g) was repeatedly washed 3 times for 3 h each time, and the %RE values for the metals were as follows: Cu: 98, Pb: 81, Sn: 83, and Zn: 50 (Figure 6a). The extractant-washed WFS was further analyzed using FE-SEM and EDX to determine the extent and efficiency of the decontamination (Figures 6b and 6c), and microwave-assisted digestion followed by ICP-OES analysis was used to determine the quantitative content of residual PTEs (Figure 6a). The total mass balance (Eq 11) during the multi-stage washing treatment of WFS is also shown in Figure 6a.

Mass balance (%) = 1st + 2nd + 3rd + Residual (11)

In Eq 11, the %RE at each sequential step in the EDTA-NaOH-NH$_3$ assisted washing treatment are referred to as '1st', '2nd', and '3rd', and the term 'Residual' represents the residual ratio of PTEs in the chemically washed WFS. The cumulative values of the mass balance (%) of Cu, Pb, Sn, and Zn were 101, 107, 91, and 69, respectively, and the surplus values for Cu and Pb may be due to the passive re-adsorption of PTEs on the surface of the WFS during the multi-stage washing. An unexpected decrease in the mass balance was observed for Zn (~31%). The Zn element was predominantly attached to the fine particles in the WFS, and therefore, the loss of these particles during the operational steps of multi-stage treatments (e.g., decantation and incomplete centrifugation) may have occurred. This result also suggests significant adsorption of Zn^{2+} and/or Zn-EDTA complexes on the easily floatable fine particles.

3.2.4 *Effect of rinsing the EDTA-NaOH-NH$_3$ washed WFS samples with water*

The EDTA-NaOH-NH$_3$ washed WFS samples (0.5 g) were rinsed using purified water (5 mL). The pH of the water was varied in from acidic (pH 3) to neutral (pH 7) and basic (pH 11) to explore the extent of metal leaching under various conditions. The content of leachable metals (Cu, Pb, Sn, and Zn) from the pH-varied water-rinsed WFS samples is shown in Figure 7. The leachable metals from the washed WFS rinsed with water that had a neutral pH were high compared to that rinsed with water at a pH of 3 or 11. The re-adsorption of some elements in the WFS as metal-chelate complexes during the washing process may be due to its corresponding presence in the rinsed supernatant. These residues of the PTEs could easily diffuse into the environment. Therefore, the rinsing step using water was incorporated in the proposed WFS decontamination methodology to eliminate the environmental release of elemental or complexed PTEs that remained on the WFS surface after chemically assisted washing. The mass balance (%) of the PTEs after rinsing was calculated using Eq 12.

Mass balance (%) = 1st + 2nd + 3rd + Rinsed + Residual (12)

In Eq 12, 'rinsed' represents 'removed-PTEs during rinsing', and the other terms are same as those in Eq 11. The rinsing step using acidic water may remove the surface-adsorbed metals via an ion-exchange reaction between the adsorbed metal and the protons, and water at a basic pH can promote the dissolution of the chelant as well as the metal-chelate complexes from the surface of WFS. Therefore, effective rinsing with water is possible at acidic and alkaline pH values, and a rinsing step using water with a pH of 11 is recommended.

3.3 Evaluation of the treated WFS for environmental hazardous impact

The total content of PTEs in the raw and EDTA-NaOH-NH_3 washed WFS after rinsing were determined via microwave-assisted digestion followed by ICP-OES analysis, and the results are listed in Table 3 along with the leaching test results conducted using water (pH adjusted to 5.8–6.3) or a 1 mol L^{-1} HCl solution according to the recommended standard methodology. The mass ratio of HCl-leached PTEs to raw WFS was high, which may represent the contents that are insoluble during the chelant-assisted washing of the WFS. In addition, the mass ratio of water-leached PTEs to raw WFS was very low. Therefore, the water-leachable PTEs were identified as weakly adsorbed species on the surface of the WFS.

The leaching test results have been compared to regulatory standards provided by the monitoring authorities of Japan, China and the US to confirm the efficiency of the method with no after-treatment environmental hazardous impact. For example, the suggested limit of water-leachable Pb from waste in Japan is 0.3 mg L^{-1} but the water-leached-Pb from the WFS treated using current method was 0.12 mg L^{-1}.
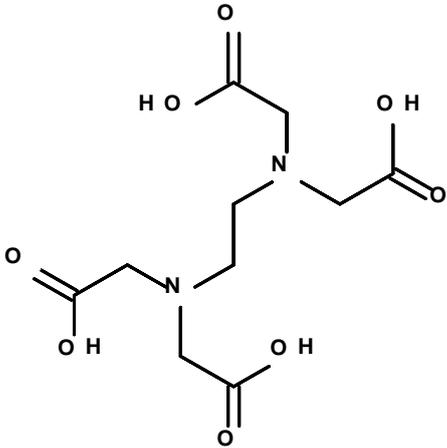
4.0 Conclusion

