Washing agents from sewage sludge: efficiency of Cd removal from highly contaminated soils and effect on soil organic balance

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Abstract

Purpose To compare Cd removal from different soils with three washing agents recovered from sewage sludge (dissolved organic matter (DOM), soluble humic-like substances (HLS), soluble humic substances (SHS)). Also, to investigate how washing with these agents changes soil organic-matter composition (OM).

Materials and methods Sandy clay loam (S1) and clay (S2) highly contaminated with Cd (300 mg kg⁻¹) were washed with DOM, HLS, or SHS solutions at various pHs, and with various washing times and washing modes (single or double). Cd distribution and OM composition were determined (including content of humic substances (HS), fulvic fraction (FF), labile humic acids (L-HA), and stable humic acids (S-HA)).

Results and discussion Cd removal proceeded with pseudo-second-order kinetics. Equilibrium was reached in 30 min (S1) and 60 min (S2). DOM, HLS, and SHS removed 75–82% of Cd from S1, and 80–87% from S2. The most mobile fraction of Cd was removed after one wash. S2 retained more OM, including HS, than S1. Although washing did not change the HA/FF ratio in most variants, washing with DOM and HLS increased the percentage of L-HA in both soils. Washing with SHS increased S-HA content in both soils, but the percent content of S-HA was similar to that in the unwashed soil.

Conclusions DOM, HLS, and SHS derived from sewage sludge can effectively remediate clay and sandy clay soils highly contaminated with Cd. Washing with an SHS solution can increase the content of the most stable carbon forms (HA), which is beneficial for carbon sequestration in remediated soils.

Keywords Cadmium · Clay soil · Soil washing · Humic substances · Sandy clay soil · Soil organic balance

1 Introduction

Remediation of contaminated soils via chemical extraction with both conventional and unconventional washing agents (WAs) has been frequently studied and is still considered a

useful method because it can remove contaminants efficiently and rapidly clean up a contaminated site. This method is especially useful for remediation of soils contaminated with mobile heavy metals (HMs). For example, in HM-contaminated soils, Cd is highly mobile even at a slightly acidic pH, which facilitates its uncontrolled migration in the environment, and Cd that is present at high concentrations can be difficult to effectively immobilize. Thus, it would be more beneficial to remove it from soil.

Although a relatively large amount of information is available about removal of HMs, including Cd, with acids (Gu et al. 2018) and chelating agents (Wang et al. 2016; Wei et al. 2018), some of these WAs harm soil properties. For example, EDTA removed 46–82% Cd from contaminated soil (Chen et al. 2015; Wang et al. 2017), but it can cause some ecological problems in the soil environment due to its persistence or slow degradation. Moreover, it degraded soil fertility

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and decreased the content of organic matter, total nitrogen, and exchangeable K, Na, Ca, and Mg (Wang et al. 2017). As an alternative, natural plant biosurfactants (e.g., saponin) can also be used to remediate soil without the negative effects of EDTA. However, they are relatively expensive, and their availability is limited because only a few plant species contain saponins at concentrations high enough to make their recovery profitable. If a WA is to be used at technical scale, it should be both effective and relatively cheap. Preferably, it would also be recovered from waste, and some WAs of organic waste origin have recently been tested (Chiang et al. 2016; Dai et al. 2017). Sewage sludge may constitute another waste source of WAs.

Sewage sludge is a potential source of soluble organic matter and soluble humic substances (SHS). The use of WAs from sewage sludge has a number of potential advantages. First, sewage sludge is rich in organic matter and macroelements, so the use of WAs recovered from sewage sludge might simultaneously remove HMs and improve soil fertility after remediation. Second, these WAs are easily obtainable, due to the large amount of sewage sludge that is produced all over the world. It should be noted that the HMs present in sewage sludges are not extracted to WA solutions (Gusiatin et al. 2017), which means that these WAs are not a source of secondary soil pollution with HMs. In fact, the WAs can be recovered even from sewage sludge with elevated concentrations of HMs that would make the sludge unsuitable for agricultural use and composting.

When selecting a WA, priority should be given to the effectiveness of the WA, but if possible, soil valorization should also be considered, including the effect of the WA on soil organic matter content. Recently, studies have begun to consider the changes in soil nutrient and organic matter content after soil washing (Chen et al. 2014; Chiang et al. 2016; Wang et al. 2016).

Some of these studies indicate that soil washing led to loss of soil organic matter. For example, Wang et al. (2016) have shown that *N,N*-bis(carboxymethyl)-L-glutamic acid, EDTA, and EDDS decreased the organic matter content in farmland soil from 2.4 to 2.0, 1.8, and 2.2%, respectively, and in mine soil from 1.9 to 1.6, 1.5, and 1.8%, respectively. Other authors indicate, however, that depending on the type of WA, the content of organic matter in remediated soil can increase (Chen et al. 2014; Chiang et al. 2016). It should be mentioned that, in washed soil, not only total organic matter is important but also the forms of its occurrence. It is known that soils should be rich in humic substances (HS). HS are recalcitrant to biodegradation so they can be stored in soil for a long time. This characteristic means that HS play an important role in determining the characteristics of a soil by influencing its chemical, physical, and biological properties. Soil organic matter, which includes HS, is important for improving soil

tilth, pH buffering, and improving air-water conditions in soil, and it serves as a large pool of carbon and other plant essential nutrients (Schindler et al. 2007; Kobierski et al. 2018). It is known that even small increases of soil organic carbon over very large areas will substantially reduce net carbon dioxide emissions. For this reduction to be long-lasting, organic matter would have to be in the more stable or resistant fractions. Thus, it is important that the possible increase of organic matter in remediated soil does not cause a considerable change in the relative amounts of carbon forms or increase the contents of stable and resistant fractions of organic matter (e.g., in HS) compared with unwashed soil.

To the best of our knowledge, information about the influence of a soil WA on the changes it causes in HS and their fractions (humic acids, HA and fulvic fraction, FF) are not documented. These changes in HS, HA, and FF should be more deeply studied because they provide useful information about changes in organics in soil after introducing exogenic substances (WAs).

