

Review

# Remediation of Heavy Metal-Contaminated Soils with Soil Washing: A Review

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**Abstract:** Soil with heavy metals' contamination has caused worldwide concern, and there is an increasing interest in the application of washing agents for the remediation of soils with heavy metals' contamination. The review summarizes the recent findings about soil washing with different washing agents. For soil washing technologies, the solubilizing capability, toxicity, and biocompatibility of agents are essential concerns. Washing agents can enhance heavy metals' desorption and removal from soil. Inorganic acids/bases/salts, synthetic surfactants, and synthetic chelators are often limited due to their adverse effects on soil. Biosurfactants, HAs (humic acids), and LMWOA (low-molecular-weight organic acids) are suggested washing agents, but the limitation of their low production needs to be conquered. Moreover, both washing with a mixture agent and sequential washing have often been adopted to improve the overall capacity of the washing agent for decontamination. Mixture washing can obtain the synergetic effect for soil washing and increase washing efficiency. Sequential washing can apply an agent with a high heavy metals removal rate. However, this may cause environmental risks in the early stage, and then remove the washing agent injected in the early stage by the secondary washing stage. Overall, the already known cases reveal the good prospect of soil washing for soil remediation.

**Keywords:** soil washing; washing agent; heavy metals; review



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## 1. Introduction

Chromium (Cr), cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As), and copper (Cu) are classified as heavy metals (HMs). These HMs, enriched in soil and exceeding the background content value, will lead to soil HMs contamination [1]. Soil HMs contamination has caused global concern due to their significant disruption to sustainable development. HMs in the soil are persistent, unbiodegradable, and toxicant. A previous study reported that excessive HMs in the soil can not only ruin soil functions and inhibit plants and microorganisms but also prevent migration by the food chain and damage human health [2]. About 20 million hectares, over 19% of China's cultivated land, has suffered metal pollution, and 12 million t/year of contaminated grains have been produced [3,4]. The national commune of soil pollution survey of China has reported the total exceeding the standard rate of soil in China was 16.1%, and the exceeding the standard rates of Cd, Hg, As, Pb, and Cr were 7.0%, 1.6%, 2.7%, 1.5%, and 1.1%, respectively [5]. Overall, soil's HM contamination poses a serious threat to the environment and humans, so it is urgent to propose effective measures to remediate it.

Soil HMs mainly include physical, chemical, and biological remediation. The physical method is generally soil replacement, simply covering the contaminated soil with clean soil

or mixing both soils and diluting the HMs' concentration. This method requires much clean soil, economic cost, and a large working volume [6]. Biological remediation is remediating soil with the growth of organisms, which needs a longer time. Chemical fixation reduces the toxicity of HMs in the short term, but is eventually be activated by rainwater leaching and can cause eco-risks. As a new technology, electrokinetic remediation has usually been limited by soil permeability and additional buffer solutions [7]. Unlike chemical fixing, chemical washing can fundamentally remove HMs from the soil without the risk caused by the secondary release.

Generally, soil washing is a time-efficient and versatile remediation method for HM-contaminated soil. Specifically, liquids are mixed with soil and remove HMs with a mechanical process. While low water solubility is grasped by HMs in soil, to improve the HMs' removal rate, additives are always added into an eluent to mobilize metals. Common additives include inorganic acid/base/salts, surfactants, and chelators. The mixture of several additives has also been used for more effective washing efficiency. Significant differences exist in the removal efficiency of different additives for HMs [8]. Moreover, soil washing technology has limitations: (1) changing the soil's physical-chemical properties [9], (2) destroying the ecological structure [10], and (3) leading to new environmental risks by adding residual washing agents in the soil [11]. Therefore, selecting a washing agent with a high metal removal rate, low toxicity, and low damage to soil properties is critical for washing technology.

Before carrying out soil washing, a systematic investigation should be conducted on the contaminated site's soil texture and pollutant distribution characteristics and the selected optimum washing methods and conditions. The washing technology is mainly divided into in situ and ex situ washing. Ex situ soil washing has a more extended history, and it evolved from industrial mining and mineral processing separation technology. Contaminated soil is excavated from the contaminated area and mixed with washing agents in specific equipment for washing. After washing, soil particles are settled and put back in place, and the washing agents can be regenerated and reused [12]. The procedure of ex situ washing technology by the United States Environment Protection Agency is as follows: (1) excavate contaminated soil, (2) screen soil and remove large-sized gravels to protect the equipment, (3) mix soil with washing agents and stirring, separating, (4) soil backfill, (5) treat the eluent phases. Ex situ soil washing can treat a broad range of metal concentrations; this technique allows a shallow concentration of HMs' residual in soil. The soil can be washed in grades if necessary because the soil has been excavated (Figure 1). Specifically, soil can be sieved and divided into several aggregate grades with different metal concentrations. More suitable washing conditions were used to improve the HMs' removal efficiency [13]. Ex situ washing is widely used in the early stage, and recently, it has been less used in large field scale soil restoration because of the complex operation process and high economic cost.

In situ soil washing is also named soil flushing, and the procedure of in situ washing is shown in Figure 2 [14]. Makino et al. [15] applied the in situ technology for Cd-contaminated paddy field remediation. They defined the washing procedure as follows: (1) agents were injected from the injection well and flowed through the contaminated area, (2) they collected the agents from the extraction well for the next step, and (3) secondary washing was conducted using deionized water to remove residual agents. Compared to ex situ washing, the in situ washing technology does not need to excavate the soil, leading to lower economic costs, and it is suitable for large-scale contaminated areas. However, the limitation is that the washing agents in the soil cannot be controlled completely. More content of agent residues in soil caused an environmental risk. Moreover, the washing efficiency was significantly influenced by soil permeability. Porous and permeable soil with hydraulic conductivity values greater than  $10^{-3} \text{ cm}\cdot\text{s}^{-1}$  was suitable for in situ washing technology. In addition, selecting a suitable washing agent has significance for the removal of HMs from soil efficiently. The comparison of different classification washing agents is shown in Table 1.

In this review, the progress on the washing agents for the remediation of contaminated soils is reviewed, and the considerations for soil washing, and the mechanism for the removal of HMs by different types of washing agents, are summarized and discussed with the purposes of providing a systematic realization about washing agents. The paper does not provide any technique in detail but instead poses an overview of soil washing as a promising alternative for HM-contaminated soils and its selected washing agent strategy.