A technique for the removal of PTEs (Pb, Cu, Sn and Zn) from WFS has been reported in this study to ensure its environmentally friendly re-utilization. The washing solution used to decontaminate the WFS includes EDTA as the main component, and NaOH and NH_3 were added to adjust the solution pH and enhance the %RE. The optimum washing performance was achieved using the following extractant composition: EDTA, 50 mmol L^{-1}; NaOH, 0.2 mol L^{-1}; and NH_3, 0.3 mol L^{-1}. The overall %RE values of the PTEs were as

follows: Cu, 98; Pb, 81; Sn, 83; and Zn, 50. Furthermore, a washing sequence that was repeated three times for 3 h each is recommended to achieve optimum %RE at a reduced duration. A post-washing rinse step with water at a basic pH is recommended to avoid leaching of elemental or complexed PTEs. The proposed process is advantageous over the available techniques because it does not require a high temperature, pressure, or any vigorous treatment protocol and decreases the possibility of post-washing hazardous effects on the environment.

Acknowledgement

Table 1: Chemical properties of EDTA and its stability constant for complexation with potentially toxic elements.

Chemical structure	pKa_n	
	$n = 1$	1.99
	$n = 2$	2.67
	$n = 3$	6.16
	$n = 4$	10.26
	log $K_{\text{M-EDTA}}$	
	Cu^{2+}	18.80
	Pb^{2+}	18.04
	Sn^{2+}	18.3
Ethylenediaminetetraacetic acid (EDTA)	Zn^{2+}	16.50

pK_a is defined as the negative common logarithm of the deprotonation constant of H_4EDTA, which is expressed as pK_{an} = -log $\frac{[H_{4-n}EDTA^{-n}][H]^n}{[H_{5-n}EDTA^{1-n}]}$ (n = 1~4). $K_{\text{M-EDTA}}$ is the stability constant between the metal ion and EDTA, which is expressed as K = $\frac{[\text{M-EDTA}^{-(4-n)}]}{[M^{n+}][EDTA^{4-}]}$.

Table 2: Contents of elements in the blank and WFS (mg kg^{-1}) determined using microwave-assisted digestion followed by ICP-OES analysis.[a, b]

Elements	Blank	WFS
Al	39 ± 12	21300 ± 100
Ca	30 ± 30	2000 ± 200
Cu	10 ± 10	21700 ± 600
Fe	11 ± 15	8400 ± 30
K	29 ± 31	1210 ± 90
Mg	30 ± 23	2860 ± 40
Mn	0.2 ± 0.2	220 ± 20
Na	< 70	2310 ± 90
Pb	18 ± 20	4100 ± 50
Sn	7 ± 8	1200 ± 40
Zn	84 ± 60	30100 ± 400

[a] The reported values are from triplicate experiments and reported as mean ± SD.

[b] The samples were analyzed for total 24 elements (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Sn, Tl, and Zn), and the elements with contents above 100 mg kg^{-1} are listed.

Table 3: Characterization of the WFS based on the leaching toxicity and comparison with regulatory limits.

Metal	Cu	Pb	Sn	Zn
(i) Raw WFS				
C_{WFS} [wt%]	2.17 ± 0.06	0.410 ± 0.005	0.120 ± 0.004	3.01 ± 0.04
$L_{Water}{}^a$ [mg L^{-1}]	12 ± 3	2 ± 6	ND	14 ± 4
$L_{HCl}{}^b$ [mg L^{-1}]	577 ± 2	94 ± 3	34 ± 3	627 ± 6
(ii) EDTA-NaOH-NH$_3$ washed and rinsed WFS				
C_{WFS} [wt%]	0.042 ± 0.003	0.078 ± 0.003	0.0136 ± 0.0008	0.15 ± 0.02
[%]^c	1.9 ± 0.2	19 ± 1	11 ± 1	5 ± 1
Total %RE [%]^d	98 ± 3	81 ± 3	83 ± 2	50 ± 2
Rinsed PTEs [%]^e	0.8 ± 0.2	7 ± 2	ND	14 ± 1
Mass-balance [%]^f	101 ± 3	107 ± 3	94 ± 3	69 ± 2
$L_{Water}{}^a$ [mg L^{-1}]	1.26 ± 0.1	0.12 ± 0.03	0.0100 ± 0.0001	8.3 ± 0.5
[%]^e	0.058 ± 0.005	0.029 ± 0.007	0.00833 ± 0.00008	0.28 ± 0.02
$L_{HCl}{}^b$ [mg L^{-1}]	10.6 ± 0.3	2.67 ± 0.03	1.45 ± 0.06	30 ± 30
[%]^e	1.63 ± 0.05	2.18 ± 0.02	4.0 ± 0.2	3 ± 3
(iii) Regulatory limits: Japan [24-26]				
$L_{Water}{}^a$ [mg L^{-1}]	NA	0.3 (0.01^i)	NA	NA
$L_{HCl}{}^b$ [mg L^{-1}]	NA	4.55^j	NA	NA
(iv) Regulatory limits: China [27, 28]				
$L_{GB5085.3-2007}{}^g$ [mg L^{-1}]	100	5	NA	100
(v) Regulatory limits: USA [29, 30]				
$L_{TCLP}{}^h$ [mg L^{-1}]	NA	5	NA	NA

