Water Science & Technology

Water Science & Technology Vol 88 No 6, 1594 doi: 10.2166/wst.2023.289

Effect of ultrasound-assisted EDTA and citric acid washing on heavy metal removal, residual heavy metal mobility, and sewage sludge quality

Hongpei Lu[a], Yonggui Wu[a,b,c,*], Youfa Luo[b,c,d], Ziran Li[a], Ziqi Wang[a], Xiaoyu Peng[a] and Yibin Qiang[a]

[a] College of Resource and Environmental Engineering, Guizhou University, Guiyang 550025, China
[b] Guizhou Kast Environmental Ecosystem Observation and Research Station, Ministry of Education, Guiyang 550025, China
[c] Guizhou Hostile Environment Ecological Restoration Technology Engineering Research Centre, Guizhou University, Guiyang 550025, China
[d] Key Laboratory of Kast Georesources and Environment, Ministry of Education, Guizhou University, Guiyang 550025, China
*Corresponding author. E-mail: ygwu72@126.com

ABSTRACT

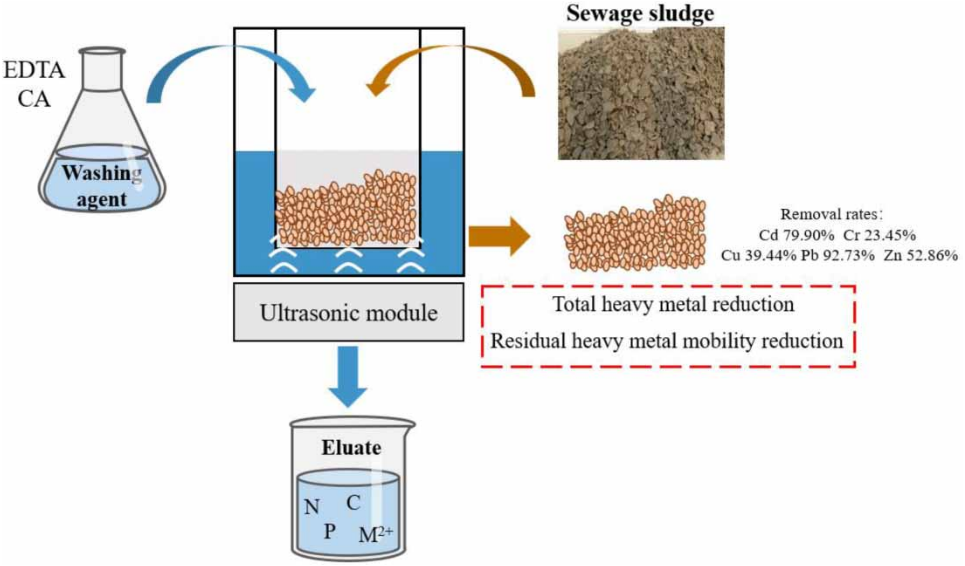
We investigated the effects of ultrasound-assisted ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) washing on heavy metal (HM) removal, residual HM mobility, and sewage sludge quality. EDTA and CA washing of sewage sludge successfully reduced the total concentration of HMs after one round of washing, but the mobility of residual HMs increased significantly. The eluate had a high concentration of HMs and nutrients (nitrogen, phosphorus, potassium, and total organic carbon), although the nutritional content of the sludge remained high. The three-phase ratio of the sludge after six rounds of washing by CA was closest to the ideal three-phase ratio, and the degree of influence on the physical structure of the soil after a land application was reduced, according to the fluctuation of generalized soil structure index (GSSI) and soil three-phase structure distance (STPSD) values. The results indicate that CA as an environmental-friendly washing agent can be the superior choice for sludge HM washing; single washing of sewage sludge may increase the mobility of residual HMs, so multiple washings should be considered for land application of sludge.

Key words: citric acid, ethylenediaminetetraacetic acid, heavy metals, sewage sludge washing, sludge quality, ultrasound

HIGHLIGHTS

- Ultrasound-assisted chemical washing is a useful and efficient solution to remove HMs from sewage sludge.
- The higher concentration ($\geq$0.4 M) of biodegradable CA eluent could effectively reduce HMs in the sewage sludge compared to the traditional non-biodegradable EDTA eluent.

GRAPHICAL ABSTRACT



1. INTRODUCTION

The management and disposal of sewage sludge is one of the most complicated tasks for wastewater treatment plants. Each stage of the sewage treatment process produces sludge, and current sludge disposal methods and utilization technologies are unable to efficiently consume large quantities of sludge, causing a huge buildup of sewage sludge. Currently, sewage sludge disposal methods include land application, disposal in landfills, incineration, and the creation of building materials (Alvarenga *et al.* 2015). To examine and dispose of sewage sludge appropriately while the conventional landfill approach is being phased out, a new mindset is urgently required (Kelessidis & Stasinakis 2012). Given that sludge contains a large amount of nutrients, the application of fertilizers in barren soil can be greatly reduced by land application of sludge (Seleiman *et al.* 2013; Hoang *et al.* 2022). The nitrogen (N) content of sewage sludge is reported to be about 4% of the dry matter (DM), while the total phosphorus (P) content is about 2% of the DM (EPA 1994). Between 15 and 85% of this, N is available to plants, while approximately 50% of P is usually available to plants (Gilbert *et al.* 2011). The toxic and detrimental components of sewage sludge, however, restrict its use in agriculture. Among all kinds of pollutants in sewage sludge, heavy metals (HMs) are particularly prominent because of their toxicity, in-degradability, portability, and accumulation in the environment and in living organisms (Rutgersson *et al.* 2020; Zhang *et al.* 2022). Hence, the development of a technology that not only quickly and effectively reduces HMs in sludge but also maintains sludge nutrients will greatly contribute to appropriate land application of sludge.

Chemical washing is one of the few permanent treatment options for removing HMs from sewage sludge (Zhang *et al.* 2018; Klik *et al.* 2021). Traditional chemical washing technology involves thorough mixing and scrubbing of sewage sludge particles with eluents. Mechanical mixing is a key step in the chemical washing of HMs. Several studies have investigated the use of ultrasound for the removal of HMs in sewage sludge washing procedures. Ultrasound has several benefits in terms of increased effectiveness in removing HMs, operation time, energy use, and washing fluid use (Son *et al.* 2012; Park & Son 2017; Choi *et al.* 2021). Due to powerful desorption at macroscopic and microscopic scales, the ultrasound washing procedure has a reasonably high removal rate for pollutants in particle pores as well as those on the surface of sewage sludge particles (Son *et al.* 2011; Wang *et al.* 2015).

Washing agents, which are crucial components of chemical washing, have been widely employed to remove HMs from sewage sludge. These include chelation agents, surfactants, organic acids, and inorganic acids (Kuan *et al.* 2010; Tang *et al.* 2018; Yang *et al.* 2021). A representative substance in washing agents, ethylenediaminetetraacetic acid (EDTA), can create solid, water-soluble complexes with alkali metals, rare earth elements, and transition metals. However, EDTA has low biodegradability in the natural environment, and only a few bacterial isolates could degrade EDTA on a laboratory scale (Bloem *et al.* 2017; Freitas & Nascimento 2017). EDTA pollutes the environment mainly through wastewater generation; the average concentration of EDTA detected in groundwater, lakes, and river water was 2–100 μg/L, and it has become a prevalent anthropogenic compound in water samples (Kari & Giger 1995; Oviedo & Rodríguez 2003; Al Sakkaf *et al.* 2021). It is thus critical and urgent to develop a washing agent that not only effectively removes HMs from sludge but is also biodegradable and environmentally friendly. Citric acid (CA), both an organic acid and a chelation agent, has been extensively explored in HM washing because it is biodegradable and does not cause secondary pollution (Kong *et al.* 2013; Bao *et al.* 2019). Ke *et al.* (2020) found that the removal efficiency of HMs was 89.1% for cadmium (Cd), 26.8% for lead (Pb), 41.7% for zinc (Zn), and 14.2% for copper (Cu) in smelter soil when 2.5 L CA (0.1 M and pH 5) solution was leached in five batches. Moreover, washing Pb-contaminated soil with a low concentration (0.01 M) of CA modified with potassium chloride resulted in a maximum Pb removal of 77.6 ± 3.4% (Etim 2019).