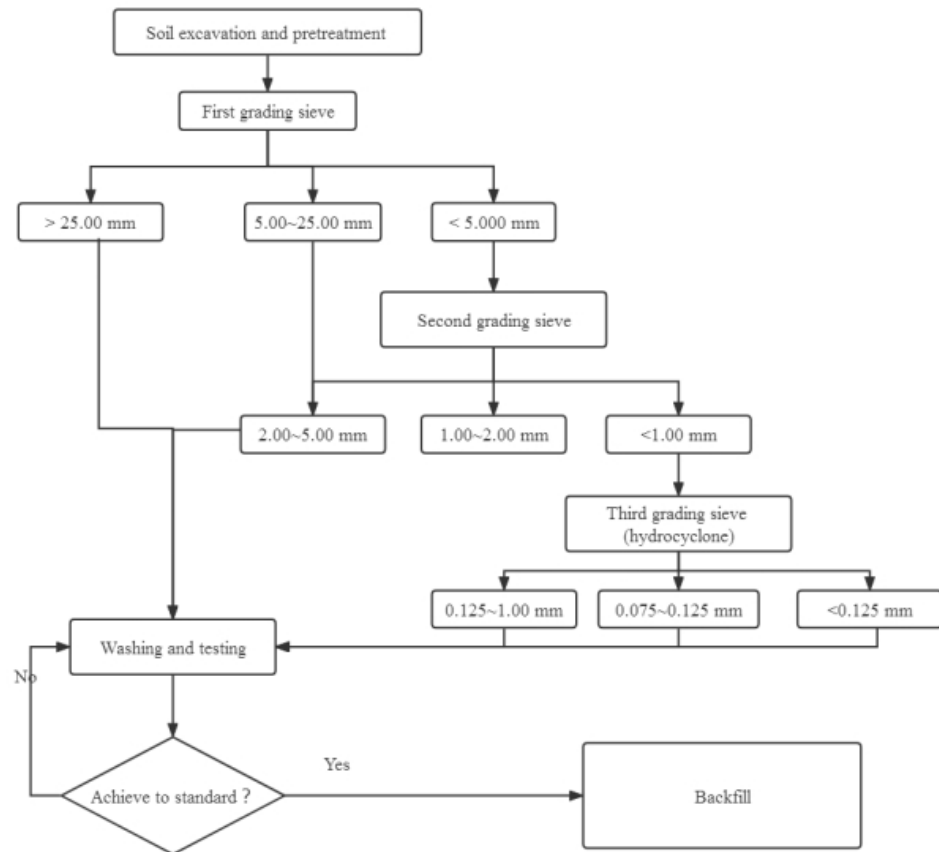


Figure 1. General procedure of ex situ washing.

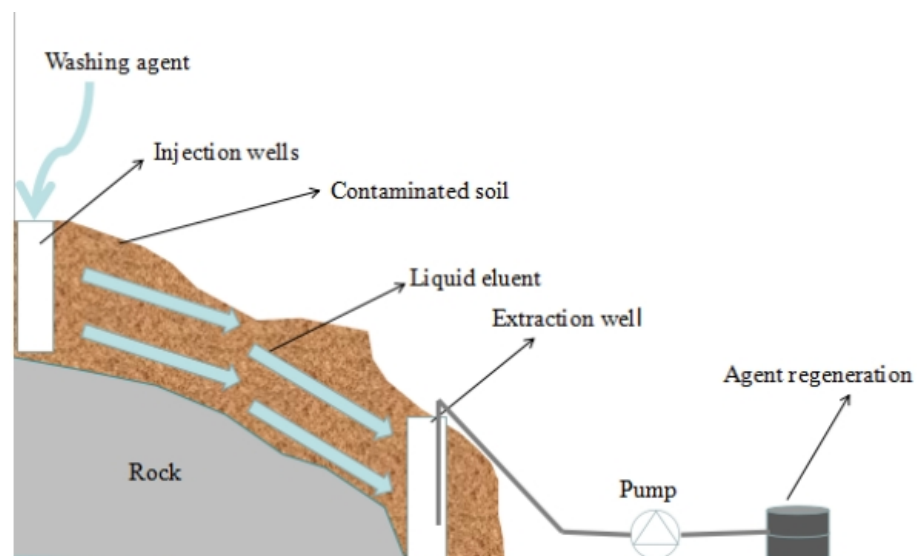


Figure 2. General procedure of in situ washing.

**Table 1.** Comparison of different washing agents.

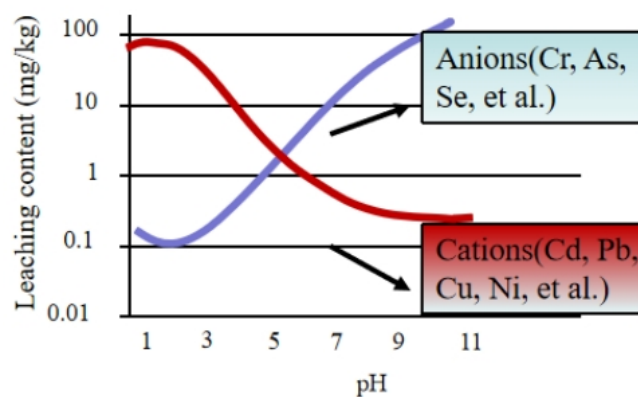
Washing Agents	Advantages	Disadvantages	Suggested Agents
Inorganic washing agents (acid, base, and salt)	High removal rate with low reaction time, except deionized water.	Destroy soil structure and cause soil nutrient loss.	FeCl <sub>3</sub>
Chemical (synthetic) surfactants	High removal rate.	High economic cost and secondary pollution.	SDS
Biosurfactants (natural surfactants)	Easily biodegradable and recyclable, it could be produced in situ and with less management.	Low production	Rhamnolipid
Humic acids	Biodegradable, in accordance with the concept of sustainable development. The structure characteristics of synthesized humic acids were controlled.	—	—
Synthetic chelators	GLDA and EDTA have high metal removal rates, and GLDA was more biodegradable than EDTA.	EDTA was not easily biodegradable and caused secondary pollution.	GLDA
Low-molecular-weight organic acids	Citric acid and tartaric acid have a high metal removal rate and are easily biodegradable.	Lower removal efficiency than synthesized chelate	CA