The present study aimed to address this gap in knowledge. Thus, the objective of this study was to examine Cd removal with soil WAs recovered from sewage sludge, and to investigate how washing with these agents changes the composition of soil organic matter. Because the effectiveness of soil washing and changes in soil organic matter can depend on soil texture, two types of soils (sandy clay loam and clay) were used in this study. For soil washing, three WAs recovered from sewage sludge were used: (i) dissolved organic matter (DOM), (ii) soluble humic-like substances (HLS), and (iii) soluble humic substances (SHS).

2 Materials and methods

2.1 Soil characterization and contamination

In this study, two soils, i.e., sandy clay loam (S1) and clay (S2), were used. Soil samples were collected from the surface layer (0–30 cm) from two locations: Baranowo (S1) and Wanguty (S2), situated in Warmia and Mazury province, north-eastern Poland. After drying at room temperature, the soils were ground and passed through a 2-mm sieve. Physicochemical characteristics of the soils are shown in Table 1.

Soil samples were spiked with Cd according to a procedure from Chaiyaraksa and Sriwiriyanuphap (2004) to obtain a total Cd concentration of 300 mg kg⁻¹. The soil was left at room temperature for 3 months, at 60–65% of its maximum water holding capacity, with frequent thorough mixing. After this period, the soil was dried at room temperature to a constant mass.

Table 1 Physicochemical characteristics of the soils ($n = 3$, $\pm$ standard deviation)

Characteristic	Unit	S1	S2
Sand	%	64 (± 1.6)	42 (± 1.3)
Silt	%	16 (± 0.16)	18 (± 0.52)
Clay	%	20 (± 0.21)	40 (± 0.95)
Texture	–	Sandy clay loam	Clay
Organic matter	%	1.6 (± 0.08)	2.1 (± 0.11)
CEC	cmol (+) kg ⁻¹	12.3 (± 0.7)	20.3 (± 1.1)
pH	–	7.1 (± 0.1)	7.2 (± 0.2)
Cd	mg kg ⁻¹	0.3 (± 0.02)	0.5 (± 0.04)
Cu		1.6 (± 0.06)	12.9 (± 1.6)
Ni		4.8 (± 0.2)	18.9 (± 2.3)
Pb		0.9 (± 0.01)	8.5 (± 0.9)
Zn		6.1 (± 0.2)	40.5 (± 3.5)

2.2 Sewage sludge and sewage sludge-derived washing agents

The sewage sludge that was the source of the WAs came from a mechanical-biological municipal wastewater treatment plant (WWTP) located in Warmia and Mazury province (Poland) with a capacity of 60,000 m³ day⁻¹. The WWTP produces sewage sludge that is a dewatered mixture of primary and biological sludges that have been anaerobically digested.

The sludge after drying at 105 °C was ground in a RETSCH SM-100 cutting mill equipped with 0.5-mm sieve. Table 2 gives a detailed characteristic of the sludge.

The sewage sludge had neutral pH (7.0 ± 0.1) and was rich in organic matter ($71.3 \pm 1.6\%$) and HS (227 ± 9.5 mg g⁻¹

Table 2 Characteristics of the sewage sludge used as the source of WAs ($n = 3$, $\pm$ standard deviation)

Characteristic	Unit	Value
pH	–	7.0 (± 0.1)
Moisture	%	83.2 (± 2.0)
Organic matter	%	71.3 (± 1.6)
Total nitrogen	%	5.4 (± 0.3)
Total phosphorous	%	2.0 (± 0.1)
Humic substances (HS)	mg C g ⁻¹ OM	227 (± 9.5)
Fulvic fraction (FF)	mg C g ⁻¹ OM	111 (± 6.5)
Humic acids (HA)	mg C g ⁻¹ OM	117 (± 6.8)
Labile HA (L-HA)	% HA	3.6 (± 0.3)
Stable HA (S-HA)	% HA	96.4 (± 2.1)
Cd	mg kg ⁻¹ d.m.	1.6 (± 0.1)
Cu		244 (± 4.3)
Ni		94.1 (± 1.9)
Pb		7.7 (± 0.8)
Zn		1083.7 (± 53.6)

OM). The contents of FF and HA were similar (111 ± 6.5 mg g⁻¹ OM and 117 ± 6.8 mg g⁻¹ OM, respectively), and in HA, stable HA (S-HA) prevailed ($> 96\%$). The concentrations of HMs in the sludge were below limits for sewage sludge in Poland.

In this study, three types of WAs were used: dissolved organic matter (DOM), soluble humic-like substances (HLS), and soluble humic substances (SHS). DOM was extracted with distilled water at 1:10 ratio (w/v). Both HLS and SHS were extracted using 0.1 M NaOH (also at the ratio of 1:10, w/v). However, before SHS extraction, from sewage sludge soluble non-humic substances (e.g., sugars and proteins) and fats, waxes and bitumens were removed by sludge washing with distilled water and defatted with a mixture of chloroform:methanol (2:1 ratio, v/v) in a microwave oven (Jouraiphy et al. 2005; Amir et al. 2006). The detailed procedure for HS extraction and fractionation (FF, HA, labile HA (L-HA), and S-HA) is given in Kulikowska and Klimiuk (2011).

The original concentrations (expressed as C) of DOM, HLS, and SHS extracted from sewage sludge were 6.8, 9.7, and 5 g C L⁻¹, respectively. However, in order to obtain the same concentrations of DOC in all WAs for comparing their effectiveness in Cd removal, they were diluted as necessary with distilled water to a concentration of 5 g C L⁻¹.

2.3 Batch soil washing

Soil washing was performed under batch conditions at a ratio of 1:40 (w/v). All WAs were used at the same concentration (5 g C L⁻¹). The suitability of WAs for removing Cd from soils was tested at different pHs: 4, 5, 6, 7, 8, 9, and 10. The pH in WAs was adjusted with HNO₃ and NaOH. Then, in order to establish the optimal extraction time, the soil was washed, under optimum pH and at specific washing times (5, 10, 15, 30, 60, 120, 180 min). After washing at each time, the samples were centrifuged and filtered through 0.45 μ m filters. In the supernatants, Cd concentration was measured.

After establishing the optimal pH and washing time, the influence of washing mode (single or double washing) was investigated. In the supernatants, Cd concentration was measured. In the double-washed soils, the following indicators were determined: Cd distribution, pH, organic matter content, total N content, content of available N and P, and concentrations of HS and their fractions (FF, HA, L-HA, and S-HA).