In addition, rather than focusing exclusively on total metal content, the mobility and bioavailability of HMs before and after washing procedures are widely used to evaluate remediation efficacy (Guo *et al.* 2018; Hazrati *et al.* 2020). However, it is noteworthy that increased mobility and plant utilization of the remaining HMs in EDTA- or CA-washed soils has been demonstrated (Lei *et al.* 2008; Zhang *et al.* 2010; Wang *et al.* 2017; Hazrati *et al.* 2020). At the same time, the successful removal of HMs resulted in a substantial relative increase in total and exchangeable nutrients (nitrogen – N; phosphorus – P; potassium – K) in sewage sludge. The magnitude of these modifications was determined by the washing agent used and the washing procedure (Wang *et al.* 2016). As a result, trade-offs between the decrease in overall metal content, rise in metal mobility, and loss of nutrients during ultrasound-assisted EDTA and CA washing of sewage sludge pose novel issues for remediation design.

We thus aimed to comprehensively evaluate the effect of using eluent (EDTA and CA) and ultrasound-assisted washing on HM removal and residual HM mobility in sewage sludge. In addition, the quality of washed sewage sludge (pH, organic matter – OM; available P – AP; available K – AK; alkali N – AN) was evaluated, and the nutrient contents in the eluate measured. We further refined the procedure for ultrasound-assisted washing of HMs from sewage sludge.

2. MATERIALS AND METHODS

2.1. Sewage sludge sampling

Samples of sewage sludge were collected from a municipal sewage treatment plant using the sequencing batch reactor-activated sludge method, which is located in Guiyang, Guizhou, China. Following collection, the sewage sludge was freeze-dried until it reached a constant weight. Prior to use, all samples were evenly mixed and passed through a standard 100-mesh sieve. The physicochemical characteristics of the sewage sludge are shown in Table 1.

2.2. Experimental methods

2.2.1. First-round washing of Cd, Cr, Cu, Pb, and Zn from the sewage sludge using CA and EDTA

Various solution concentrations, ultrasound times, and washing agents (including CA and EDTA) were used for the experiments. A solid–liquid ratio of 1:4 (g:mL), an ultrasound time between 2 and 90 min, and a CA concentration between 0.1 and 0.6 M or an EDTA concentration between 0.05 and 0.3 M were used. We employed an ultrasound system with 600 W of power and a 40-kHz ultrasound transducer module. To maintain a constant operating temperature, the reservoir was filled with 2 L of tap water and the water was replaced, since the temperature in the reservoir was slightly increased (5–7 °C) when the ultrasound was running. All washings were performed in 50 mL centrifuge tubes at room temperature (25 °C). The mixture was then washed by centrifugation at 4,000 × *g* for 10 min and filtered (0.45 μm).

2.2.2. Continuous washing of Cd, Cr, Cu, Pb, and Zn from the sewage sludge using CA and EDTA

After determining the optimal washing parameters from the first-round washing experiment, the sewage sludge was subjected to eight continuous washings. We employed washing in a solid–liquid ratio of 1:4, an ultrasound time of 30 min, and a CA concentration of 0.4 M or an EDTA concentration of 0.2 M. All washings were performed in 50-mL centrifuge tubes at room temperature (25 °C). The ultrasound system parameters were consistent with those of the first-round washing experiment. The eluents were made up to the same initial scale after each washing. The mixture was then washed by centrifugation at 4,000 × g for 10 min and filtered (0.45 μm).

2.3. Analytical methods

2.3.1. Determination of pH, nutrient content and three-phase ratio of sewage sludge

The pH values of the sewage sludge were measured at a solid–liquid ratio of 1:5 using a pH meter. Organic matter was determined by the Tyurin method. Alkali N was determined using the alkaline diffusion method. Available P was determined using the anti-spectrophotometric sodium hydrogen carbonate–Mo–Sb solution method. Available K was determined using flame photometry. The three-phase ratio of the sewage sludge was determined using soil three-phase tester.

2.3.2. Determination of HMs in sewage sludge

The total metal concentration was determined using acid digestion ($HCl/HF/HNO_3/HClO_4$) followed by coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 7000 Series ICP Spectrometer, USA). HM was extracted sequentially using the modified BCR-sequencing extraction method (Zhang *et al.* 2017). In short, four operationally defined

Table 1 | Physicochemical characteristics of the sewage sludge

Characteristic	Unit		Characteristic	Unit	
pH	/	7.18 ± 0.19	Cr	mg/kg	72.65 ± 1.39
OM	%	18.47 ± 0.31	Cd	mg/kg	0.68 ± 0.04
AP	mg/kg	219.50 ± 41.55	Zn	mg/kg	379.50 ± 4.53
AK	mg/kg	1,693.00 ± 23.07	Cu	mg/kg	73.02 ± 3.15
AN	mg/kg	1,340.50 ± 4.95	Pb	mg/kg	17.76 ± 0.76

fractions were extracted sequentially: acid exchangeable (F1, 0.11 M HAc), readily reducible (F2, 0.5 M $NH_4OH{\cdot}HCl$, pH 2.0), oxidizable (F3, 8.8 M $H_2O_2 + 1.0$ M NH_4Ac, pH 2.0), and residual fractions (F4, HCl, HNO_3, $HClO_4$, and HF).

2.3.3. Determination of nutrient contents in eluate

Total K was determined using flame atomic absorption spectrophotometry. Nitrate N was determined using UV spectrophotometry. Ammonia N was determined spectrophotometrically using Nessler's reagent. Total P was determined spectrophotometrically using ammonium molybdate. Total organic carbon (TOC) content was determined using a TOC analyser (Shanghai METSH, TOC-2000).

2.4. Data analysis

The total Cd, Cr, Cu, Pb, and Zn removal (in %) was calculated using the following equation (Zhong *et al.* 2021):

$$R_T = \frac{C_{\text{solution}} \times V}{m \times C_T} \times 100\%$$

where R_T refers to the removal efficiency of total HM, C_{solution} refers to the metal concentration in the eluate (mg/L), V refers to the eluate volume (L), m refers to the sewage sludge weight (kg), and C_T refers to the total HM concentration in the sewage sludge (mg/kg). The results of each experiment were derived and analyzed for mean and standard deviation using the above equation.

2.5. Quality assurance and statistical analysis

All experiments were repeated three times. All tubes and glassware were soaked in either dilute HNO_3 (10%) or H_2SO_4 (10%) overnight prior to the start of each experiment and rinsed with deionized water. Average values of the results are presented with error bars. Standard reference material for soil composition analysis (GBW07404 (GSS-4) was used for quality control. Matrix spikes were tested for each batch of samples, and recoveries of HMs were all within 80–120%. BCR SEP recoveries were within 85–105% via comparison of the sum of the four fractions with total metal concentration. Statistical analysis of the data was performed using SPSS 22.0 software (SPSS Inc., Chicago, IL, USA). The experimental results were presented as mean ± standard deviation (SD). Least significant difference tests were used to separate means where ANOVA showed significance at $P < 0.05$.

3. RESULTS AND DISCUSSION

3.1. Effects of washing agent concentration and ultrasound time on HM washing

Sewage sludge is a biosolid composed of a diverse range of microbial communities and adsorbed organic or inorganic materials. One goal of sewage sludge washing is to permanently and significantly reduce the amount, toxicity, or mobility of contaminants. As shown in Figure 1, 0.05 M of EDTA had a good effect on the removal of Pb, with a maximum removal of 53.87%, whereas the removal of Cd, Cr, Cu, and Zn was poor, with percentages below 30.00% (Figure 1(a)). Treatment with 0.1 M CA had almost no effect on the removal of the target HMs at lower concentrations, with a removal below 10% (Figure 1(e)). When the ultrasound time was longer than 10 min, the removal of target HMs increased significantly with increasing CA and EDTA concentrations. The best removal of Cd, Cr, Cu, Pb, and Zn by EDTA was 30.00, 2.12, 18.18, 64.14, and 27.43%, respectively (Figure 1(d)), and the best removal of Cd, Cr, Cu, Pb, and Zn by CA was 14.71, 26.42, 1.10, 40.84, and 31.02%, respectively (Figure 1(h)).