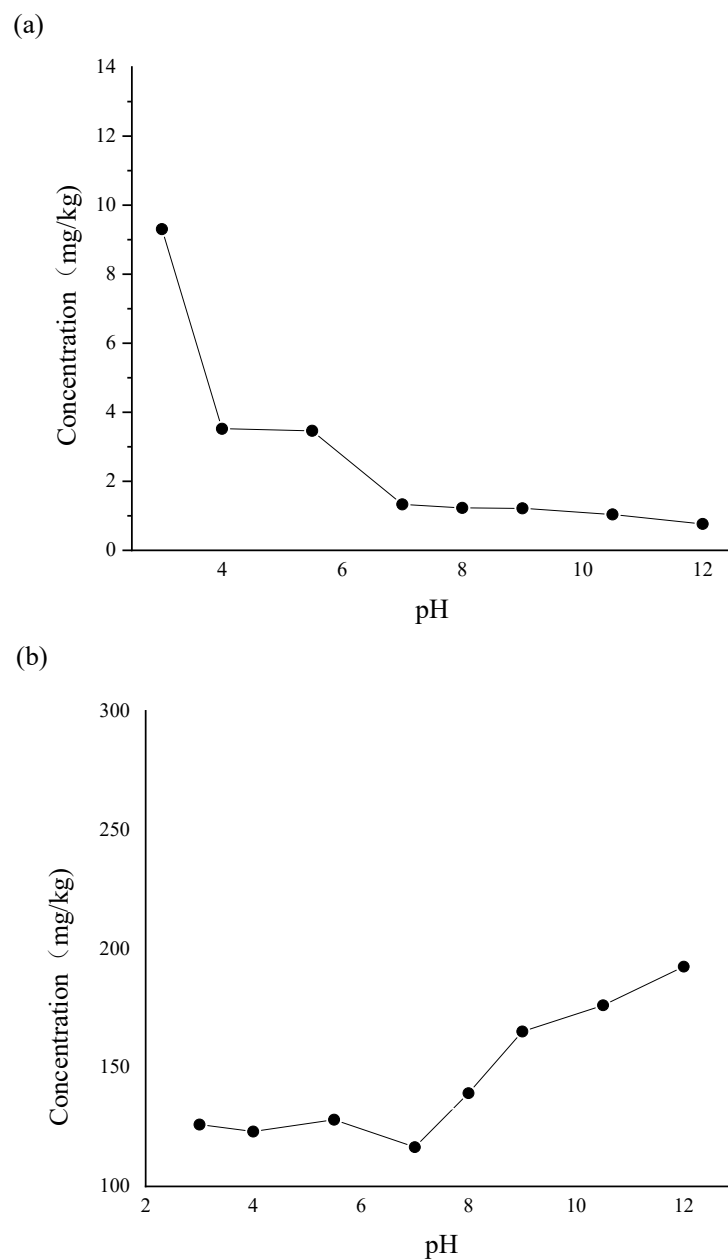
## 2. Remedial Applications of Washing Agents

### 2.1. Inorganic Washing Agents

#### 2.1.1. Acid and Base Solutions

At an early stage, acid, base, and salt were commonly used as washing agents for HMs' removal from contaminated soil, and were classified as inorganic washing agents. These washing agents could suppress the adsorption of metals onto soil particles, and then the metals could be extracted by washing agents. According to a previous study, a low percentage of water-soluble fraction metals exist in the soil. In other words, distilled water has a low removal rate for HMs [15]. Most studies have revealed that pH is a critical parameter controlling the leaching ability of metals [16]. The HMs in the soil are combined with solid residues through adsorption/desorption on mineral or organic surfaces, which is dominated by pH. The pH-dependent leaching tendency of HMs in soil could be regarded as follows: the release of cations increases with increased pH, and anions have an opposite tendency, as shown in Figure 3. According to our previous study, the regularity of Cd and W release from the soil is shown in Figure 4 (unpublished). This might be the mechanism of HMs' removal from soil by chemical washing with acid and/or base solutions, and different washing agents being used to removing various pollutants.

**Figure 3.** The schematic of leaching heavy metal ions as a function of pH.



**Figure 4.** The schematic of the leaching ability of W (a) and Cd (b) as a function of pH.

Protons in inorganic acids are the main contributors to metal removal. At the same time, some soil has a high acid buffering ability, which may lead to a lower removal rate for acid solutions, particularly for low concentration acid solutions. Moreover, the ability of HMs' retention on soil particles is positively correlated with the release of soil colloid, and more release of soil colloid was observed in acidic conditions. Thus, the loss of soil colloid may contribute to HMs' removal by washing with acid solutions [17]. Wang et al. [18] assessed the efficiency of six washing solutions ( $\text{H}_3\text{PO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_3\text{COOK}$ ,  $\text{HNO}_3$ ,  $\text{KNO}_3$ ,  $\text{KH}_2\text{PO}_4$ ) at different concentrations to find a washing solution that could minimize the damage of HMs to soil quality, and the result showed that 1%  $\text{HNO}_3$  was the optimum washing solution, which has 75.7% and 60.6% removal rates for Cd and Pb, respectively, and with the lowest cost and risks to the soil. The ligand displacement reaction of hydroxyl ions with As species, e.g.,  $\text{AsO}_4^{3-}$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{H}_2\text{AsO}_4^-$ , could be regarded as the main reason for the ability to extract As for sodium hydroxide [19]. Generally, it could be considered that an alkali solution could be used as a washing agent to extract metallic oxyanions (e.g.,  $\text{AsO}_4^{3-}$ ,  $\text{WO}_4^{2-}$ , et al.). In addition, although alkali solutions can be properly

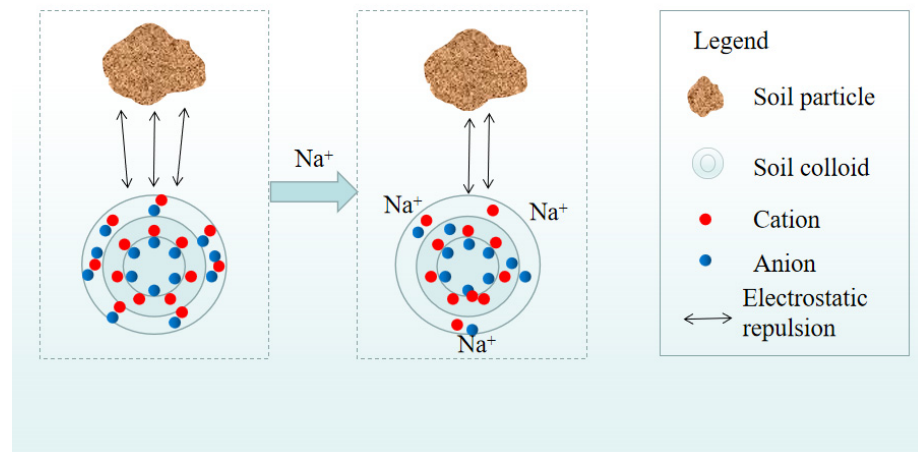
conducted to extract anionic metals such as As, the extraction rate of cationic metals such as Cd, Pb, Cu, and Zn is too low. Based on the background that most sites have multi-metal contamination, especially containing anionic metals and cationic metals simultaneously, researchers have been more willing to use acidic solutions as soil washing agents than alkali solutions.