The abbreviations are defined as follows: C_{WFS} is the content of PTEs in the WFS based on microwave-assisted digestion and ICP-OES analysis; ND stands for "Not detected or Below Detectable Limit"; and NA stands for "Not available".

^{a} L_{Water}: Leachable metal due to leaching by water (pH 5.8–6.3); ^{b}L_{HCl}: Leachable metal due to 1 mol L^{-1} HCl lixiviant.; ^{c}Mass ratio of PTEs in washed WFS to raw WFS; ^{d}Total %RE from WFS after multi-stage washing with EDTA-NaOH-NH$_3$; ^{e}Mass ratio of rinsed PTEs from washed WFS to raw WFS; ^{f}Mass ratio of (washed PTEs + Rinsed PTEs + Residual PTEs) to total PTEs in raw WFS; ^{g}$L_{GB5085.3-2007}$: Leachable metal due to H$_2$SO$_4$/HNO$_3$ mixed lixiviant adjusted to pH 3.20 ± 0.05.; ^{h}L_{TCLP}: Leachable metal due to acetic acid or acetate buffer lixiviant adjusted to pH 2.88 or 4.93.; ^{i}Environmental limitation of natural soil; ^{j}Original value is 150 mg-PTEs kg^{-1}-Waste.
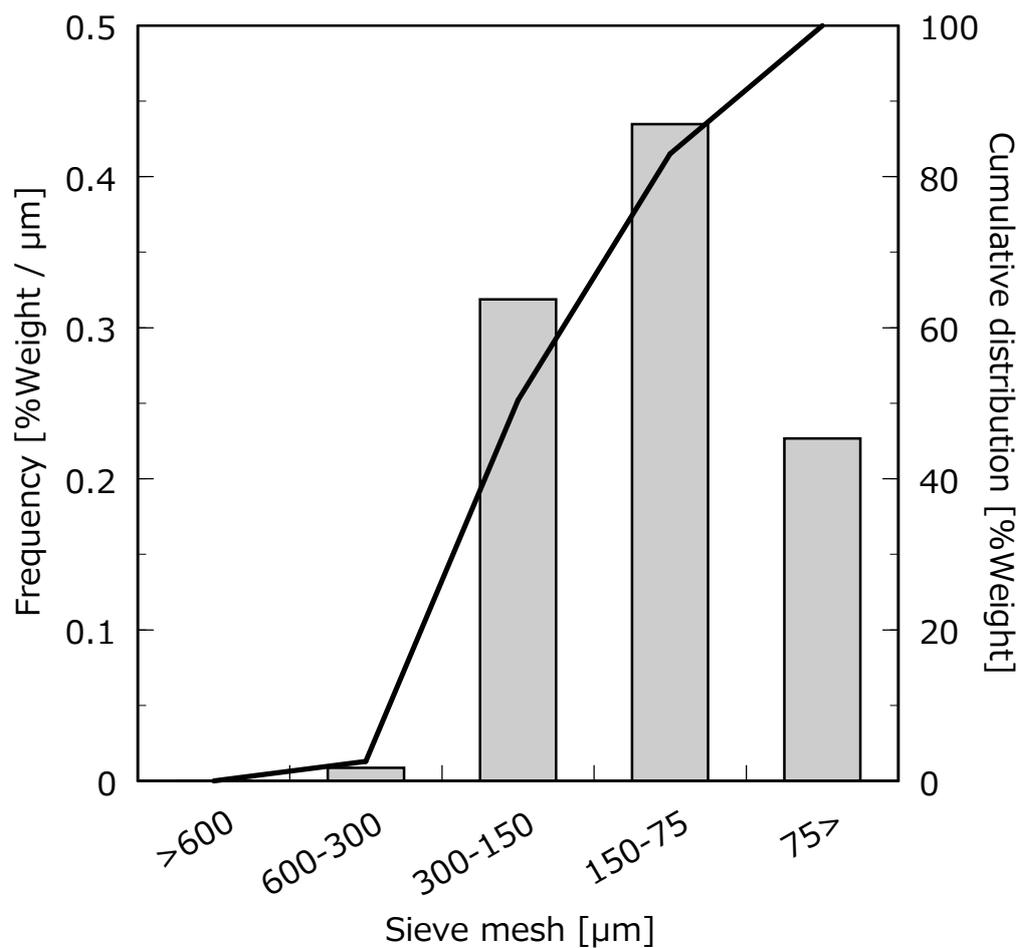
Figure 1: Particle size distribution of the WFS sample (column, size frequency of particles, solid line, and cumulative distribution of particles during sieving).
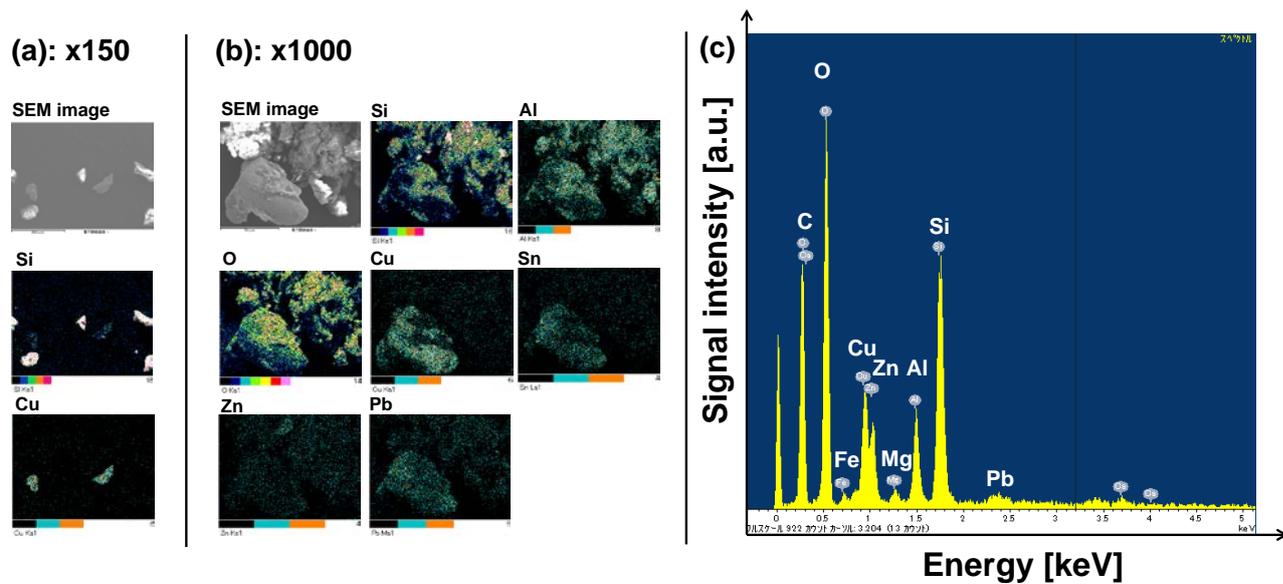
Figure 2: Element mapping images of the WFS samples using FE-SEM and EDX. (a), (b) Mapping images of the WFS particles. (c) X-ray fluorescence spectrum of the