The role of CA (both chelating agent and weak acid) in the removal of HMs may be the result of two mechanisms: acid dissolution and metal complexation. On the one hand, only HMs that form more stable complexes with the chelator than with functional groups in the sewage sludge can be washed out (Wang *et al.* 2015); on the other hand, H^+ ions can compete with HM ions for adsorption sites and affect the adsorption of HMs, thus promoting the desorption of HM ions from the sewage sludge (Zhai *et al.* 2018). At lower concentrations, CA forms complexes with HMs to chelate them from the sewage sludge. With increasing CA concentrations, HMs were gradually removed due to acid dissolution and HM chelation. Therefore, HM removal via organic acids is not only due to their acidity but also due to their chelating properties. EDTA is a strong chelator, and its mechanism in HM washing is similar to that of conventional chelators.

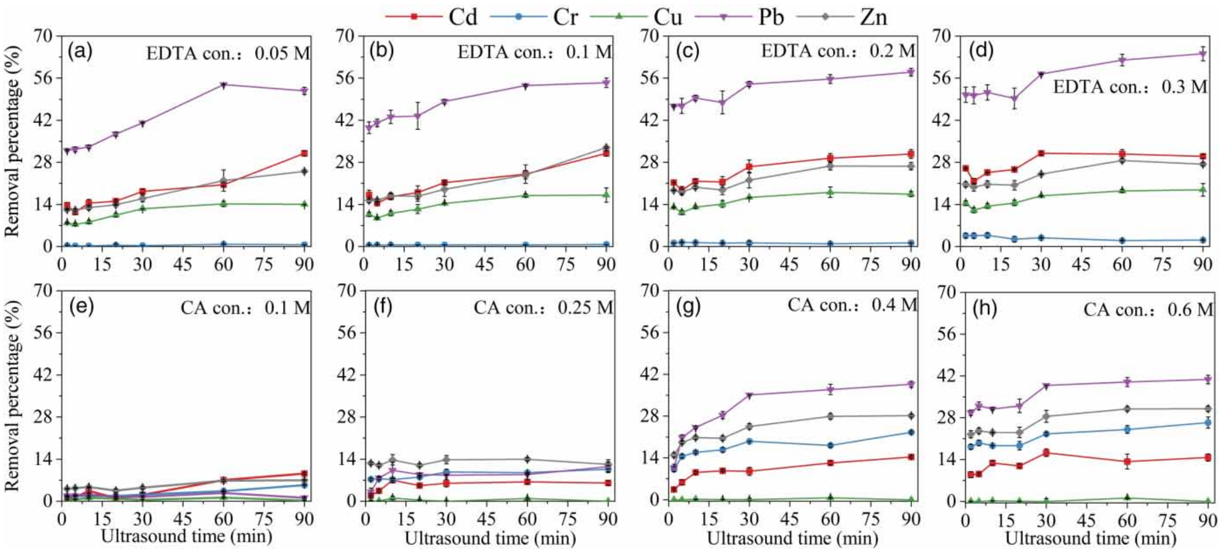


Figure 1 | Effects of EDTA concentration, CA concentration, and ultrasound time on the removal of Cd, Cr, Cu, Pb, and Zn.

In this study, the ultrasound-assisted HM washing experiments using CA and EDTA yielded the following sequence of HM removal efficiencies:

$$\text{CA: Pb} > \text{Zn} > \text{Cr} > \text{Cd} > \text{Cu} \quad (1)$$

$$\text{EDTA: Pb} > \text{Cd} > \text{Zn} > \text{Cu} > \text{Cr} \quad (2)$$

CA and EDTA were both efficient in Pb removal, as shown by Equations (1) and (2). CA washing, however, did not completely remove Cd and Cu from the sewage sludge. This indicates that these HMs were present as very strong adsorption cations and formed more stable complexes with biosolids as compared to CA. The same was true for Cu and Cr washing with EDTA. However, when compared to CA, EDTA was more efficient in removing Pb at low concentrations (e.g., <0.1 M, Pb removal $>31\%$). The removal of Cd, Cr, Cu, and Zn did not increase significantly with increasing EDTA concentration ($P > 0.05$), similar to the patterns observed for CA. This could be due to the co-solubilization effect of target HMs and co-existing metals (Fe, Ca, Mg, and Mn) (Wu *et al.* 2015).

It is worth noting that the percentage of removed HMs increased with increasing ultrasound time and tended to stabilize after a while. A previous study reported entrapment of dissolved gas molecules in pores during ultrasound-assisted washing, which enhanced the micro-scale contact of the washing liquid in the interior of sewage sludge particles (Choi *et al.* 2021). The acoustic-physical effects of ultrasound (including micro-jets and shock waves) may also break particles into smaller ones with a larger surface area (Son *et al.* 2012). However, it has been reported that pollutants that are strongly bonded to soil particles via trenching in pores could hardly be desorbed by mechanical mixing alone (Son *et al.* 2011). This may also pertain to sewage sludge. When compared to traditional mechanical mixing, however, ultrasound-assisted washing was 7–10 times faster and more energy efficient (Zhang *et al.* 2017; Kou *et al.* 2020). This could save time, reduce energy consumption, and improve HM removal efficiency from sewage sludge in a short period of time.

3.2. Effects of ultrasound-assisted washing on the chemical fractionation of Cd, Cr, Cu, and Zn in sewage sludge

The washing agent-induced washing process altered the chemical forms in the sewage sludge (Figure 2). Before washing, Cr, Cu, Pb, and Zn were mainly present in the more stable fractions (F3 and F4), while Cd was mainly present in the readily reducible fraction (F2). The mobile fractions of the target HMs increased to varying degrees after washing with EDTA and CA. Notably, the removal of target HMs by the two eluents was proportional to the ratio of the mobile fraction (F1) in these HMs. For example, the percentage of the mobile fraction of Pb after washing with 0.3 M EDTA and an ultrasound time of 30 min was 68%, while the removal was 57%. Moreover, the percentage of the mobile fraction of Pb after washing with