### 2.1.2. Salt Solutions

The potent acid washing agents have a strong negative effect on the soil environment, as they acidify the soil and destroy the soil structure. Conversely, inorganic salt (e.g.,  $\text{FeCl}_3$ ) eluents have a less negative effect on the soil environment, with a good leaching effect. Common salt solutions used for soil washing include  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and  $\text{FeCl}_3$ . The metallic cations and anions in salt solutions might contribute to the extraction of HMs in the washing process. Chen et al. [20] reported that  $\text{FeCl}_3$  has a higher removal rate for Cd in clay soil than  $\text{NaCl}$  and  $\text{CaCl}_2$  solutions. After optimizing the leaching conditions,  $\text{FeCl}_3$  has a high removal efficiency of HMs. For example, Alaboudi et al. revealed that after leaching with 0.5 M  $\text{FeCl}_3$  solution for 1 h, the highest removal rate of Pb, Cd, and Cr in sandy soil can reach 93.79%, 97.4%, and 81.75%, respectively, and the mechanism was regarded as improved metal solubility after  $\text{H}^+$  was released by the hydrolysis of  $\text{FeCl}_3$ . A previous study [10] reported that As removal was enhanced with the simultaneous extraction of Zn and Ni after acid solution washing, which was attributed to the competitive oxyanions such as phosphate and sulfate decreasing the number of sites on mineral or organic surfaces for As. Beesley et al. [21] figured out that the dissolved phosphorus increased As mobility in the soil after biochar was applied to the soil, which was promoted by competitive adsorption between P and As. Thus, a phosphate solution can specifically remove As in soil, and the mechanism can be regarded as a similar structure to those of  $\text{PO}_4^{3-}$  and  $\text{AsO}_4^{3-}$  [22]. Moreover,  $\text{Cl}^-$  has a significant effect on leaching Cd and Pb from soil [23]. The study [24] reported that  $\text{Cl}^-$  can form stable complexes with  $\text{Cd}^{2+}$ , which has higher mobility than  $\text{Cd}^{2+}$ , thus, the  $\text{Cl}^-$  in a salt solution contributed to a high Cd removal rate.  $\text{FeCl}_3$  is not the optimal choice for Pb-contaminated soil washing due to the precipitation of  $\text{PbCl}_2$ , and  $\text{Fe}(\text{NO}_3)_3$  may perform better than  $\text{FeCl}_3$  for Pb removal [25]. Overall, anions in a salt solution can promote the leaching of HMs in the soil in the following ways: (1) competitive adsorption with metal oxyanion, (2) forms soluble complexes with metal cations, and (3) change the properties of soil, such as soil pH. However, the precipitation process should be considered.

In addition, Makino et al. [26] reported the efficiency of cationic chloride solutions for extracting Cd from the soil, and the results showed that the extraction efficiency of the cations of the four chlorides decreased in the following order:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ . These cations can promote ion exchange with metallic cations on the surface of soil particles and mobilize Cd in soil. Makino [27] reported the remediation of Cd-contaminated paddy soil by leaching with 0.1 M  $\text{CaCl}_2$  solution in a field scale; their remediation procedure included three steps: (1) leaching the contaminated paddy field with  $\text{CaCl}_2$  solution, (2) leaching the contaminated paddy field with water for removal of Cd and  $\text{CaCl}_2$  solutions, and (3) collecting leaching eluent for further disposal. After leaching by  $\text{CaCl}_2$  solution, 66% Cd in the original soil was removed. The presence of  $\text{Na}^+$  in the aqueous solution destroys the electrostatic balance in the diffusion double electron layer of colloidal particles and reduces the electrostatic repulsion between soil particles and soil colloids (Figure 5) [28]. After that, the loss of soil colloid and the HMs' removal rate decreased. In addition, Diao et al. [12] reported that coexisting  $\text{Na}^+$  or  $\text{Ca}^{2+}$  can enhance the washing capacity of biosurfactants, and the  $\text{Ca}^{2+}$  effect is greater than that of  $\text{Na}^+$ . However, whether other cations have a similar effect has not been studied.