area in (b). The signal corresponding to carbon was due to the carbon tape used as a background material.
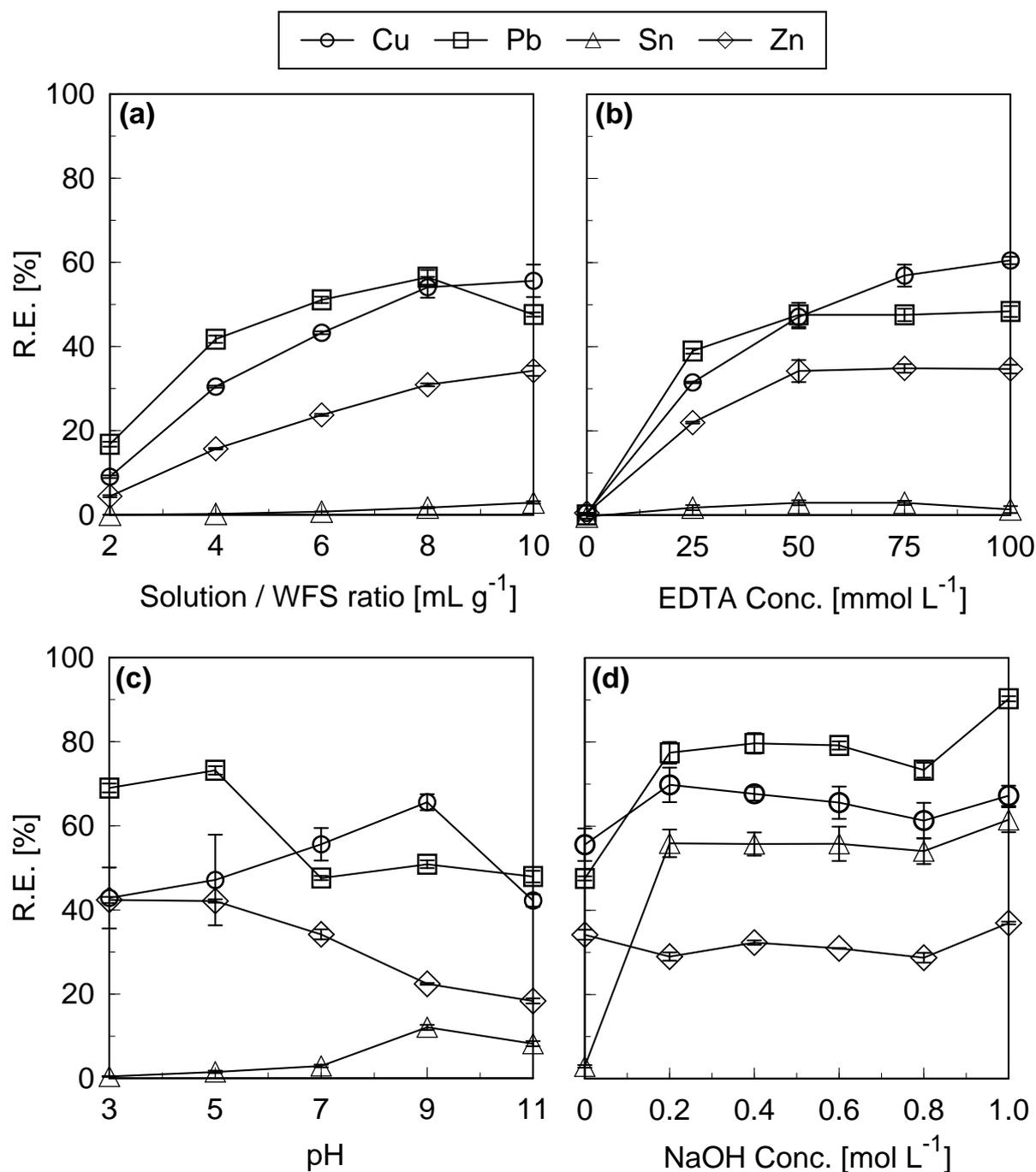
Figure 3: Removal efficiency of PTEs (%RE; points, mean of a triplicate experiment; bars, SD) from WFS during EDTA-induced treatment. (a) Effect of solution/WFS ratio, C_{EDTA} = 50 mmol L^{-1}, pH = 7. (b) Effect of EDTA concentration, solution/WFS ratio = 10 mL g^{-1}, pH = 7;.(c) Effect of pH, solution/WFS ratio = 10 mL g^{-1}, C_{EDTA} = 50 mmol L^{-1}. (d) Effect of NaOH concentration, solution/WFS ratio = 10 mL g^{-1}, C_{EDTA} = 50 mmol L^{-1}.
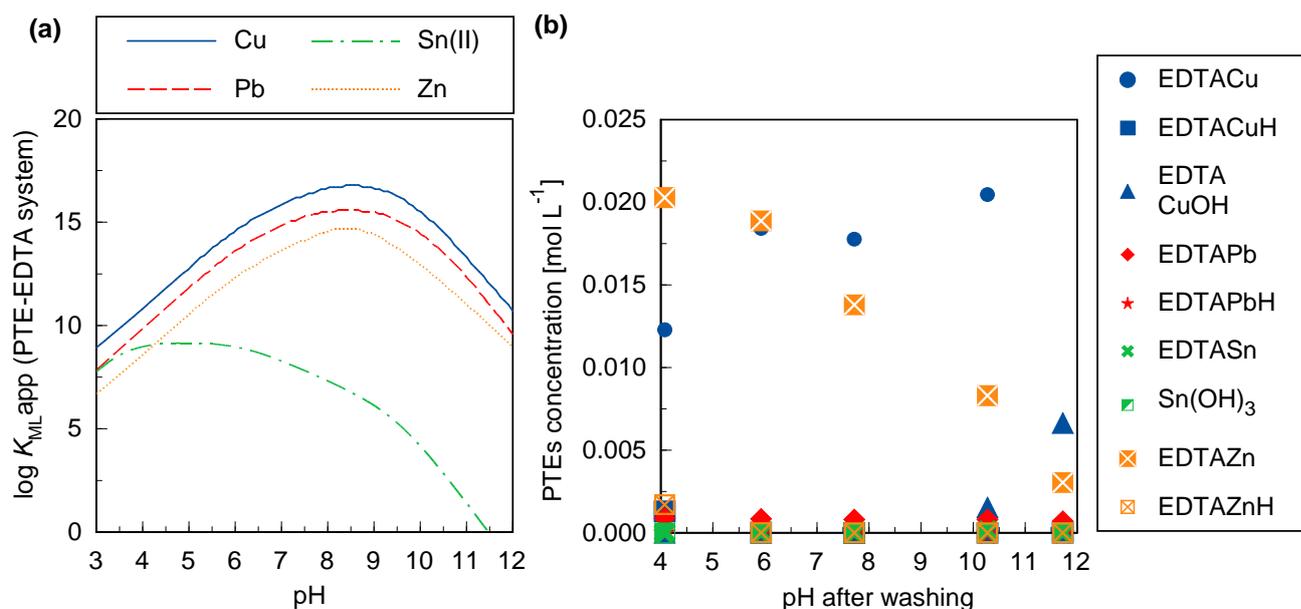