2.4 Analytical methods

Soil texture was determined based on soil particle size analysis (Mastersizer 2000 particle size analyzer). The content of organic matter in soil was analyzed according to Tiurin method, and the cation exchange capacity (CEC) according to Kappen's method (Ostrowska et al. 1991). The pH and electrical conductivity of soil were determined with a

potentiometric method, using soil and distilled water mixture (1:2.5 ratio, *w/v*).

In the aqueous solutions of DOM, HLS, and SHS, the following were measured: concentration (based on total organic carbon) with a Shimadzu Liquid TOC-V_{CSN} analyzer, and surface tension (Krüss K100 tensiometer, Wilhelmy plate method). To estimate the aromaticity of tested WAs, the SUVA₂₅₄ was determined (Hansen et al. 2016). The SUVA₂₅₄ is the UV absorption at 254 nm normalized to the organic carbon concentration in a given WA.

In addition, the WAs were characterized by FTIR. Attenuated total reflectance ATR (FT-IR/ATR) spectra were recorded in the 3600–400 cm^{-1} range, resolution 4 cm^{-1} , at room temperature using Nicolet 6700 spectrometer and Meridian Diamond ATR accessory (Harrick). Dried (60 °C, 24 h) samples were directly applied onto the diamond crystal, and close contact was made with the surface by a pressure tower. Interferograms of 256 scans were average for each spectrum. Dry potassium bromide (48 h, 105 °C) was used as a reference material to collect ATR spectra. All ATR spectra were corrected for water vapor and carbon dioxide and ATR correction was applied. No smoothing functions were used.

Total metal concentration (Cd, Cu, Pb, Zn) in WAs and total Cd concentration in soils was measured using a flame atomic absorption spectrometer (FAAS) (Varian, AA280FS). The soils were previously digested in a mixture of concentrated HCl and HNO₃ (3:1 ratio, *v/v*) in a microwave oven. Both in unwashed soils and soils double-washed with DOM, HLS, and SHS, Cd was fractionated into four fractions: exchangeable and acid-soluble (F1), reducible (F2), oxidized (F3), and residual (F4) according to a modified BCR (Community Bureau of Reference) procedure. The detailed description of metal fractionation is given in Pueyo et al. (2008).

All measurements were performed in triplicate. The results on Cd removal efficiency depending on pH in WAs, Cd fractionation, and organic balance in soils were analyzed statistically (STATISTICA 13.1, StatSoft). To elucidate significant differences between means ($p < 0.05$), post hoc comparisons were made using Tukey's HSD test.

3 Results and discussion

3.1 Washing agent characteristics

Based on the extraction procedure of a given WA from sewage sludge, it can be assumed that DOM contained mainly low-molecular organics and fulvic acids, and HLS contained both low-molecular organics and macromolecular compounds (fulvic and humic acids), whereas SHS contained only fulvic and humic acids. Using the SUVA₂₅₄ indicator (Table 3), it can be concluded that the aromaticity and molecular weight of WAs increased in the order DOM < HLS < SHS.

The WAs extracted from sewage sludge had different pHs, which was related to the type of extractant used. DOM had neutral pH (6.9) because it was extracted with distilled water, whereas HLS and SHS were alkaline (pH 11.7 and 12.3, respectively) as they were extracted with NaOH (Table 3). After extraction, HLS was present at the highest concentration (9.7 g L^{-1}), and SHS was present at the lowest (5 g L^{-1}). The WAs also differed in electrical conductivity. The WAs extracted with NaOH (HLS and SHS) had higher electrical conductivity than DOM. However, after DOM and HLS were diluted to concentrations of 5 g L^{-1} , they had lower electrical conductivity (20 mS cm^{-1} , on average) than SHS, which meant that SHS had a greater effect on soil salinity than DOM or HLS. Too high concentration of sodium in soil might increase the possibility of its toxicity to plants and it might cause soil aggregates to crumple and spread which leads to poor water retention (Mohamed et al. 2018).

Infrared spectroscopy was used for the determination of the quality features of DOM, HLS, and SHS. This method is a very important tool used in the environmental analyses for characterization of complex organic compounds. The FT-IR/ATR spectra in Fig. 1 provide information about specific molecular structures and various functional groups in WAs.

All presented spectra are characterized by several principal bands. The band at about 3267 cm^{-1} is attributed to the “free” O–H groups of carboxylic acids (Socrates 2001). The band at about 3066 cm^{-1} is associated with =C–H stretching mode of aromatic structures, which can be confirmed by the presence of relatively intense band at 1580 cm^{-1} and the presence of multiple bands within 960–700 cm^{-1} range (out-of-plane bending modes of aromatic structures). However, the band at ~3066 cm^{-1} may be the result of overlapping of stretching mode of aromatic hydrocarbons, unsaturated aliphatic hydrocarbons (Yang and Simms 1995), and N–H symmetric stretching in residual peptides, probably not removed by sludge extraction. The described bands have the highest intensity in the DOM spectrum and the maximum of the band at ~3066 cm^{-1} in HLS and SHS spectra is shifted to 3030 cm^{-1} in the DOM spectrum. The bands of aliphatic C–H stretching, mostly methyl substituents of aromatic rings (–CH₃; 2957, 2873 cm^{-1}) and methylene linkages linking aromatic rings (–CH₂–; 2931 cm^{-1}), are also present in all the spectra. The band at ~3188 cm^{-1} may be probably due to N–H symmetric stretching of peptide groups and/or H-bonded O–H in COOH groups (Shouliang et al. 2008; Montusiewicz et al. 2018).