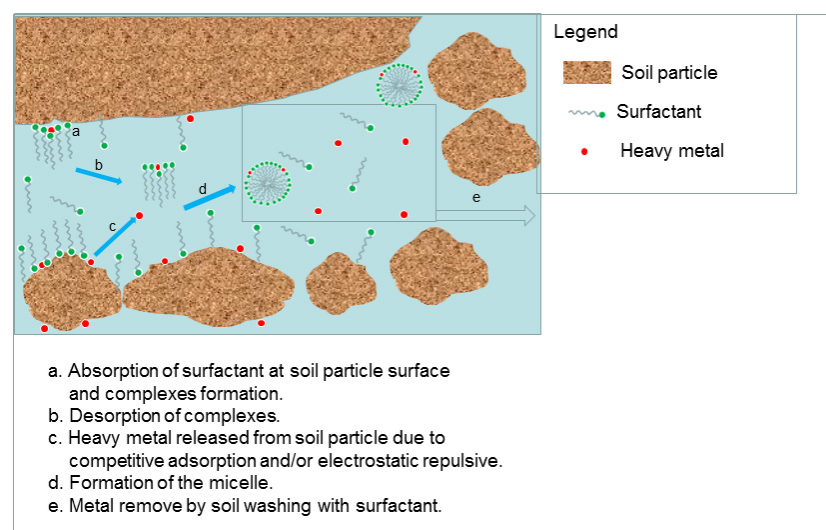




**Figure 5.** Influence of  $\text{Na}^+$  on electrostatic repulsion between soil particle and soil colloid.

## 2.2. Surfactants

Surfactants, a group of amphiphilic chemicals that contain both hydrophilic and hydrophobic parts in the molecular structure simultaneously, have proven to be promising washing agents for the remediation of HM-contaminated soil. Generally, surfactants comprise two categories in terms of the resource: chemical (synthetic) surfactants and biosurfactants (natural surfactants). Specifically, cationic, anionic, zwitterionic, and non-ionic surfactants belong to different categories because of their different hydrophilic head groups [29]. HMs in soil are generally adsorbed on the surface of soil particles, mainly in the form of ions or precipitated metal compounds. The surfactant can assist the desorption and dispersion of contaminants from soils via surfactant-associated complexation and ionic exchange [12]. Thus, surfactant-enhanced washing can be applied to remove HMs from contaminated soils. Slizovskiy et al. [30] reported that cationic surfactant DPC, nonionic surfactant Ammonyx KP, and ionic biosurfactant JBR-425 can enhance HMs' removal by the washing technic. Surfactants can not only improve the washing efficiency but also contribute to the bio-extraction of HMs from soil [31]. Hu et al. [32] studied the impact of APG surfactant on the HMs' accumulation in *Scirpus triqueter*. APG induced more HMs to gather on the root surface in co-contamination and increased accumulation amounts of Pb (9.7-fold) and Cd (1.0-fold) in the root significantly. The mechanism of soil washing for metal removal by surfactants is shown in Figure 6. In Table 2, cases regarding the use of surfactants for the remediation of site-specific contaminated soils are summarized.



**Figure 6.** Schematic of surfactant-enhanced soil washing for heavy metal-contaminated soil.

**Table 2.** Application cases of surfactants for the remediation of contaminated soil.

Surfactants	Pollutants	Application Condition			Effectiveness of Remediation	Refs
		Content	Solid–Liquid Ratio:	Washing Time		
SDS	Cd	0.01 M	—	—	Remove 94% of total Cd.	[33]
Saponin	Cu	3%	1:40	24 h	The removal rates of Cu, Cd, and Zn were 96%, 98%, and 100%, respectively.	[34]
Biosurfactant from <i>Pseudomonas</i> sp. CQ <sub>2</sub>	Cd, Cu, Pb	3%	1:30	5 days	The removal rates of Cd, Cu, and Pb were 78.7%, 65.7%, 56.9%, respectively.	[35]
Lignosulfonate	Pb, Cu	8%	1:10	6 h with 4 times	The removal rates of Pb and Cu were 67.4%, 73.2%, respectively.	[36]
Rhamnolipids	Cu, Cd	3 g TOC/L	1:40	24 h	The removal rates of Cu and Cd were 24% and 62%, respectively.	[37]
Humic acids	Hg, Cu	1%	1:10	24 h	The removal rates of Cu and Hg were 67% and 57%, respectively.	[38]
Humic acids	Cu, Pb	2%	1:8	6 h	The removal rates of Cu and Pb were 60.3% and 48%, respectively.	[39]
Humic acids	Pb, Cd	—	—	5 h	The removal rates of Cd and Pb were 70% and 40%, respectively.	[40]
Rhamnolipid	Pb	0.7%	—	—	The removal rate of Pb was 16%.	[41]
The <i>Paenibacillus</i> sp. D9 lipopeptide biosurfactant	Cu, Pb, Zn	0.4%	1:5	48 h	The removal rates of Cu, Pb, and Zn were 84.4%, 96.4%, and 57.9%, respectively.	[42]
SLES	Cd, Zn	40 mmol/L	1:5	8 h	The removal rates of Cd and Zn were 45.2% and 47.7%, respectively.	[43]
A biosurfactant by the yeast <i>Candida tropicalis</i>	Zn, Cu, Pb	1%	1:25	24 h	The removal rates of Cu, Pb, and Zn were 70%, 15%, and 80%, respectively.	[44]
SLES and rhamnolipid	Cd, Pb	40 mmol/L for rhamnolipid, 100 mmol/L for SLES	1:10	0.5 h	Rhamnolipid removed 62% of total Pb, SLES removed 89% of Cd and 88% of Pb.	[45]
SLES and rhamnolipid	Cd, Pb	40 mmol/L	—	—	Rhamnolipid removed 82.8% of Pb and 99.99% of Cd, SLES removed 98.7% of Cd and 99.8% of Pb.	[46]



Table 2. Cont.

Surfactants	Pollutants	Application Condition			Effectiveness of Remediation	Refs
		Content	Solid–Liquid Ratio:	Washing Time		
Rhamnolipid	Cu, Cd, Pb, Cr	0.8%	1:10	12 h	80.21, 86.87, 63.54, and 47.85% of Cu, Cd, Pb, and Cr were removed, respectively.	[47]
LED3A	Pb, Zn	0.7%	1:10	5 h	Decreased the percentage of Pb and Zn, respectively, from 52.1 to 22.8% and from 61.8 to 19.2% in the mobile fractions.	[48]
Biosurfactant from <i>Candida sphaerica</i> UCP0995	Zn, Pb	2.5%	1:10	24 h with 3 times	The biosurfactant removed 90% Zn, 79% Pb	[49]
cocamidopropyl betaine	As, Cr, Cu,	1%	1:10	2 h	The removal rates of As, Cr, and Cu, were 60%, 32%, and 77%, respectively.	[50]
SDBS	Zn, Cd, Pb	0.09 mmol/L for SDBS, 7% for Tween-80	—	—	SDBS removed Zn, Cd and Zn, for 84%, 74%, and 4%, respectively. Tween-80 removed Zn, Cd and Zn, for 57%, 83%, and 43%, respectively.	[51]

### 2.2.1. Chemical (Synthetic) Surfactants

Typical chemical surfactants include anionic, anionic, and zwitterionic surfactants. Zeng et al. reported that HMs in soil exist in the form of ions or precipitation, and surfactants can extract metals from the soil particle dominantly via associated complexation and ion exchange [52]. Cationic surfactants can prompt cationic metal dissolution by cation exchange. After that, the metal cations are released and are more accessible to be removed from the soil. Anionic surfactants are formatted metal–surfactant complexes by complexation and adsorption processes, and have better water solubility. The basic information of several typical synthetic surfactants is shown in Table 3. Most synthetic ionic surfactants have a molar weight ranging from 350 to 500 g/mol.