Figure 4: (a) Apparent stability constants (log K_{MLapp}) of the PTE-EDTA complexes at different pH values. The log K_{MLapp} is defined as (log K_{ML} + log K_{MLH} − log K_{MH} − log K_{LH}), K_{ML}: stability constant of PTE-EDTA, K_{MLH}: stability constant of PTE-EDTA-H (or OH) complex, K_{MH}: hydrolysis constant of PTE-OH, K_{LH}: protonation constant of EDTA. (b) Chemical speciation of the PTE-EDTA complexes in the EDTA-spiked washing solution at different pH values, solution/WFS ratio = 10 mL g^{-1}, C_{EDTA} = 50 mmol L^{-1}.
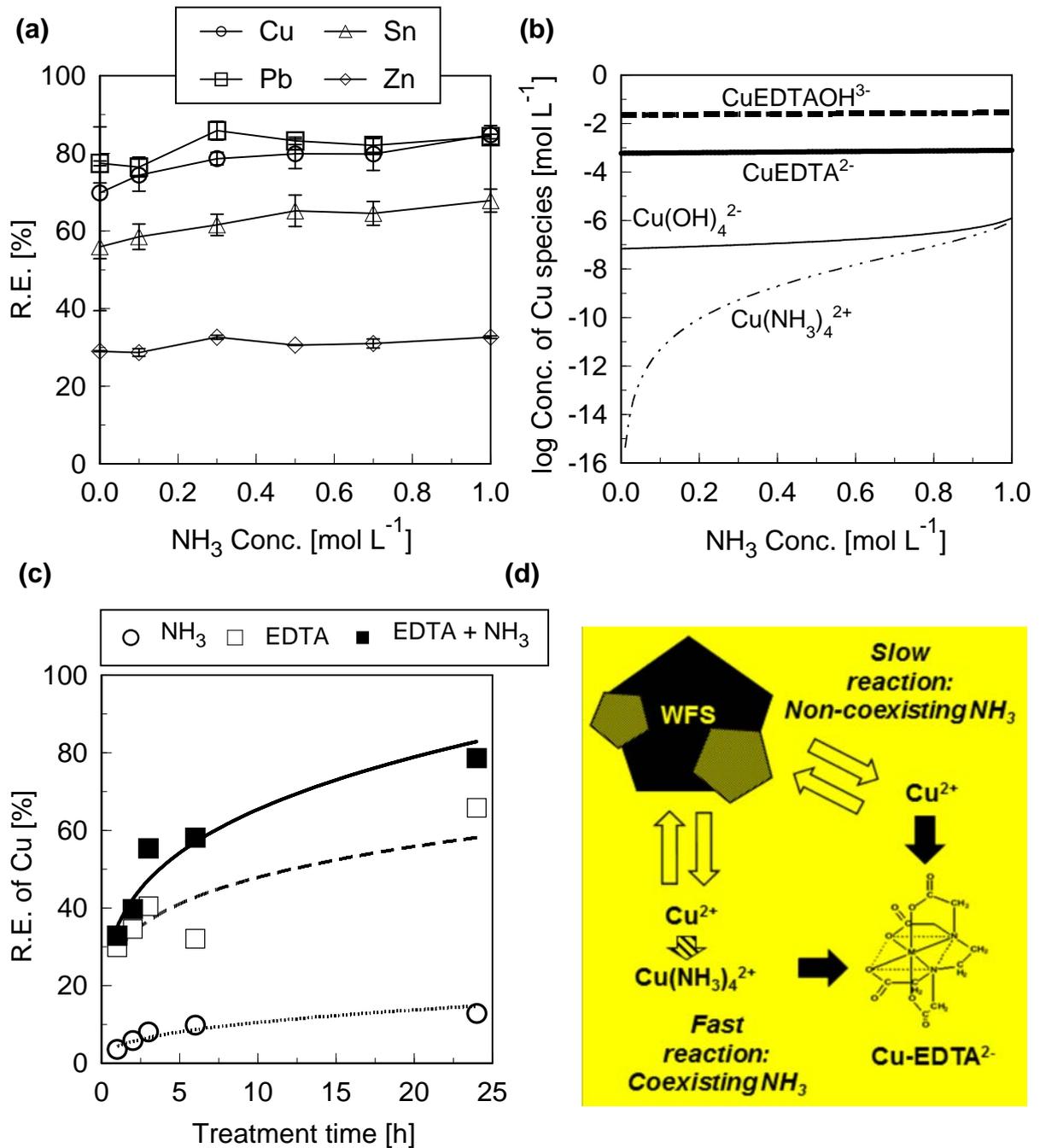
Figure 5: Removal efficiency of PTEs (% RE; points, mean of a triplicate experiment; bars, SD) from WFS during (EDTA + NH$_3$)-induced