Within 2000–400 cm^{-1} range (Fig. 1), there are several bands indicating i.a. the presence of carboxylates and amides. The band at ~1644 cm^{-1} is typical of symmetric C=O vibrations in carboxylates and amides, while the bands at 1404 cm^{-1} and 1330 cm^{-1} indicate the presence of the asymmetric COO[–] vibrations. The COOH vibration is practically missing (low-intensity shoulder at ~1740 cm^{-1}), what may be caused by the presence of Na ions and relatively high pH of

Table 3 Characteristics of WAs ($n = 3$, $\pm$ standard deviation)

Characteristic	Unit	DOM	HLS	SHS
pH	–	6.9 (± 0.08)	11.7 (± 0.13)	12.3 (± 0.11)
Concentration ^a	g C L ⁻¹	6.8 (± 0.24)	9.7 (± 0.42)	5.0 (± 0.19)
Surface tension	mN m ⁻¹	45.02 (± 0.08)	40.45 (± 0.11)	42.45 (± 0.09)
Electrical conductivity	mS cm ⁻¹	26.4 (± 0.43)	39.7 (± 0.52)	36.2 (± 0.61)
Cu	mg L ⁻¹	1.1 (± 0.05)	2.3 (± 0.12)	4.7 (± 0.19)
Pb		0.0	0.0	0.0
Zn		0.7 (± 0.08)	1.3 (± 0.12)	3.6 (± 0.32)
Cd		0.0	0.0	0.0
SUVA ₂₅₄ ^b	L mg ⁻¹ m ⁻¹	1.60	1.94	2.40

^a Original concentrations after extraction from sewage sludge^b For 0.5 g L⁻¹ DOM, HLS, and SHS solutions

some WAs (Table 3). The band at 1580 cm⁻¹ may be the result of the presence of both C=O stretching in amide I and/or aromatic C=C conjugated with C=O of COO⁻. Additionally, the band at 1404 cm⁻¹ may also be assigned to C–H and OH of COOH in hydroxyl or amine compounds (Zhai et al. 2012). The bands at 1515 and 1450 cm⁻¹ are characteristic for aromatic skeletal, C–H vibrations, and C–N and N–H vibrations in amide II (Socrates 2001; Liu and Chen 2013). An intense band at ~ 1047 cm⁻¹ points to the presence of C–O stretching

vibrations in aromatic ethers (Liu and Chen 2013). Both the carboxyl (dissociated and undissociated) and unprotonated amino groups were the most abundant in the described IR spectra (Fig. 1). All described bands have the highest intensity in the DOM spectrum and the lowest in the SHS spectrum.

All WAs showed some surface activity and are characterized of surface tension in a range between 40.45 and 45.02 mN m⁻¹. The surface tension of SHS depends on the source from which the SHS originate. For example, SHS extracted from leonardite

Fig. 1 FT-IR/ATR spectra of DOM, HLS, and SHS in 3600–400 cm⁻¹ range

reduced surface tension of water to 55 mN/m^{-1} (Meng et al. 2017). Changes in the surface properties of WA by decreasing both surface and interfacial tensions can reduce the adhesion between HMs and soil particles, facilitate the transport of HMs from soil into solution, and prevent re-adsorption of HM-WA complexes in soil (Liu et al. 2017).

It is worth to emphasize that, despite the presence of HMs in sewage sludge (Table 2), only trace concentrations were detected in the WAs. This is because most HMs have low mobility during washing at high pH. The fact that HMs are not washed from the sludge is important because, even when WAs are extracted from sewage sludge with elevated concentrations of HMs, there is no risk of secondary soil pollution.

3.2 The influence of pH on Cd removal from soils

Regardless of the type of soil and the WAs, Cd removal from both soils was much higher at acidic pH than that at alkaline pH (Fig. 2). This could be related to the distribution of Cd in the soils (Section 3.5), as it was mostly bound to oxides, and metal oxides decompose to a greater extent at acidic pH than at alkaline pH. Cd is more soluble and mobile in acidic than that in alkaline pH (Hong et al. 2002).

The substantial effect of pH on the effectiveness of soil washing in the present study is consistent with the results of other researchers who have investigated its effect on the mobility of both Cd and other HMs in soils (Liu and Chen 2013; Kulikowska et al. 2015a; Meng et al. 2017). In the present study, Cd removal efficiency was highest at pH 4 with all WAs and both soils: with S1, the efficiency was 67%, 66%, and 60%, with DOM, HLS, and SHS, respectively; with S2, it was 69%, 67%, and 67%, respectively. Although the efficiency of Cd removal was lower at alkaline pH than that at acidic pH, it increased slightly when the pH was increased from 9 to

10, except with SHS and S1. Based on these results, pH 4 was selected for further investigations.

3.3 Kinetics of Cd removal from soils

Despite the high concentration of Cd in soils, its removal proceeded relatively quickly; Fig. 3 shows the amount of Cd removed over time, and Table 4 gives the kinetic parameters (q_e and k) calculated from the pseudo-second-order kinetics model. With all WAs, equilibrium was reached after 30 min with S1, and after 60 min with S2. The rate constants (k) for removal of Cd from S1 were higher than those for removal from S2, which may be due to weaker Cd bonding in S1 than in S2. Unlike S1, S2 had some properties facilitating higher Cd sorption, i.e., clay texture, caused by a 2 times higher content of the clay fraction, and higher CEC. In comparison with other studies, the time to reach equilibrium in the present study was extremely short. For example, Meng et al. (2017) reported that the optimal washing time for Cd removal using HS extracted from leonardite was 2 h (with an initial Cd concentration of 6.57 mg kg^{-1}). This is because the lower the metal concentration in soil, the higher its binding strength (Han et al. 2003).

In this study, the q_e values were similar in both soils, especially those for washing with DOM and HLS (Table 4). The q_e values for SHS were slightly lower than those for DOM and HLS. Cd removal with tested WAs proceeded with higher k rate constants from soil S1 than S2. Similarly, high values of k ($0.232 \text{ kg mg}^{-1} \text{ h}^{-1}$) were reported by Kulikowska et al. (2015b) for washing of sandy clay loam contaminated with Cd, Cu, Ni, Pb, and Zn with SHS extracted from compost. For Cd removal from silty loam with SHS extracted from leonardite, Meng et al. (2017) determined k values 3.2–11.8 times lower than those in this study. In their study, however, the concentration of Cd was several times lower.