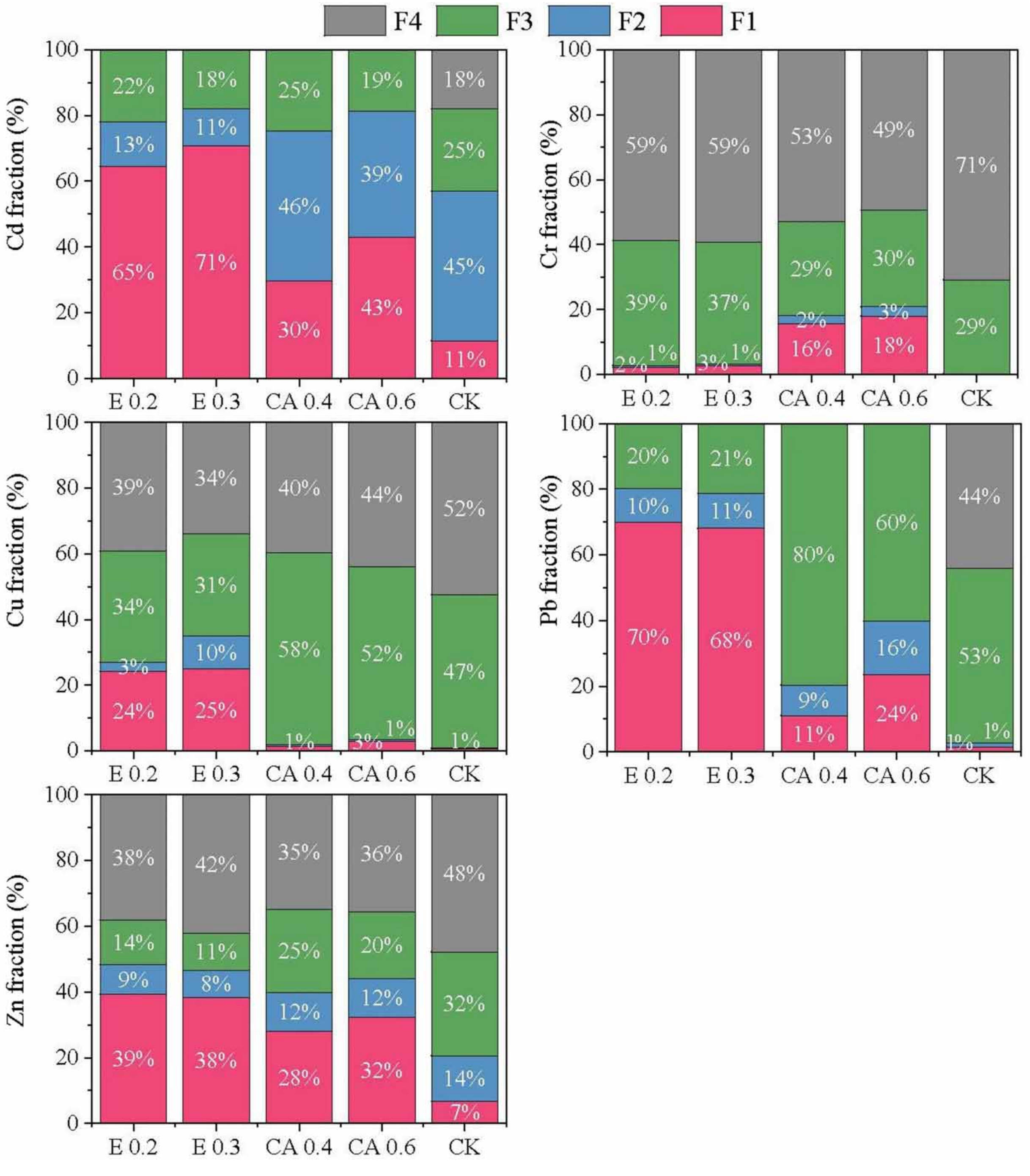


Figure 2 | Fractions of Cd, Cr, Cu, Pb, and Zn in unshed sewage sludge (CK) and sewage sludge washed with EDTA or CA (0.2, 0.3 or 0.4, 0.6 M, respectively) for 30 min assisted with ultrasound.

0.6 M CA and an ultrasound time of 30 min was 24%, and the removal percentage was 39%. As mentioned above, this indicates that CA and EDTA can almost completely release Pb from the sewage sludge biosolid. Furthermore, the washing agents removed unstable HMs from sewage sludge and interfered with the chemical equilibrium of the remaining HMs. To maintain equilibrium, residual HMs are frequently converted to more unstable forms (Udovic & Lestan 2009). CA and EDTA washing had little effect on the mobile fraction of Cr and Cu. This indicates that Cr and Cu form more stable complexes with biosolid functional groups or exist as poorly soluble inorganic precipitates.

The first round of ultrasound-assisted washing for 30 min significantly reduced the total amount of HMs (Figure 2) but could not reduce environmental risks because the sewage sludge contained more HMs in the mobile fraction (Beiyuan *et al.* 2018). Continuous washing could be used to reduce HM bioavailability.

3.3. Effects of continuous washing on HMs in sewage sludge

Based on the results for the different concentrations of washing solutions, the ultrasound time, and washing costs for the removal of HMs from sewage sludge, we further investigated the effect of continuous washing. We chose CA (0.4 M), EDTA (0.2 M), and an ultrasound time of 30 min for continuous washing. The removal of HMs gradually increased as the number of washings increased, while the rate of increase gradually decreased. After the sixth round of washing, the removal of the target HMs tended to be stable (Figure 3). After six rounds of CA washing, the cumulative removal for Cd, Cr, Cu, Pb, and Zn was 66.18, 30.22, 9.59, 70.89, and 50.38%, respectively. EDTA also demonstrated a good effect after six washing cycles, with a cumulative removal of 79.90, 23.45, 39.44, 92.73, and 52.86% for Cd, Cr, Cu, Pb, and Zn, respectively. However, CA washing removed less Pb and Cd than EDTA washing, particularly for Pb. The differences in Pb removal were likely associated with the stability constants of $R-Pb^{2+}(COOH)_m$ (log $K = 12.30$) and $EDTA-Pb^{2+}$ (log $K = 17.90$). Yet, the stability constants of metal chelators are not the only factor in the extraction of HMs from sewage sludge (Beiyuan *et al.* 2018). For example, although the stability constants of $R\text{-}Cu^{2+}(COOH)_m$ (log $K = 18.00$) and $EDTA-Cu^{2+}$ (log $K = 18.80$) were similar, compared to EDTA, CA had almost no ability to remove Cu in this study. A number of previous studies have demonstrated that a variety of factors can influence HM removal, such as washing agent properties, sewage sludge characteristics (e.g., HM morphology, OM content, and properties), and operating parameters (e.g., washing time, solid-to-liquid ratio, solution pH, and temperature) (Ke *et al.* 2020; Klik *et al.* 2021; Zhu *et al.* 2021). In general, CA and EDTA have distinct advantages in removing various HMs from sewage sludge, while CA is a better alternative to EDTA in terms of environmental friendliness.

3.4. Effect of the washing process on sewage sludge nutrients

Washing affected the quality of sewage sludge (pH, OM, AP, AK, and AN), but the magnitude and direction of quality changes depended on the washing agents used (Table 2). Because the washing agents were acidic, the pH in the sewage sludge was significantly lower ($P < 0.05$) after six rounds of washing (the pH decreased by 1.52, on average, after washing with EDTA; and by 4.2 after washing with CA) as compared to the original sludge. The OM content of sewage sludge increased significantly ($P < 0.05$) after six rounds of washing; unwashed sewage sludge had an OM content of 18.47%, which increased by 4.64% after washing with EDTA and by 8.1% after washing with CA. In a previous study, Wang *et al.* (2015) also observed

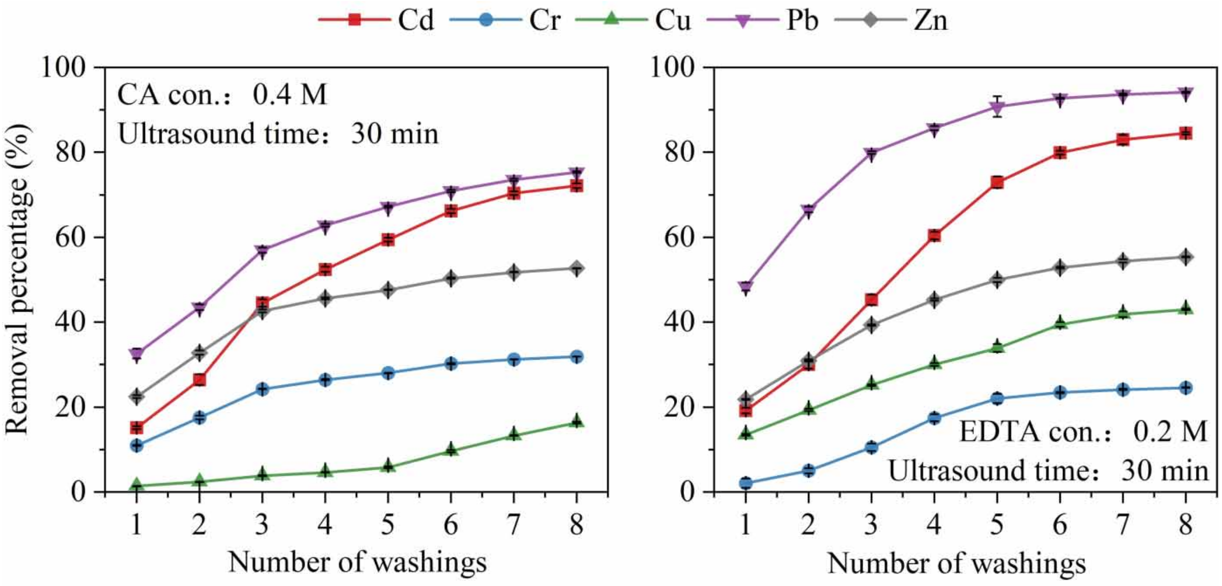


Figure 3 | Removal of HMs by continuous washing with 0.4 M CA and 0.2 M EDTA with an ultrasound time of 30 min.