**Table 3.** The information on the several commonly used chemical surfactants.

Type	Abbreviation	Molecular Formula/mol. wt.
Cationic surfactant	DPC	C <sub>17</sub> H <sub>30</sub> CIN/283.88
	DDAC	C <sub>22</sub> H <sub>48</sub> CIN/362.08
	Ammonyx KP	C <sub>27</sub> H <sub>46</sub> CINO/436.11
	CATB	C <sub>16</sub> H <sub>33</sub> (CH <sub>3</sub> ) <sub>3</sub> NBr/364.45,
	HTAB	C <sub>16</sub> H <sub>33</sub> (CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> NBr/406.53 C <sub>19</sub> H <sub>42</sub> BrN/364.45
Anionic surfactant	PFOA	C <sub>7</sub> F <sub>15</sub> COOH/414.07
	SLES	C <sub>12</sub> H <sub>25</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>n</sub> OS <sub>3</sub> Na
	SDS	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> Na/288.38
	SDHS	C <sub>16</sub> H <sub>29</sub> NaO <sub>7</sub> S/388.45
	SDBS	C <sub>18</sub> H <sub>29</sub> NaO <sub>3</sub> S/348.48
	Texapon-40	C <sub>16</sub> H <sub>33</sub> NaO <sub>6</sub> S/376.48
	AOT	C <sub>20</sub> H <sub>37</sub> NaO <sub>7</sub> S/444.56
	Spolapon AOS 146	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>n</sub> CH = CHSO <sub>3</sub> Na & CH <sub>3</sub> (CH <sub>2</sub> ) <sub>n</sub> CH(OH)CH <sub>2</sub> SO <sub>3</sub> Na (n = 9–13)
	SLES	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> Na/382
Nonionic	Tween 80	C <sub>64</sub> H <sub>124</sub> O <sub>26</sub> /1310
	Brij-35	C <sub>12</sub> H <sub>25</sub> (OC <sub>2</sub> H <sub>4</sub> ) <sub>23</sub> OH/1198
	Triton X-100	C <sub>5</sub> H <sub>17</sub> C <sub>6</sub> H <sub>4</sub> O(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>9.5</sub> H/628

n, the number of functional group.

For HMs' removal, the existing form of the HMs should be pointed out. Typical forms of chromium and arsenic are negatively charged oxoanionic and positively charged cationic for Cd, Pb, Cu, Ni, and Zn. Specifically, cationic surfactants are not acceptable for soil contaminated by metallic oxyanion. Cationic surfactants may contribute to oxyanion retention in soils by the complexation process. Gładysz-Płaska et al. [53] investigated the mechanism of cationic surfactant sorption onto clay and restrained Cr (VI) migration. It was observed that cationic surfactants with longer tails increased chromate retention in soil. It suggested that cationic surfactants can anchor to the clay surface through the hydrophobic attraction and further immobilize the negatively charged Cr (VI), decreasing chromium removal. More recently, anionic surfactants have been used more for chromium and arsenic removal from contaminated soils. Several mechanisms might contribute to arsenic/chromium oxyanions being removed from soil by anionic surfactants: (1) anionic surfactants compete with arsenic/chromium oxyanions for the adsorption sites on soil particles, (2) there is an anion exchange reaction between arsenic/chromium oxyanions and anionic surfactants, (3) the retention of anionic surfactants in soil increase zeta potential of the soil particles and the arsenic/chromium oxyanions are mobilized by electrostatic repulsive interactions. Compared to anionic surfactants, cationic surfactants are easily adsorbed to soil-bearing particles because of the negative charge on most soil colloid particles. For this reason, more cases that use anionic surfactants for soil flushing rather than cationic surfactants were reported.

SDS is one of the most common anionic surfactants, which can elute HMs from soil [54]. Chen et al. found that the best removal efficiencies of Cd in artificially contaminated soil were obtained with 1 h washing time, and the Cd removal rate was achieved at 81.2% [55]. SDS can bind with metals and prompt their desorption from soil particles [56]. Other commonly used surfactants include DPC, DDAC, SDBS, Ammonyx KP, CATB, etc. (Table 3). Although nonionic surfactants are widely used for the remediation of contaminated soil, few studies have been applied to the research on HMs' contamination and research for organic pollutants. Compared with ionic surfactants, nonionic surfactants are easier to micellize and it is unnecessary for higher concentrations to be used to overcome the electrostatic repulsion between surfactant headgroups [57]. The ionizing process hardly occurs in water for nonionic surfactants. Some possible mechanisms of metal removal may not occur for nonionic surfactants, such as ion exchange and electrostatic repulsion. Thus, nonionic surfactants always show a lower metal removal efficiency. Mongkolchai et al. [43] reported that ionic surfactants (SLES, SDS, DTAB) possess a greater efficacy than nonionic surfactants (Tween 80) for Zn removal, and the surfactant potential for Cd removal was SLES > SDS > DTAB > Tween 80. Torres et al. [58] found that the highest removal rate of Cd, Zn, and Cu were obtained with the addition of 20 mL 0.5% of Tween 80 to 6 g soil with 23 h stirring on a laboratory scale. The best removal efficiencies of Cd, Zn, and Cu by Tween 80 achieved 85.9%, 85.4%, and 81.5%, respectively. Generally, the use of chemical surfactants on a field scale is limited due to their easy retention in the soil, high economic costs, and uncertain toxicity. Recently, with the progress of industrialization, the price of synthetic surfactants has gradually decreased. Thus, it is helpful to develop low toxicity, easily biodegradable surfactants.

#### 2.2.2. Biosurfactants (Natural Surfactants)

To avoid new pollution, which is caused by residual chemical surfactants in the soil, more researchers have used biosurfactants for soil washing. Biosurfactants are bio-available compounds with a surface-active chemical property, which not only has high HM removal ability but is also easily biodegraded, thereby avoiding secondary pollution. In recent studies, researchers found that biosurfactants have an efficient extraction rate for HMs from contaminated soil. Technically, biosurfactants can also be categorized as ionic and nonionic surfactants. Most biosurfactants are obtained from the life activity of organisms, such as the fermentation of microbials and the metabolism of animals or plants. For example, *Pseudomonas aeruginosa* can secrete rhamnolipid [59], teasaponin can be extracted from the seed of *Camellia oleifera* Abel [60], and sophorolipid can be produced by *Candida* [61].