Fig. 2 Efficiency of Cd removal (η) from soils with washing agents at different pHs. a S1. b S2

Fig. 3 Plots of the pseudo-second-order kinetic model for Cd removal from soils with DOM, HLS, and SHS. **a** S1. **b** S2

3.4 Removal of Cd during single and double soil washing

With both soils and all WAs, Cd removal was more effective with double washing than single washing (Fig. 4). However, the efficiency was high with just a single washing (for S1: 67.3% DOM, 64.3% HLS, 56.7% SHS; for S2: 67.5% DOM, 65% HLS, 60.7% SHS), which shows that Cd can be easily removed from soils and transferred into WAs. After a second washing, Cd removal from S1 increased by 14.3% (DOM), 15.1% (HLS), and 18.5% (SHS), and the efficiency of its removal from S2 increased by 19.3% (DOM), 15.9% (HLS), and 18.9% (SHS) ($p < 0.05$). However, process efficiency in the first washing was higher than that in the second washing. This is because this HM was present mostly in the exchangeable and reducible fractions, which have the highest potential to be removed during soil washing. Therefore, these two fractions mostly affected Cd removal and indicate that the Cd content in the fractions from which this metal can be released was considerably diminished. Therefore, it is not advisable to use more than two washings with these WAs. Finally, with DOM, HLS, and HS, respectively, the efficiency of Cd removal after double washing was 81.6%, 79.4%, and 75.3% for S1, and 86.8%, 81%, and 79.6% for S2.

The high effectiveness of all tested WAs may be related to their content of functional groups. As it is known that HS have a high content of carboxylic $-\text{COOH}$ and phenolic $-\text{OH}$ groups, which are important for the formation of metal-

humic complexes (Spark et al. 1997; Conte et al. 2005), we expected SHS and HLS to have high efficiency. The high efficiency of DOM, especially in Cd removal, can be related to the high content of the FF in DOM. Due to its solubility in aqueous solutions throughout the pH range, FF has also been extracted from DOM. And the role of FF in the binding of HMs is confirmed by numerous studies. For example, Borůvka and Drábek (2004) determined the distribution of organically bound Cd, Pb, and Zn between HA and fulvic acids (FA) in heavily polluted Fluvisols. They found that all HMs were bound predominantly to the FA. A similar observation was made by Donisa et al. (2003). Those authors analyzed 11 elements, including Cd, in 3 different soils (andosols, cambisols, and podzols) and showed that FA was generally the main humic fraction reacting with the HMs. Other authors showed that sorption sites in organic matter can be highly specific (Adriano 2001; Heredia et al. 2002). Angehrn-Bettinazzi et al. (1989) reported that Pb was likely to form complexes with insoluble HS, while Cd and Zn formed complexes with mobile organic substances of low-molecular weight. In the present study, the carboxyl (dissociated and undissociated) and unprotonated amino groups were the most abundant in WAs. These groups can serve as coordination and electrostatic interaction sites for adsorbing HMs (Wu et al. 2001). Because DOM had higher intensity of these groups than HLS and SHS, it was more effective in Cd removal ($p < 0.05$) compared with other WAs. Similarly, Liu and Chen (2013) found that DOM from wine-processing waste

Table 4 Coefficients and goodness-of-fit (R^2) of pseudo-second-order kinetics model for Cd removal from soils S1 and S2 with DOM, HLS, and SHS

Value	Unit	S1			S2		
		DOM	HLS	SHS	DOM	HLS	SHS
q_e	mg kg^{-1}	208.3	200.1	172.4	208.3	200.0	192.3
k	$\text{kg mg}^{-1} \text{h}^{-1}$	0.230	0.250	0.280	0.134	0.192	0.096
R^2	—	0.9999	0.9998	0.9999	0.9996	0.9994	0.9993

Fig. 4 Efficiency of Cd removal (η) from soils after single and double washing. **a** S1. **b** S2. Different letters indicate significant differences ($p < 0.05$) between washing agents and between first and second washings

sludge was effective in Cd removal from soil due to chelating reactions between Cd and the carboxyl and amide groups present in DOM.

3.5 The effect of washing agents from sewage sludge on Cd distribution

The number of soil washings affected Cd removal from individual fractions. Figure 5 shows that initial distribution patterns of Cd were quite similar in both soils and the largest amount of Cd was found in the reducible fraction. The differences in soil properties had some effect on Cd distribution in the other fractions. In clay soil (S2), the Cd concentration in F1 fraction was lower, but that in F3 and F4 fractions was higher than in sandy clay soil (S1).

During a single washing, all WAs removed Cd mainly from F2 fraction in both soils. This suggests that the initial Cd concentration in individual fractions was crucial for HM removal. A second washing further decreased Cd mobility (based on F1 fraction removal) ($p < 0.05$), but the amount of reduction in mobility depended on the WA that was used. The best results were obtained with DOM (both soils) and SHS (S2). Moreover, a second washing also removed more Cd from the F2 fraction, mainly from soil S1. The effect of soil washing on Cd content in F3 fraction differed depending on the soil. With S1, Cd content in F3 fraction increased after a single washing and then remained about the same after a second washing. With S2, Cd content in F3 fraction decreased after a single washing and then either remained about the same (with DOM) or increased back to about its initial level before washing (with HLS and SHS). This increase in Cd content in F3 fraction may be related to an increase in organic matter content in the washed soils (see Section 3.6). The changes in Cd content in F4 fraction were minor, as this fraction contained the lowest Cd concentrations.

The kind of WA that is used affects the removal of Cd from individual fractions. Cd removal with EDTA is similar to the removal with the WAs used in the present study. Begum et al. (2012) found that, when Cd was present at a total concentration of 132 mg kg^{-1} and mostly in the F2 (55%) and F1 (42%) fractions, the content of Cd in F1 and F2 fractions decreased significantly, but that in F3 fraction increased after washing with EDTA. Hong et al. (2002), who used the Tessier fractionation procedure, found that saponin removed 83% of Cd from the exchangeable and carbonate fractions (equivalent to F1 fraction in the present study), and 33% of Cd from the Fe–Mn oxide fraction, but had little effect on the content of Cd in the organic fraction. Cao et al. (2017) found that an aqueous extract from *Coriaria nepalensis*, *Clematis brevicaudata*, *Pistacia weinmannifolia*, and *Ricinus communis* plants at pH 4 was only able to decrease the Cd concentration in F1 fraction.