Table 2 | Comparison of the quality of washed and unwashed sewage sludge (CK) after six rounds of ultrasound-assisted washing for 30 min with 0.2 M EDTA and 0.4 M CA (standard deviation from the mean value, $n = 3$)

	pH	OM (%)	AP (mg/kg)	AK (mg/kg)	AN (mg/kg)
CK	7.18 ± 0.19a	18.47 ± 0.31a	219.50 ± 41.55a	1,693.00 ± 23.07a	1,340.50 ± 4.95a
EDTA	5.66 ± 0.10b	23.11 ± 1.25b	177.40 ± 42.74a	136.20 ± 8.17b	882.00 ± 9.90c
CA	2.98 ± 0.09b	26.57 ± 0.68c	44.54 ± 3.10b	105.30 ± 4.27c	1,207.50 ± 4.95b

Different letters indicate significant differences in nutrient content in unwashed and washed sewage sludge ($P < 0.05$).

an increase in OM after CA washing, which could be attributed to changes in sludge structure and residual CA as a possible source of OM. However, Ren *et al.* (2015) found that EDTA washing resulted in a decrease in the OM content, which is contrary to the results of the present study.

The nutrient content required for plant growth needs to be considered in addition to pH and OM when applying sewage sludge to land. We found that the contents of AN and AK were significantly lower ($P < 0.05$) after six rounds of EDTA and CA washing as compared to the untreated sludge; yet, the effect of EDTA washing on the AP content was smaller. It has to be noted that many factors (e.g., pH, redox potential, washing) can affect the removal of N, P, and K from sludge, from which the pH (CA treatment pH between 1.5 and 2.5 and EDTA treatment pH between 5.0 and 6.0) was likely the most important factor that affected the dissolution and conversion of sludge AN, AP, and AK in the present study (Ren *et al.* 2015).

3.5. Effect of the washing process on three-phase ratio of sewage sludge

The three-phase ratio is usually the ratio of the volumes of solid, gas, and liquid phases in the soil, which constitute the whole soil body, and is an important indicator of the looseness of the soil structure. In this paper, the effect of washing process on the physical properties of municipal sludge is judged by the three-phase ratio, mainly considering that the change of physical and chemical properties of sludge after washing process will affect the effect and direction of subsequent land use. If the physical properties of the sludge after washing process are similar to those of the soil, the lower the degree of impact on the physical properties of the soil after its land use, the better the land-use effect.

As can be seen in Figure 4, ultrasound-assisted washing of sewage sludge resulted in a change in the sludge. The change trend is related to the type of washing agents. Before washing process, the sludge three-phase ratio was 40.28:44.96:14.76 (solid:gas:liquid); after one and six rounds of washing by EDTA, the sludge three-phase ratio was 36.02:43.57:20.41 and 31.42:47.13:21.45, respectively; after one and six rounds of washing by CA, the sludge three-phase ratio was 41.30:37.19:21.51 and 42.59:23.86:33.55, respectively.

The generalized soil structure index (GSSI) is a structural change indicator that measures the ratio of solid, gas and liquid phases in the soil. The larger the value, the more desirable the three-phase structure is in that state. Soil three-phase structure distance index (STPSD) is also a measure of the structural change of soil three-phase structure. In contrast to GSSI, the smaller the change in STPSD value, the more desirable the three-phase structure is in that state. These two values can indirectly respond to the trend of washing process on the change of sludge three-phase structure and provide the theoretical basis for the subsequent sludge resource utilization.

The left axis of Figure 5 shows that the GSSI of CK was 82.22. After washing by CA once and six times, the sewage sludge GSSI increased significantly ($P < 0.05$) compared to CK, by 9.24 and 7.66, respectively, but the number of CA washing did not have a significant effect on GSSI. After washing by EDTA once and six times, the sludge GSSI increased significantly ($P < 0.05$) compared to CK, by 5.62 and 3.08, respectively. The right axis in Figure 5 shows that the sludge STPSD decreased more significantly after washing by CA than EDTA chemical elution.

In summary, both ultrasound-assisted chemical washing positively influenced the change of sludge three-phase ratio. In terms of washing agent, the three-phase ratio was closer to the ideal state after CA washing of sewage sludge compared to EDTA. In terms of the number of washing, the number of times CA-washed sewage sludge did not change the three-phase ratio significantly ($P < 0.05$), while the number of times EDTA washed sewage sludge changed the three-phase ratio more significantly ($P < 0.05$).

3.6. Effect of the washing process on the mobility of residual HMs

After single or multiple rounds of ultrasound-assisted washing for 30 min, all washing agents reduced the total content of the target HMs (Figure 3). However, assessing sewage sludge quality solely based on the total HM content is insufficient because

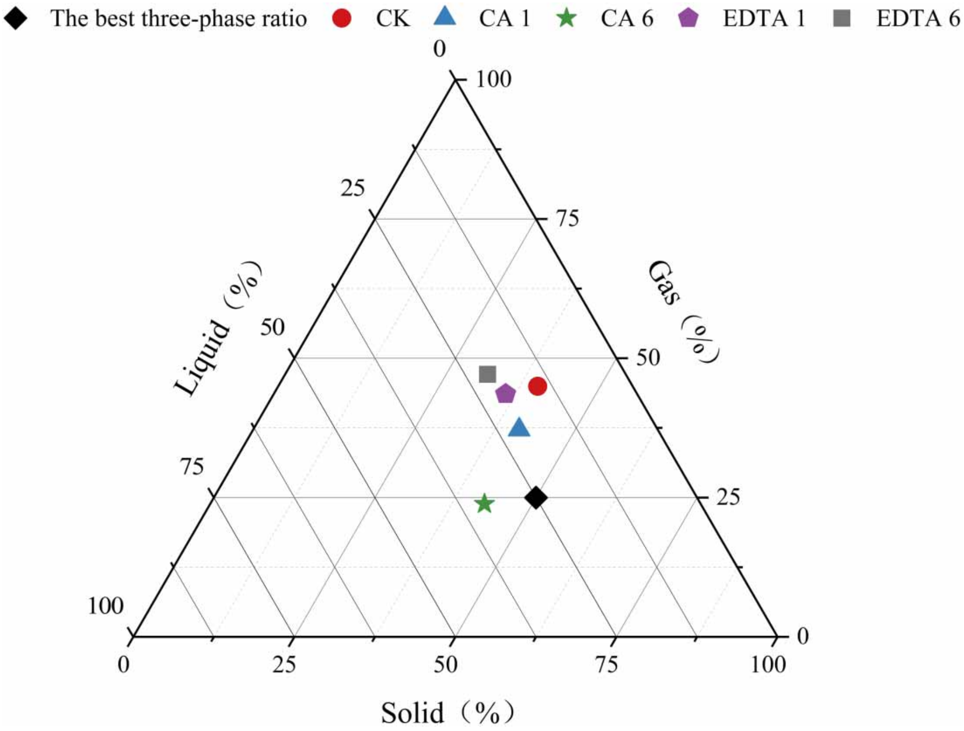


Figure 4 | Effect of ultrasound-assisted washing process on the three-phase ratio of sewage sludge.

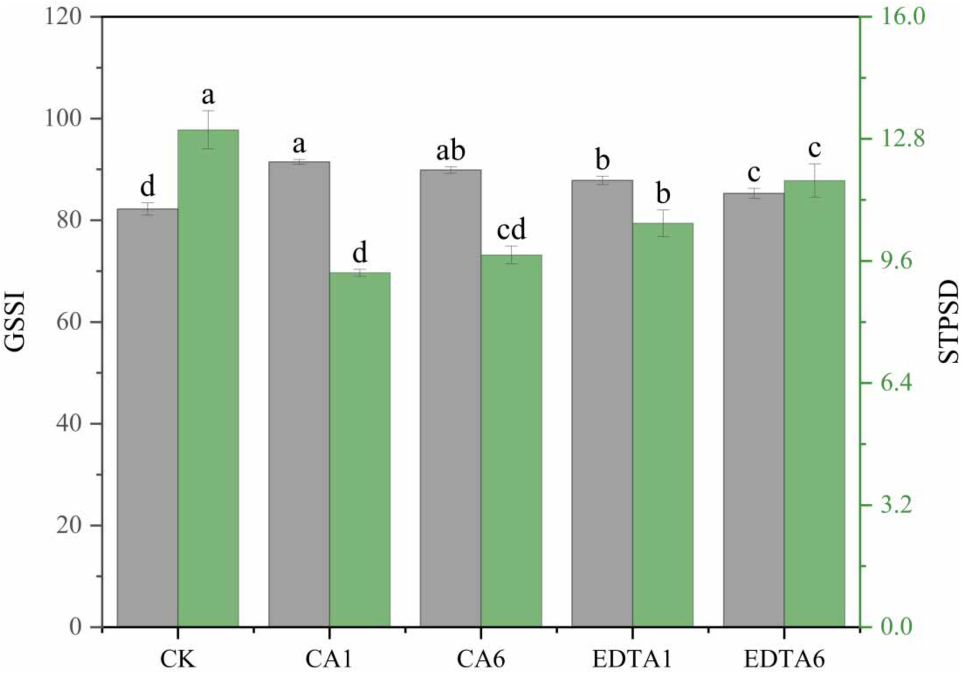


Figure 5 | Trends in the modification of sludge three-phase ratio by ultrasound-assisted washing. Different letters indicate significant differences between the treatment groups ($P < 0.05$).