Currently, the most commonly used biosurfactants include glycolipid (e.g., rhamnolipids, fructose lipids, sophorolipids), lipopeptide (e.g., surfactin, polymyxin), and glycoside (e.g., saponin) compounds [62]. Rhamnolipid is the most studied glycolipid biosurfactant, consisting of one or two rhamnose groups (hydrophilic part) and up to three hydroxy fatty acids (hydrophobic part). However, the main rhamnolipid-producing species is the gram negative bacterium of *Pseudomonas aeruginosa*. Several microbes (e.g., *Nocardia* spp., *Serratia rubidaea*, *Enterobacter* spp.) can secrete rhamnolipid [63]. A low critical micelle concentration enables rhamnolipids to reduce the surface tension of the solution significantly. The hydroxyl and carboxyl groups in the molecule can also be complexed with metal ions in the soil so that the HMs are released from the soil particle [64]. Juwarkar et al. [65] revealed that 92% and 88% removal rates for Cd and Pb, respectively, in soil was observed after 36 h of washing with rhamnolipid, and the microbial population of the contaminated soil was increased after washing. As an anionic surfactant, rhamnolipid can bind with cationic metals (Zn, Cd, Cu, Pb, Ni) due to its negative charge. The complex of rhamnolipid–metals has a stronger stabilizing ability than the complex of metals and soil particles. As an anion surfactant, the possible mechanism of soil washing with rhamnolipid has been listed in Section 2.2.1. More research has showcased the non and low toxicity of rhamnolipid for organisms and soil. Johann et al. [66] reported that rhamnolipid indicated low toxicity to *Aspergillus niger*. Kim et al. [67] indicated that rhamnolipid ex-

tracted from *Pseudomonas aeruginosa* strain B5 not only has low toxicity but also protects pepper from *phytophthora blight* and suppresses the *C. orbiculare* development on cucumber leaves. Many pieces of research have confirmed the efficient degradability of rhamnolipid. Chrzanowski et al. [68] studied the biodegradation of rhamnolipids, and the results indicated that rhamnolipid was quickly degradable under aerobic, anoxic, and anaerobic conditions. Saponin is the most studied glycoside biosurfactant. Mukhopadhyay et al. [69] explored the feasibility of a biodegradable plant-based surfactant (saponin) for soil washing and compared the metal removal rate of saponin and SDS (chemical surfactant). The result revealed that saponin attained up to 86 percent As removal efficiency, which was significantly higher than SDS, and saponin was suggested as a soil washing agent for removing As even from soil with high Fe content for its efficient washing rate and being biodegradable. Most kinds of biosurfactants have low toxicity and low application risk for soil washing. Thus, it has a good application prospect.

### 2.2.3. Humic Acids (HAs)

HAs are important components of soil that have amphiphilic properties, and they could be used as biosurfactants for soil remediation. Traditionally, HAs are not exactly surfactants. However, HAs have many characteristics of surfactants, so they are often used as soil washing agents to remove HMs. Therefore, researchers can broadly classify them into the category of surfactants. Generally, HAs can be extracted from agricultural waste biomass and municipal solid wastes [70], and this is in accordance with the concept of sustainable development. HAs can also be produced by chemical synthesis [71]. Thus, HAs include two categories: natural and synthetic. HAs can not only improve soil properties but also remove various soil pollutants. Therefore, more research has recently focused on washing soil with natural HAs for HMs' removal because of abundant oxygen-containing functional groups such as carboxylic [72] and phenolic-OH groups [73]. Zhang et al. [74] studied natural HAs produced by composting sesame straw for Cd removal from the soil with a washing technic. Under optimum washing conditions (optimum HA concentration, equilibrium time, pH, solid-to-liquid ratio), which were showcased by batch desorption experiments, a triple washing procedure can remove 74.16 and 42.91% of Cd and Ni from the soil, respectively. It is certain that the adverse effects of HA residues in the soil could be ignored. This is an unparalleled advantage for soil washing.

Different functional groups, such as the carboxyl group, are contained in HAs, such as acyl hydroxy, carbonyl, amine, etc., which can be complexed with metals. There are differences in the complexation stability of HAs from different sources to a selected HM ion, which is caused by the natural characteristic of HAs. While HAs obtained from various sources have different group types, amounts, and properties for complexation. Alkaline HAs with high molecular weight can stabilize HMs, specifically, (1) they stabilize HMs directly by an ion exchange reaction and complexion, (2) they stabilize HMs indirectly by changing soil properties, such as soil pH, CEC, organic matter, and microorganisms, while weakly acidic HAs with low molecular weight can mobilize HMs in the soil as a surfactant. Thus, weakly acidic HAs have been commonly used for soil washing to enhance HMs' removal. However, not all kinds of HMs can be removed by HAs. Tsang et al. [75] reported the limited effectiveness of HAs for soil HMs' removal, and they attributed this to the low metal binding affinity for natural HAs and the adsorption of HAs onto soil [76,77]. Meanwhile, Borggaard et al. [78] revealed that natural HAs extracted up to 45% and 54% of total Cd and Cu, respectively, but extracted only 4% and 7% of total Pb and Ni, respectively.

Synthetic HAs were synthesized by abiotic humification rather than biotic humification. Specifically, humic precursors transform into HAs by the catalyzation of metallic oxide. Moreover, soil washing with HAs increased the concentration of total organic matter, total nitrogen, and phosphorus. Otherwise, the quality of the soil was improved. Compared to natural HAs, synthesized HAs have the advantage of having controlled structural characteristics, which can change by changing the species of the precursors, pH, temperature, and the ratio of the catalyst. Additionally, natural HAs can be sulfonated or oxidized to

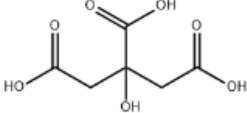
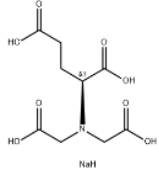
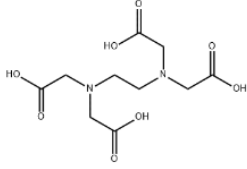
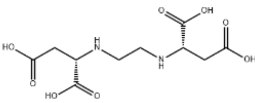
produce sulfonated HAs, nitro-sulfonated HAs, etc., and it can increase the hydrophilicity of HAs. Yang et al. [71] reported a new synthesized HA with high -COOH content for soil washing and optimized its washing condition. The result shows that 45.2% and 34.6% of Cu and Zn, respectively, were removed with single washing under optimum conditions, and HAs mainly removed HMs in the exchangeable and acids soluble and reducible fraction (BCR sequence extraction). Therefore, HAs contain specific functional groups and can be obtained by technical methods to improve the removal efficiency of HMs. The development of a specific synthesis method of HAs and exploration of the mechanisms of washing with HAs will be helpful to the wide application of Has.