3.6 Soil organic balance in soil

As a source of WAs, sewage sludge that had been subjected to methane fermentation was used instead of raw excess sludge for two reasons. First, although HS are present in raw sewage sludge because humification occurs during sewage treatment (Riffaldi et al. 1982; Unsal and Sozudogru Ok 2001; Réveillé et al. 2003), HS content is higher in fermented sewage sludge (Kulikowska et al. 2019). Second, fermented sewage sludge contains a low concentration of low-molecular-weight organic compounds. Réveillé et al. (2003) investigated the distribution of HS and lipids in raw and fermented sewage sludge and found that lipid extract from raw sludge consisted mainly of fatty acids, whereas that from fermented sludge consisted predominantly of steroids. This difference in composition is important because an increase in the content of low-molecular-weight organic compounds in the soil after washing could cause an oxygen deficit in the soil.

Fig. 5 Cd distribution in soil before and after washing. **a** Soil S1. **b** Soil S2. Different letters indicate significant differences ($p < 0.05$) between washing agents ((a)–(d)), and between first and second washings ((A),

(B)). F1 is exchangeable and acid-soluble fraction, F2 is reducible fraction, F3 is oxidizable fraction, and F4 is residual fraction

In this study, soil washing decreased soil pH from neutral to slightly or moderately acidic (Table 5). A decrease in soil pH always accompanies soil washing, but the size of the change

in soil pH depends on the type of WA. For example, a WA at pH 4 (DOM extracted with 3 M NaOH from wine-processing waste sludge) decreased soil pH from 5.8 to 4.6 (Liu and Lin

Table 5 pH and organic matter before and after soil washing with DOM, HLS, and SHS ($n = 3$, $\pm$ standard deviation). For a given characteristic, significant differences between the unwashed and washed soil are indicated with different letters (ANOVA followed by Tukey's HSD test, $p < 0.05$)

Soil	pH	Organic matter (%)
Unwashed S1	7.1 (± 0.11)a	1.6 (± 0.09)a
Washed S1 with DOM	6.08 (± 0.08)b	1.72 (± 0.10)a
Washed S1 with HLS	6.14 (± 0.10)b	2.11 (± 0.14)b
Washed S1 with SHS	5.81 (± 0.09)c	4.22 (± 0.12)c
Unwashed S2	7.2 (± 0.12)a	2.1 (± 0.06)a
Washed S2 with DOM	5.42 (± 0.09)b	3.25 (± 0.21)b
Washed S2 with HLS	5.46 (± 0.11)b	3.59 (± 0.18)b
Washed S2 with SHS	5.21 (± 0.12)b	5.75 (± 0.14)c

2013), whereas a FeCl_3 solution decreased soil pH to a greater extent, from pH 5.92 to 4.05 (Makino et al. 2008).

In soils after washing, the content of organic matter (OM) had increased, and the content was greater in soil

S2 than that in soil S1 (Table 5). This increase was related to sorption of organic compounds from WAs in soil. Soil S2 contained two times more clay fraction and had a CEC that was nearly two times higher (Table 1), which facilitated sorption of organics from WAs. This is in agreement with the results obtained by Shen (1999), who found that a high content of clay in soil favored the sorption of dissolved organic matter. In the present study, the increase in OM content after double washing with SHS caused the classification of S2 to change from mineral to mineral-organic soil. An increase in OM after washing with organic WAs is a rather typical phenomenon. Chen et al. (2014) found an increase (1.7–2.3 times in the topsoil and 2.6–3.0 times in the subsoil) in OM content after washing Pb-contaminated soils with DOC derived from wine-processing waste sludge. Chiang et al. (2016) observed a slight increase in OM content after soil washing with a liquid fertilizer from food-waste composting. Using a DOC solution at a concentration of 1.5 g/L^{-1} and pH 2 or pH 3, the content of OM in topsoil increased from 6.2 to 6.5% or 6.9%, respectively,

Fig. 6 Changes in concentration of HS and distribution of FF and HA fractions in unwashed and washed soils. **a** HS in soil S1. **b** FF and HA in soil S1 (as % of HS). **c** HS in soil S2. **d** FF and HA in soil S2 (as % of HS). For HS in a particular soil, concentrations followed by the same letters do

not differ significantly at $p < 0.05$. For FF in a particular soil, percent contents followed by the same letters do not differ significantly at $p < 0.05$. Similarly, percent contents of HA in a particular soil that are followed by the same letters do not differ significantly at $p < 0.05$

Fig. 7 Changes in HA/FF ratio in unwashed and washed soils. For a particular soil, HA/FF ratios under the same letters do not differ significantly at $p < 0.05$

and in subsoil from 4.0 to 4.3% or 4.6%, respectively. The increases in OM were attributed to the DOC remaining on the soil particles.

Soil organic matter is important for a wide variety of chemical, physical, and biological properties of soil. As soil organic matter increases, so does the soil's CEC, total N content, and

other properties, such as water holding capacity and microbiological activity (Horneck et al. 2011).

Re-generation of HS through humification of OM from diverse soil additives may be the way to re-build the protective function of the soil barrier, and consequently to reduce environmental risks in areas under anthropopressure

Fig. 8 Changes in concentration of L-HA and S-HA and their share of total HA in unwashed and washed soils. **a** L-HA and S-HA contents in soil S1. **b** Percent content of L-HA and S-HA in HA in soil S1. **c** L-HA

and S-HA contents in soil S2. **d** Percent content of L-HA and S-HA in HA in soil S2. For L-HA and S-HA in a particular soil, their contents do not differ significantly at $p < 0.05$ if they are followed by the same letter

(Kwiatkowska-Malina 2018). However, although some researchers have reported changes in soil properties after washing, they have analyzed mostly basic soil properties and soil fertility. Moreover, the reported organic balances were based only on total OM content, and changes in HS and their fractions were not documented, even though it is known that the quality of HS or of their fractions can be changed by soil management practices (Reddy et al. 2014; Galantini et al. 2014).

In the present study, soil washing increased the content of HS in soil, which confirms that these substances are sorbed in soil. As would be expected, the increase in HS was the highest when these substances were used as the WA: after washing with SHS, HS concentrations were about 3 times higher in soils S1 and S2 than before washing. Washing with DOM and HLS also significantly increased the content of HS in soil S2 ($p < 0.05$) (Fig. 6). Both before and after soil washing with each of the three WAs, soil S1 had a higher HA/FF ratio than soil S2, and soil washing did not significantly change this ratio in soil S1 ($p > 0.05$) (Fig. 7). In contrast, washing with HLS and SHS significantly increased the HA/FF ratio in soil S2 ($p < 0.05$), although washing with DOM did not have a statistically significant effect ($p > 0.05$).