the mitigation risk of HMs arises from their availability and mobility, not from their total content. In land application of sewage sludge, the HM content of the F1 fraction is a good indicator of HM contamination because the HMs in this fraction have the highest mobility and availability and pose the greatest risk to the environment (Klik *et al.* 2021). In this study, in the case of Cd, Cr, Cu, Pb and Zn, respectively, the respective contents of the HMs in the F1 fraction were 0.08, 0.52, 0.27 and 25.35 mg/kg (Figure 6). However, the contribution of each HM to the F1 fraction increased significantly ($P < 0.05$) after the first round of washing. This is surprising because many studies have found that the F1 content of HM-contaminated soil decreased significantly after the first round of washing (Zhang *et al.* 2017; Wang *et al.* 2018). This finding is an important reference for future sewage sludge HM washing. Besides the washing agents that interfere with the chemical equilibrium of residual HMs, pH is also a major factor affecting the stability of HMs in washed sewage sludge. Under low pH conditions, HMs are easily converted to forms with greater mobility and higher bioactivity (e.g., F1) (Zhai *et al.* 2018). Because the fraction F1 contains the metals which are weakly adsorbed to the solid surface through relatively weak electrostatic interactions, the HM content of the F1 fraction was significantly reduced after six rounds of washing with eluents ($P < 0.05$).

Despite the fact that the total HM content of sewage sludge varied greatly, multiple washings dramatically decreased the HMs in the F1 fraction. Multiple washing appears to be the best method for removing all target HMs and reducing their mobility at the same time.

3.7. Nutrient contents in eluate after continuous washing

Washing of sewage sludge results in nutrient loss. The nutrient content of the eluate was altered by both washing agents, but the magnitude and direction of this alteration were distinct between the two (Figure 7). The K content stabilized after five rounds of washing for both agents, but was 508 mg/L for EDTA and 462 mg/L for CA. The contents of NO_3-N and NH_4-N in the eluate of both washing agents increased slowly after the first round of washing. After continuous washing with CA and EDTA, the TOC content in the eluate gradually increased. The accumulated TOC content in the CA eluate reached 224 g/L, while that in the EDTA eluate reached 175 g/L after eight rounds of washing.

It is worth noting that the P content of the CA eluent was lower than that of the EDTA eluent. After eight rounds of continuous washing, the content of TP in the CA eluate was 114 mg/L, while it was 438 mg/L in the EDTA eluate. This is most

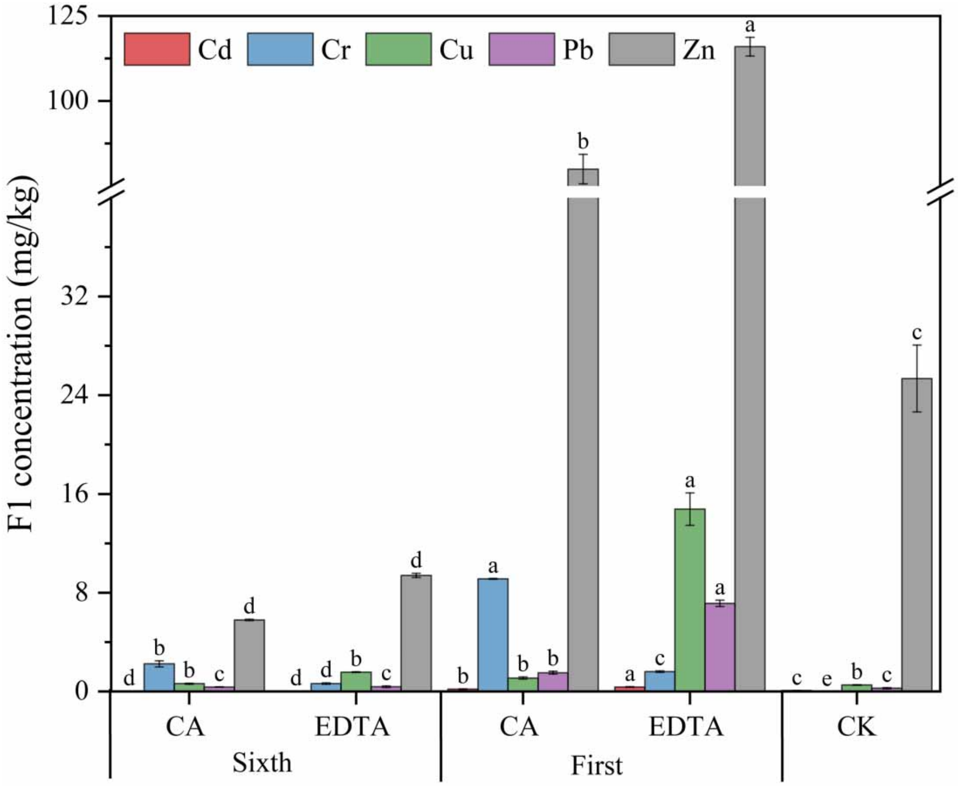


Figure 6 | Changes in the acid exchangeable fraction of HMs in sewage sludge before and after washing with 0.4 M CA and 0.2 M EDTA. CK indicates unwashed sewage sludge, sixth indicates six rounds of ultrasound-assisted washing for 30 min, and first indicates the first round of ultrasound-assisted washing for 30 min. Different letters indicate significant differences in each HM component of F1 in unwashed and washed sewage sludge ($P < 0.05$).

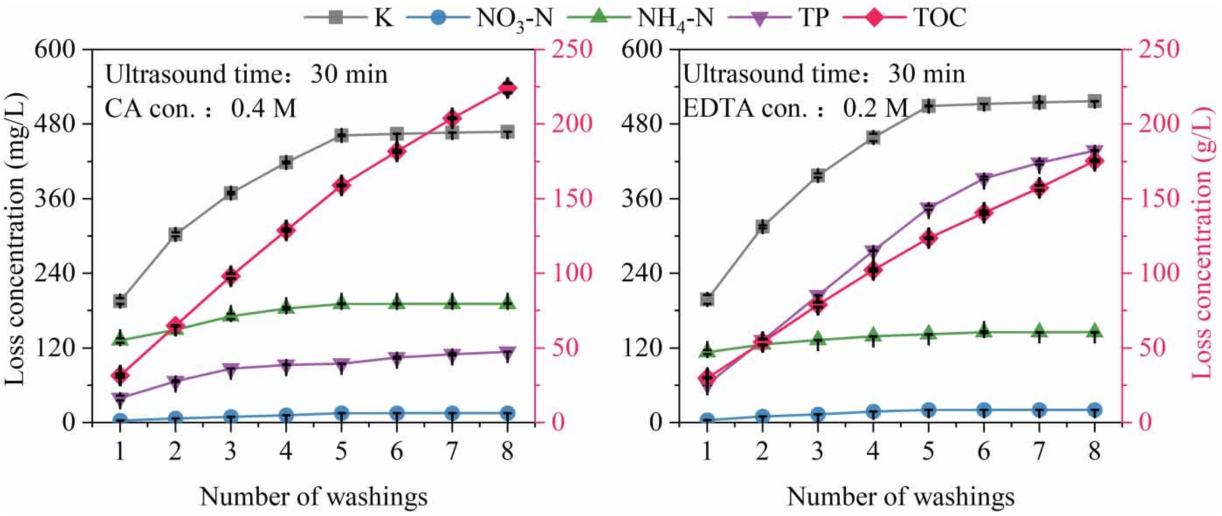


Figure 7 | Nutrient contents in eluate after continuous ultrasound-assisted washing for 30 min by 0.4 M CA and 0.2 M EDTA (the second *y*-axis indicates the TOC content).

likely due to the fact that phosphoric acid is more acidic than CA, preventing the latter from dissolving phosphide, thus reducing the loss of TP.