treatment, C_{EDTA} = 50 mmol L^{-1}, solution/WFS ratio = 10 mL g^{-1}. (a) Effect of NH$_3$ concentration, C_{NaOH} = 0.2 mol L^{-1}. (b) Simulation of Cu speciation in the washing solution. (c) Rate of Cu removal during EDTA-assisted washing treatment without or with NH$_3$ in the solution: C_{EDTA} = 50 mmol L^{-1}, C_{NaOH} = 0.2 mol L^{-1}, Conc. of NH$_3$ = 0.3 mol L^{-1}. (d) Mechanism of enhanced Cu removal with the addition of NH$_3$ to the solution (schematic view).
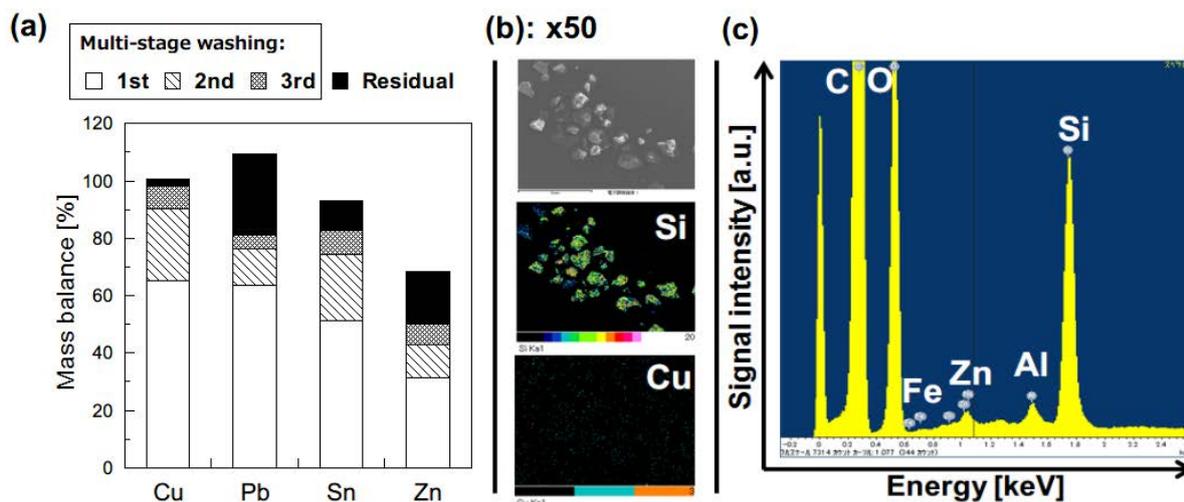
Figure 6: Effect of the multi-stage washing treatment. (a) Mass balance of PTEs during the multi-stage washing treatment under the optimum operation