In soil, there are both labile and stable HA (L-HA and S-HA, respectively). According to Schnitzer and Schuppli (1989), L-HA are more aromatic than S-HA. Similarly, Gieguzynska et al. (2009) reported that L-HA are weakly bound, aromatic macromolecules of small or medium size, while S-HA are larger aliphatic macromolecules. In the present study, soil washing with DOM, HLS, and HS affected the percent content of labile HA and stable HA in the soil (Fig. 8). Soil washing with SHS increased the percentage of S-HA in HA in sandy clay loam (soil S1) from 86 to 91% and decreased it in clay soil from 82 to 73%. However, soil washing with DOM and HLS increased the percentage of L-HA in sandy clay loam to a greater extent than in clay soil (Fig. 8b).

4 Conclusions

DOM, HLS, and SHS derived from sewage sludge are effective WAs for remediation of both clay and sandy clay soils highly contaminated with Cd. After a single soil washing, the process efficiency was high (57–67%), and it increased to 75–87% after double washing. The small difference between washings indicates that most of the mobile Cd was already removed after the first washing. All WAs increased organic matter content (including HS content). Although DOM and HLS increased the percent content of labile HA in both soils, the ratio of HA-to-FF in most washed soils was similar to that in the unwashed soils. The SHS solution significantly increased the content of stable HA in soil, although the percentage of HS in this fraction was similar to that in the unwashed

soil. Thus, soil washing with HS solution can increase carbon sequestration in soil.

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References

- Adriano DC (2001) Trace elements in terrestrial environments. Springer New York, New York, NY
- Amir S, Hafidi M, Lemee L et al (2006) Structural characterization of fulvic acids, extracted from sewage sludge during composting, by thermochemolysis-gas chromatography-mass spectrometry. *J Anal Appl Pyrolysis* 41:410–422
- Angehrn-Bettinazzi C, Thoni L, Hertz J (1989) An attempt to evaluate some factors affecting the heavy metal accumulation in a forest stand. *Int J Environ Anal Chem* 35:69–79
- Begum ZA, Rahman IMM, Tate Y, Sawai H, Maki T, Hasegawa H (2012) Remediation of toxic metal contaminated soil by washing with biodegradable aminopolycarboxylate chelants. *Chemosphere* 87:1161–1170
- Borůvka L, Drábek O (2004) Heavy metal distribution between fractions of humic substances in heavily polluted soils. *Plant Soil Environ* 50: 339–345
- Cao Y, Zhang S, Wang G, Huang Q, Li T, Xu X (2017) Removal of Pb, Zn, and Cd from contaminated soil by new washing agent from plant material. *Environ Sci Pollut Res* 24:8525–8533
- Chaiyaraksa C, Sriwiriyanuphap N (2004) Batch washing of cadmium from soil and sludge by a mixture of $\text{Na}_2\text{S}_2\text{O}_5$ and Na_2EDTA . *Chemosphere* 56:1129–1135
- Chen Y-M, Lin W-H, Lin Y-A et al (2014) Remediation of lead-contaminated soil using dissolved organic carbon solutions prepared by wine-processing waste sludge. *Geoderma* 235–236:233–239
- Chen C, Chen Y, Xie T, Wang MK, Wang G (2015) Removal, redistribution, and potential risks of soil Cd, Pb, and Zn after washing with various extractants. *Environ Sci Pollut Res* 22:16881–16888
- Chiang P-N, Tong O-Y, Chiou C-S, Lin YA, Wang MK, Liu CC (2016) Reclamation of zinc-contaminated soil using a dissolved organic carbon solution prepared using liquid fertilizer from food-waste composting. *J Hazard Mater* 301:100–105
- Conte P, Agretto A, Spaccini R, Piccolo A (2005) Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils. *Environ Pollut* 135:515–522
- Dai S, Li Y, Zhou T, Zhao Y (2017) Reclamation of heavy metals from contaminated soil using organic acid liquid generated from food waste: removal of Cd, Cu, and Zn, and soil fertility improvement. *Environ Sci Pollut Res* 24:15260–15269
- Donisa C, Mocanu R, Steinnes E (2003) Distribution of some major and minor elements between fulvic and humic acid fractions in natural soils. *Geoderma* 111:75–84
- Galantini JA, Duval ME, Iglesias JO, Kruger H (2014) Continuous wheat in semiarid regions. *Soil Sci* 179:284–292
- Gieguzynska E, Amine-Khodja A, Trubetskoy OA, Trubetskaya OE, Guyot G, ter Halle A, Golebiowska D, Richard C (2009) Compositional differences between soil humic acids extracted by