We discovered that the eluate had a substantial quantity of nutrients produced from sewage sludge, which can have a negative influence on the groundwater ecosystem if not managed appropriately.

4. CONCLUSION

Ultrasound-assisted chemical washing is a useful and efficient solution to remove HMs from sewage sludge, instead of stabilizing mobile fractions without reducing the overall amount of HMs. The higher concentration ($\geq$0.4 M) of biodegradable CA eluent could effectively reduce HMs in the sewage sludge compared to the traditional non-biodegradable EDTA eluent. However, 0.4 M CA had a lower single-washing efficiency than 0.2 M EDTA at a solid-liquid ratio of 1:4 and an ultrasound time of 30 min. Ultrasound-assisted washing can reduce the treatment time by 7–10 times as compared to traditional mechanical mixing. Furthermore, during the first round of washing, the mobile fractions (F1) of HMs increased, posing a potential threat to the environment. After continuous washing with CA and EDTA, the total amount of HMs and the F1 fraction was significantly reduced. CA can be a better alternative to EDTA for the removal of HMs from sewage sludge, based on a combination of washing efficiency and removal of mobile fractions. When concentrating on HM removal, it is also important to monitor the quality and three-phase ratio of sewage sludge used for land application (pH, OM, AP, AK, AN, solid: gas: liquid). The type of washing agent utilized had an effect on the quality of the sewage sludge after washing. Furthermore, because the eluate had a significant concentration of HMs (Cd, Cr, Cu, Pb, Zn, etc.) and nutrients (N, P, K, TOC, etc.), secondary contamination and potential recovery should be considered.

CONSENT FOR PUBLICATION

All authors agreed to publish this research (including any individual details, images or videos) in *Water Science and Technology*.

FUNDING

This research has been supported by the Technology R&D project of Guohui Group-GZU (20180726), Guizhou Central Leading Local Science and Technology Development Funds Project ([2022] 4022): Guizhou Karst Environmental Ecosystem Ministry of Education Field Scientific Observation and Research Station Capacity Enhancement Construction, and the high-level innovation talents in Guizhou ([2020] 6002).

AUTHORS' CONTRIBUTIONS

All authors contributed to the study conception and design. The first draft of the manuscript and the drawing of the diagram were completed by H. L. and all authors commented on previous versions of the manuscript. Manuscript writing guidance and the first draft revision was completed by the corresponding author Y. W., Y. L., and X. P. Experimental operation, data collation and sample collection were performed by Z. L., Z. W., and Y. Q. All authors read and approved the final manuscript.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Al Sakkaf, R., Palmisano, G., Delclos, T., López-Muñoz, M. J. & Scandura, G. 2021 In situ DRIFTS-MS study of EDTA photocatalytic degradation. *Catalysis Today* **361**, 2–10. https://doi.org/10.1016/j.cattod.2019.10.002.

Alvarenga, P., Mourinha, C., Farto, M., Santos, T., Palma, P., Sengo, J., Morais, M. C. & Cunha-Queda, C. 2015 Sewage sludge, compost and other representative organic wastes as agricultural soil amendments: benefits versus limiting factors. *Waste Management* **40**, 44–52. https://doi.org/10.1016/j.wasman.2015.01.027.

Bao, Y., Guo, A., Ma, J., Pan, C. & Hu, L. 2019 Citric acid and glycine reduce the uptake and accumulation of Fe_2O_3 nanoparticles and oxytetracycline in rice seedlings upon individual and combined exposure. *Science of the Total Environment* **695**, 133859. https://doi.org/10.1016/j.scitotenv.2019.133859.

Beiyuan, J., Tsang, D., Valix, M., Baek, K., Ok, Y. S., Zhang, W., Bolan, N. S., Rinklebe, J. & Li, X. D. 2018 Combined application of EDDS and EDTA for removal of potentially toxic elements under multiple soil washing schemes. *Chemosphere* **205**, 178–187. https://doi.org/10.1016/j.chemosphere.2018.04.081.

Bloem, E., Haneklaus, S., Haensch, R. & Schnug, E. 2017 EDTA application on agricultural soils affects microelement uptake of plants. *Science of the Total Environment* **577**, 166–173. https://doi.org/10.1016/j.scitotenv.2016.10.153.

Choi, J., Lee, D. & Son, Y. 2021 Ultrasound-assisted soil washing processes for the remediation of heavy metals contaminated soils: the mechanism of the ultrasonic desorption. *Ultrasonics Sonochemistry* **74**, 105574. https://doi.org/10.1016/j.ultsonch.2021.105574.

EPA 1994 *Land Application of Sewage Sludge*. Environmental Protection Agency, Washington DC, USA.

Etim, E. U. 2019 Batch leaching of Pb-contaminated shooting range soil using citric acid-modified washing solution and electrochemical reduction. *International Journal of Environmental Science and Technology* **16**, 3013–3020. https://doi.org/10.1007/s13762-018-1909-2.

Freitas, E. V. & Nascimento, C. 2017 Degradability of natural and synthetic chelating agents applied to a lead-contaminated soil. *Journal of Soils and Sediments* **17**, 1272–1278. https://doi.org/10.1007/s11368-015-1350-9.

Gilbert, P., Thornley, P. & Riche, A. B. 2011 The influence of organic and inorganic fertiliser application rates on UK biomass crop sustainability. *Biomass and Bioenergy* **35**, 1170–1181. https://doi.org/10.1016/j.biombioe.2010.12.002.

Guo, X., Zhao, G., Zhang, G., He, Q., Wei, Z., Zheng, W., Qian, T. & Wu, Q. 2018 Effect of mixed chelators of EDTA, GLDA, and citric acid on bioavailability of residual heavy metals in soils and soil properties. *Chemosphere* **209**, 776–782. https://doi.org/10.1016/j.chemosphere.2018.06.144.

Hazrati, S., Farahbakhsh, M., Heydarpoor, G. & Besalatpour, A. A. 2020 Mitigation in availability and toxicity of multi-metal contaminated soil by combining soil washing and organic amendments stabilization. *Ecotoxicology and Environmental Safety* **201**, 110807. https://doi.org/10.1016/j.ecoenv.2020.110807.

Hoang, S. A., Bolan, N., Madhubashani, A. M. P., Vithanage, M., Perera, V., Wijesekara, H., Wang, H., Srivastava, P., Kirkham, M. B., Mickan, B. S., Rinklebe, J. & Siddique, K. H. M. 2022 Treatment processes to eliminate potential environmental hazards and restore agronomic value of sewage sludge: a review. *Environmental Pollution* **293**, 118564. https://doi.org/10.1016/j.envpol.2021.118564.

Kari, F. G. & Giger, W. 1995 Modeling the photochemical degradation of ethylenediaminetetraacetate in the River Glatt. *Environmental Science and Technology* **29**, 2814–2827. https://doi.org/10.1021/es00011a018.

Ke, X., Zhang, F. J., Zhou, Y., Zhang, H. J., Guo, G. L. & Tian, Y. 2020 Removal of Cd, Pb, Zn, Cu in smelter soil by citric acid leaching. *Chemosphere* **255**, 126690. https://doi.org/10.1016/j.chemosphere.2020.126690.

Kelessidis, A. & Stasinakis, A. S. 2012 Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. *Waste Management* **32**, 1186–1195. https://doi.org/10.1016/j.wasman.2012.01.012.

Klik, B., Gusiatin, Z. M. & Kulikowska, D. 2021 Quality of heavy metal-contaminated soil before and after column flushing with washing agents derived from municipal sewage sludge. *Scientific Reports* **11**, 15773. https://doi.org/10.1038/s41598-021-95441-5.

Kong, L. J., Tian, S. H., Luo, R. S., Liu, W., Tu, Y. T. & Xiong, Y. 2013 Demineralization of sludge-based adsorbent by post-washing for development of porosity and removal of dyes. *Journal of Chemical Technology and Biotechnology* **88**, 1473–1480. https://doi.org/10.1002/jctb.3989.