conditions; extractant, EDTA (50 mmol L^{-1}) + NaOH (0.2 mol L^{-1}) + NH$_3$ (0.3 mol L^{-1}); Washing solution/WFS ratio, 100 mL/10 g; Treatment time, 3 h per cycle. (b) Mapping images of solvent-treated WFS. (c) X-ray fluorescence spectrum on the area in (b). The signal corresponding to carbon was due to the carbon tape used as a background material.
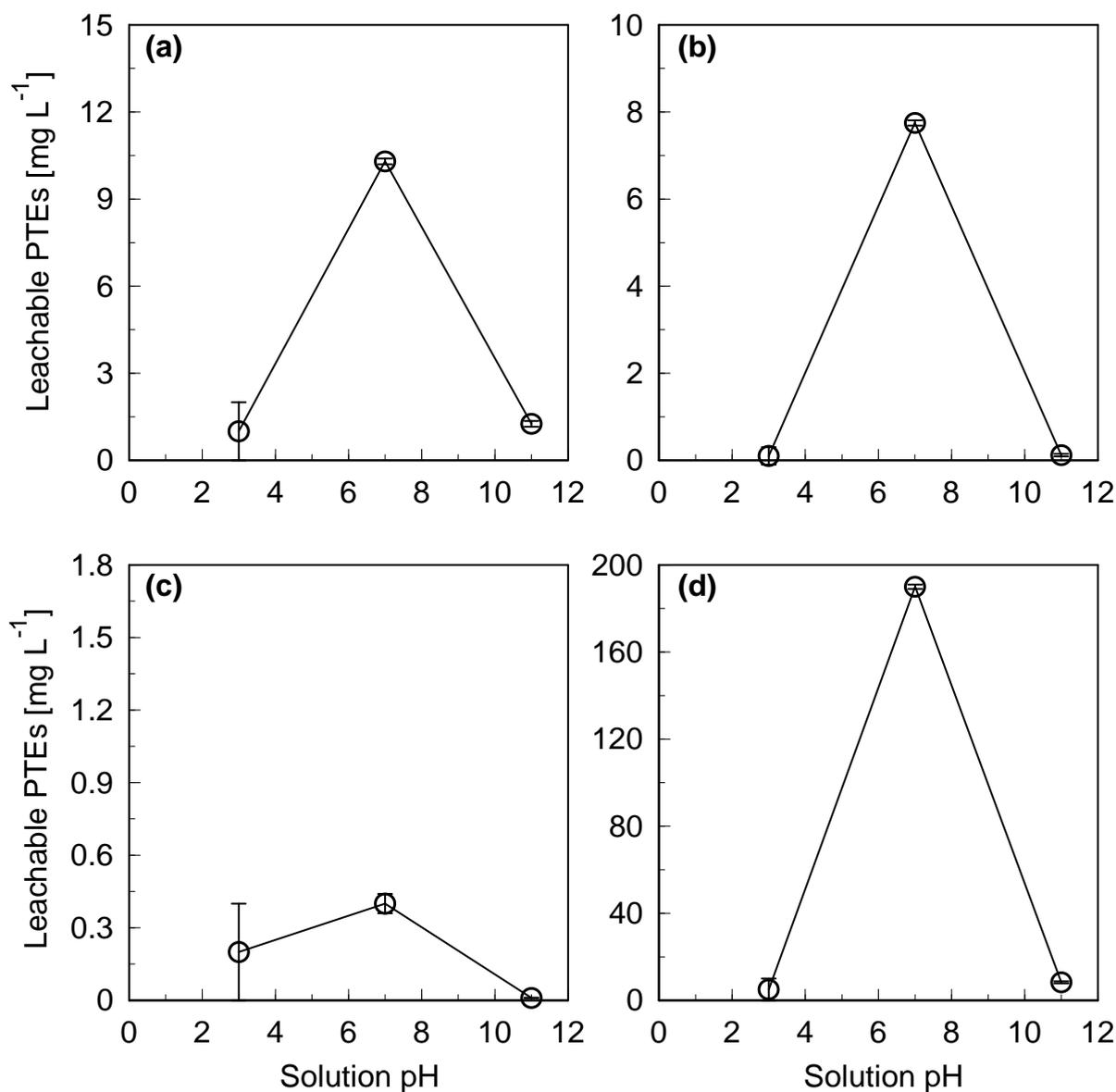
Figure 7: Effect of the rinsing solution pH (solvent: purified water) used to test leaching of PTEs from the EDTA-NaOH-NH$_3$ washed WFS: (a) Cu, (b) Pb, (c) Sn, and (d) Zn (points, mean of a triplicate experiment; bars, SD).

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