- various methods as evidenced by photosensitizing and electrophoretic properties. *Chemosphere* 75:1082–1088
- Gu F, Zhang Y, Tang Q, Lu C, Zhou T (2018) Remediation of Zn(II)- and Cu(II)-contaminated soil using citric acid and citric acid-containing wastewater. *Int J Civ Eng* 16:1607–1619
- Gusiatin ZM, Kulikowska D, Klik B (2017) Suitability of humic substances recovered from sewage sludge to remedy soils from a former As mining area – a novel approach. *J Hazard Mater* 338:160–166
- Han FX, Banin A, Kingery WL, Triplett GB, Zhou LX, Zheng SJ, Ding WX (2003) New approach to studies of heavy metal redistribution in soil. *Adv Environ Res* 8:113–120
- Hansen AM, Kraus TE, Pellerin BA et al (2016) Optical properties of dissolved organic matter (DOM): effects of biological and photolytic degradation. *Limnol Oceanogr* 61:1015–1032
- Heredia W, Peirano P, Borie G, Aguilera M (2002) Soil organic matter–metal interactions in Chilean volcanic soils under different agronomic management. *Commun Soil Sci Plant Anal* 33:2083–2099
- Hong K-J, Tokunaga S, Kajiuchi T (2002) Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils. *Chemosphere* 49:379–387
- Horneck DA, Sullivan DM, Owen JS, Hart JM (2011) Soil test interpretation guide. Oregon State University Extension. Publication EC 1478
- Jouraphy A, Amir S, El Gharous M et al (2005) Chemical and spectroscopic analysis of organic matter transformation during composting of sewage sludge and green plant waste. *Int Biodeterior Biodegrad* 56:101–108
- Kobierski M, Kondratowicz-Maciejewska K, Banach-Szott M, Wojewódzki P, Peñas Castejón JM (2018) Humic substances and aggregate stability in rhizospheric and non-rhizospheric soil. *J Soils Sediments* 18:2777–2789
- Kulikowska D, Klimiuk E (2011) Organic matter transformations and kinetics during sewage sludge composting in a two-stage system. *Bioresour Technol* 102:10951–10958
- Kulikowska D, Gusiatin ZM, Bułkowska K, Kierklo K (2015a) Humic substances from sewage sludge compost as washing agent effectively remove Cu and Cd from soil. *Chemosphere* 136:42–49
- Kulikowska D, Gusiatin ZM, Bułkowska K, Klik B (2015b) Feasibility of using humic substances from compost to remove heavy metals (Cd, Cu, Ni, Pb, Zn) from contaminated soil aged for different periods of time. *J Hazard Mater* 300:882–891
- Kulikowska D, Klik BK, Gusiatin ZM, Hajdukiewicz K (2019) Characteristic of humic substances from municipal sewage sludge: a case study. *Desalin Water Treat* 144:57–64
- Kwiatkowska-Malina J (2018) Functions of organic matter in polluted soils: the effect of organic amendments on phytoavailability of heavy metals. *Appl Soil Ecol* 123:542–545
- Liu C-C, Chen G-B (2013) Reclamation of cadmium-contaminated soil using dissolved organic matter solution originating from wine-processing waste sludge. *J Hazard Mater* 244–245:645–653
- Liu CC, Lin YC (2013) Reclamation of copper-contaminated soil using EDTA or citric acid coupled with dissolved organic matter solution extracted from distillery sludge. *Environ Pollut* 178:97–101
- Liu Z, Li Z, Zhong H, Zeng G, Liang Y, Chen M, Wu Z, Zhou Y, Yu M, Shao B (2017) Recent advances in the environmental applications of biosurfactant saponins: a review. *J Environ Chem Eng* 5:6030–6038
- Makino T, Takano H, Kamiya T, Itou T, Sekiya N, Inahara M, Sakurai Y (2008) Restoration of cadmium-contaminated paddy soils by washing with ferric chloride: Cd extraction mechanism and bench-scale verification. *Chemosphere* 70:1035–1043
- Meng F, Yuan G, Wei J, Bi D, Wang H (2017) Leonardite-derived humic substances are great adsorbents for cadmium. *Environ Sci Pollut Res* 24:23006–23014
- Mohamed RM, Al-Gheethi AA, Noramira J et al (2018) Effect of detergents from laundry greywater on soil properties: a preliminary study. *Appl Water Sci* 8:1–7
- Montusiewicz A, Bis M, Pasieczna-Patkowska S, Majerek D (2018) Mature landfill leachate utilization using a cost-effective hybrid method. *Waste Manag* 76:652–662
- Ostrowska A, Gawliński S, Szczubińska Z (1991) Analysis of soils and plants. Institute of Environmental Protection – National Research Institute, Warsaw, Poland
- Pueyo M, Mateu J, Rigol A, Vidal M, López-Sánchez JF, Rauret G (2008) Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environ Pollut* 152:330–341
- Reddy SB, Nagaraja MS, Punith TS, Police Patil AS (2014) Elemental analysis, E4/E6 ratio and total acidity of soil humic and fulvic acids from different land use systems. *Ann Plant Soil Res* 16:89–92
- Réveillé V, Mansuy L, Jardé É, Garnier-Sillam É (2003) Characterisation of sewage sludge-derived organic matter: lipids and humic acids. *Org Geochem* 34:615–627
- Riffaldi R, Sartori F, Levi-Minzi R (1982) Humic substances in sewage sludges. *Environ Pollut Ser B, Chem Phys* 3:139–146
- Schindler FV, Mercer EJ, Rice JA (2007) Chemical characteristics of glomalin-related soil protein (GRSP) extracted from soils of varying organic matter content. *Soil Biol Biochem* 39:320–329
- Schnitzer M, Schuppli P (1989) Method for the sequential extraction of organic matter from soils and soil fractions. *Soil Sci Soc Am J* 53:1418
- Shen Y-H (1999) Sorption of natural dissolved organic matter on soil. *Chemosphere* 38:1505–1515
- Shouliang H, Beidou X, Haichan Y et al (2008) Characteristics of dissolved organic matter (DOM) in leachate with different landfill ages. *J Environ Sci* 20:492–498
- Socrates G (2001) Infrared and Raman characteristic group frequencies. In: Tables and charts. John Wiley & Sons, Ltd., Chichester
- Spark KM, Wells JD, Johnson BB (1997) Sorption of heavy metals by mineral-humic acid substrates. *Soil Res* 35:113
- Unsal T, Sozudogru Ok S (2001) Description of characteristics of humic substances from different waste materials. *Bioresour Technol* 78:239–242
- Wang G, Zhang S, Xu X et al (2016) Heavy metal removal by GLDA washing: optimization, redistribution, recycling, and changes in soil fertility. *Sci Total Environ* 569–570:557–568
- Wang Y, Ma F, Zhang Q, Peng C, Wu B, Li F, Gu Q (2017) An evaluation of different soil washing solutions for remediating arsenic-contaminated soils. *Chemosphere* 173:368–372
- Wei H, Zhang W, Zhuang L, Wang S, Tsang DCW, Qiu R (2018) Two-stage multi-fraction first-order kinetic modeling for soil Cd extraction by EDTA. *Chemosphere* 211:1035–1042
- Wu FC, Tseng RL, Juang RS (2001) Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. *Water Res* 35:613–618
- Yang CQ, Simms JR (1995) Comparison of photoacoustic, diffuse reflectance and transmission infrared spectroscopy for the study of carbon fibers. *Fuel* 74:543–548
- Zhai Y, Peng W, Zeng G, Fu Z, Lan Y, Chen H, Wang C, Fan X (2012) Pyrolysis characteristics and kinetics of sewage sludge for different sizes and heating rates. *J Therm Anal Calorim* 107:1015–1022