Kou, Y., Zhao, Q., Cheng, Y., Wu, Y., Dou, W. & Ren, X. 2020 Removal of heavy metals in sludge via joint EDTA-acid treatment: effects on seed germination. *Science of The Total Environment* **707**, 135866. https://doi.org/10.1016/j.scitotenv.2019.135866.

Kuan, Y. C., Lee, I. H. & Chern, J. M. 2010 Heavy metal extraction from PCB wastewater treatment sludge by sulfuric acid. *Journal of Hazardous Materials* **177**, 881–886. https://doi.org/10.1016/j.jhazmat.2009.12.115.

Lei, M., Liao, B. H., Zeng, Q. R., Qin, P. F. & Khan, S. 2008 Fraction distributions of lead, cadmium, copper, and zinc in metal-contaminated soil before and after extraction with disodium ethylenediaminetetraacetic acid. *Communications in Soil Science and Plant Analysis* **39**, 1963–1978. https://doi.org/10.1080/00103620802134776.

Oviedo, C. & Rodríguez, J. 2003 EDTA: the chelating agent under environmental scrutiny. *Química Nova* **26**, 901–905. https://doi.org/10.1590/S0100-40422003000600020.

Park, B. & Son, Y. 2017 Ultrasonic and mechanical soil washing processes for the removal of heavy metals from soils. *Ultrasonics Sonochemistry* **35**, 640–645. https://doi.org/10.1016/j.ultsonch.2016.02.002.

Ren, X., Yan, R., Wang, H., Kou, Y., Chae, K., Kim, I. S., Park, Y. & Wang, A. 2015 Citric acid and ethylene diamine tetra-acetic acid as effective washing agents to treat sewage sludge for agricultural reuse. *Waste Management* **46**, 440–448. https://doi.org/10.1016/j.wasman.2015.07.021.

Rutgersson, C., Ebmeyer, S., Lassen, S. B., Karkman, A., Fick, J., Kristiansson, E., Brandt, K. K., Flach, C. & Larsson, D. G. J. 2020 Long-term application of Swedish sewage sludge on farmland does not cause clear changes in the soil bacterial resistome. *Environment International* **137**, 105339. https://doi.org/10.1016/j.envint.2019.105339.

Seleiman, M. F., Santanen, A., Kleemola, J., Stoddard, F. L. & Makela, P. S. 2013 Improved sustainability of feedstock production with sludge and interacting mycorrhiza. *Chemosphere* **91**, 1236–1242. https://doi.org/10.1016/j.chemosphere.2013.02.004.

Son, Y., Cha, J., Lim, M., Ashokkumar, M. & Khim, J. 2011 Comparison of ultrasonic and conventional mechanical soil-washing processes for diesel-contaminated sand. *Industrial and Engineering Chemistry Research* **50**, 2400–2407. https://doi.org/10.1021/ie1016688.

Son, Y., Nam, S., Ashokkumar, M. & Khim, J. 2012 Comparison of energy consumptions between ultrasonic, mechanical, and combined soil washing processes. *Ultrasonics Sonochemistry* **19**, 395–398. https://doi.org/10.1016/j.ultsonch.2011.11.002.

Tang, J., He, J. G., Xin, X. D., Hu, H. Z. & Liu, T. T. 2018 Biosurfactants enhanced heavy metals removal from sludge in the electrokinetic treatment. *Chemical Engineering Journal* **334**, 2579–2592. https://doi.org/10.1016/j.cej.2017.12.010.

Udovic, M. & Lestan, D. 2009 Pb, Zn and Cd mobility, availability and fractionation in aged soil remediated by EDTA leaching. *Chemosphere* **74**, 1367–1373. https://doi.org/10.1016/j.chemosphere.2008.11.013.

Wang, X., Chen, J., Yan, X., Wang, X., Zhang, J., Huang, J. & Zhao, J. 2015 Heavy metal chemical extraction from industrial and municipal mixed sludge by ultrasound-assisted citric acid. *Journal of Industrial and Engineering Chemistry* **27**, 368–372. https://doi.org/10.1016/j.jiec.2015.01.016.

Wang, G., Zhang, S., Xu, X., Zhong, Q., Zhang, C., Jia, Y., Li, T., Deng, O. & Li, Y. 2016 Heavy metal removal by GLDA washing: optimization, redistribution, recycling, and changes in soil fertility. *Science of the Total Environment* **569–570**, 557–568. https://doi.org/10.1016/j.scitotenv.2016.06.155..

Wang, H., Liu, T. Z., Tsang, D. & Feng, S. 2017 Transformation of heavy metal fraction distribution in contaminated river sediment treated by chemical-enhanced washing. *Journal of Soils and Sediments* **17**, 1208–1218. https://doi.org/10.1007/s11368-016-1631-y.

Wang, G., Zhang, S., Zhong, Q., Xu, X., Li, T., Jia, Y., Zhang, Y., Peijnenburg, W. J. G. M. & Vijver, M. G. 2018 Effect of soil washing with biodegradable chelators on the toxicity of residual metals and soil biological properties. *The Science of the Total Environment* **625**, 1021–1029. https://doi.org/10.1016/j.scitotenv.2018.01.019.

Wu, Q., Cui, Y., Li, Q. & Sun, J. 2015 Effective removal of heavy metals from industrial sludge with the aid of a biodegradable chelating ligand GLDA. *Journal of Hazardous Materials* **283**, 748–754. https://doi.org/10.1016/j.jhazmat.2014.10.027.

Yang, Z. B., Wang, D., Wang, G. Y., Zhang, S. R., Cheng, Z., Xian, J. R., Pu, Y. L., Li, T., Jia, Y. X., Li, Y., Zhou, W. & Xu, X. X. 2021 Removal of Pb, Zn, Ni and Cr from industrial sludge by biodegradable washing agents: caboxyethylthiosuccinic acid and itaconic-acrylic acid. *Journal of Environmental Chemical Engineering* **9**. https://doi.org/10.1016/j.jece.2021.105846.

Zhai, X., Li, Z., Huang, B., Luo, N., Huang, M., Zhang, Q. & Zeng, G. 2018 Remediation of multiple heavy metal-contaminated soil through the combination of soil washing and in situ immobilization. *Science of The Total Environment* **635**, 92–99. https://doi.org/10.1016/j.scitotenv.2018.04.119.

Zhang, W., Huang, H., Tan, F., Wang, H. & Qiu, R. 2010 Influence of EDTA washing on the species and mobility of heavy metals residual in soils. *Journal of Hazardous Materials* **173**, 369–376. https://doi.org/10.1016/j.jhazmat.2009.08.087.

Zhang, H. J., Gao, Y. T. & Xiong, H. B. 2017 Removal of heavy metals from polluted soil using the citric acid fermentation broth: a promising washing agent. *Environmental Science and Pollution Research* **24**, 9506–9514. https://doi.org/10.1007/s11356-017-8660-y.

Zhang, X., Yang, H. & Cui, Z. 2018 Evaluation and analysis of soil migration and distribution characteristics of heavy metals in iron tailings. *Journal of Cleaner Production* **172**, 475–480. https://doi.org/10.1016/j.jclepro.2017.09.277.

Zhang, H., Qi, H., Zhang, Y., Ran, D., Wu, L., Wang, H. & Zeng, R. J. 2022 Effects of sewage sludge pretreatment methods on its use in agricultural applications. *Journal of Hazardous Materials* **428**, 128213. https://doi.org/10.1016/j.jhazmat.2022.128213.

Zhong, Q., Zhang, S., Pan, X., Wang, G., Xu, X., Li, T., Zhou, W., He, Y., Luo, L., Liu, Y. & Long, L. 2021 Efficiency and comprehensive risk assessment of soil Pb and Cd by washing technique with three biodegradable eluents. *Environmental Science and Pollution Research International* **28**, 61811–61824. https://doi.org/10.1007/s11356-021-15037-4.

Zhu, Z., Wang, J., Liu, X., Yuan, L., Liu, X. & Deng, H. 2021 Comparative study on washing effects of different washing agents and conditions on heavy metal contaminated soil. *Surfaces and Interfaces* **27**, 101563. https://doi.org/10.1016/j.surfin.2021.101563.

First received 5 July 2023; accepted in revised form 30 August 2023. Available online 7 September 2023