### 2.3. Chelators

The chelators can form stable water-soluble complexes with HMs through chelation, which can mobilize HMs from insoluble phases. Chelators have fewer adverse effects on soil structure and plant productivity, and more researchers have used chelators for soil washing. Technically, chelators can be divided into two categories: synthetic chelators and low-molecular-weight organic acids

Chelators are a class of compounds with lone electron pairs available for coordination, and they can form complexes with metal ions through coordination bonds. After complex interaction, HMs can be transformed from an insoluble form to a soluble one and become easily removed from the soil. The efficacy of chelators in metal extraction is usually assessed by the stability constant (Ks) of the chelators–metal complexes [79]. For selected HMs, the removal efficiency of the metal by different chelators can be judged by Ks. Generally, the chelators with larger Ks have a higher metal removal ability. It is impossible to compare the removal ability of a certain chelator for different metals by the value of Ks. The removal rate is influenced by the existing forms of the metals and the migration ability. A part of the common stability constants of metal–chelate complexes are listed in Table 4.

**Table 4.** Stability constants (log KML) of metal–chelate complexes in the assay mixture.

Washing Agents	General Structural Formula	Heavy Metals	Ks
CA		Cd	3.5
		Ni	3.36
		Cu	5.9
		Pb	4.1
		Zn	4.86
		Mn	2.55
GLDA		Cd	10.31
		Ni	12.74
		Cu	13.03
		Pb	11.6
		Zn	11.52
EDTA		Cd	16.5
		Ni	18.4
		Cu	18.78
		Pb	18
		Zn	16.5
EDDS		Cd	10.9
		Ni	16.7
		Cu	18.36
		Pb	12.7
		Zn	13.4

### 2.3.1. Synthetic Chelators

Aminopolycarboxylates, are category compounds with coordination groups (hydroxyl and amino). Not all kinds of aminopolycarboxylates are suitable for field scale applications of soil washing. Commonly used aminopolycarboxylate chelates for soil washing in a field scale include EDTA, EDDS, and GLDA. Additionally, some other aminopolycarboxylates are limited to the laboratory research scale, such as NTA and diethylene triamine pentaacetic acid (DTPA), because these agents are hazardous to human health and soil ecology [80,81]. Gluhar et al. [82] compared the removal rate of GLDA, IDS, and EDDS to EDTA for Pb, Zn, and Cd in multi-contaminated soil. The results found that the removal rate of GLDA is higher in the former, which achieved 78% and 33% for Cd and Ni, respectively, and it was approximately equivalent to EDTA (71% and 29% for Cd and Ni, respectively), while for Pb, EDTA has a higher removal rate (75%) than GLDA (58%). Kaurin et al. [83] also confirmed that EDTA has a slightly higher metals mobilization ability than GLDA and EDDS, which was consistent with the study of Wang et al. [84]. Generally, EDTA has high removal efficiency of HMs.

For commonly used chelate, compared to EDTA, easily biodegradable agents (such as EDDS, MGDA, and GLDA) have more potential for soil washing. EDTA has poor performance in photochemical degradation and biodegradation and is prone to long-term existence in the soil environment. It also has a negative effect on soil organic matter, total nitrogen, and available elements (K, Ca, and Na), and even inhibits the growth of organisms [20,85,86]. Soil physical characteristics are affected after EDTA washing and amendment with inorganic and organic additives. Qiao et al. [87] studied the washing efficiency of EDDS and EDTA for soil containing Cd. The results found that the removal rate of EDTA for Cd reached 92.4%, and EDDS reached 46.8%, while EDDS had less toxicity to crops. The degradation performance of EDDS in soil was researched by Khalid et al. [88]. A 100% degradation rate was observed on the 54th day after soil washing. Gao et al. [89] investigated the ability of EDTA, GLDA, and CA (citric acid) to remove Cd and Ni from polluted soil. EDTA has a higher removal rate than CA and GLDA, but the adverse effects of GLDA and CA washing on soil enzyme activity are significantly lower than EDTA. Thus, considering both leaching efficiency and ecological safety, biodegradable GLDA can be used as a good substitute for the conventional washing agent (EDTA). Moreover, IDS is also considered a new chelator, which has a good biodegradation performance. The research revealed that 80% of IDS could degrade in 7 days and lead to lower environmental toxicity.

### 2.3.2. Low-Molecular-Weight Organic Acids (LMWOA)

LMWOA has a lower molecular weight than aminocarboxylic acids. These substances can desorb or dissolve HMs from the surface of soil particles. Then HMs are diffused into the soil solution and are easier to remove from the soil by washing [90]. Commonly used LMWOA for soil washing include CA, TA, OA, AA, etc. LMWOA enhances HMs through the formation of soluble chelates, which are produced by the interaction between organic acid radicals and HMs [91]. Li et al. [92] found that CA and TA have a high removal rate for Cd, which achieved 73% and 62%, respectively. Compared to them, AA and OA were lower. Two possible reasons that may contribute to the higher removal rate of CA and TA are as follow: (1) acidic conditions, the pH values of the CA and TA solutions were 1.6 and 1.3, respectively, and were lower than AA and OA (based on the same concentration). A stronger acidic condition was beneficial to metal mobilization. (2) The chelation reaction: CA and TA have more ligands, which are conducive to chelating HMs. OA has a low removal rate for Zn, Cu, and Cd, which is attributed to the formation of insoluble oxalate precipitation [93]. Thus, the possible precipitation interactions between LMWOA and metals must be considered.

Generally, LMWOA is easily biodegradable. For example, 70% of CA can degrade in 20 days, and has few adverse impacts on soil and crops [94]. Tan et al. [95] investigated the influence of different washing parameters (washing concentration, solid-liquid ratio, time, and pH value) on the remediation efficiency for Cr-contaminated soil using CA.



Under optimal washing conditions, the Cr removal rate reached 73.52%. The optimum washing condition was as follows: a content of 0.3 mol/L CA solution, a solid–liquid ratio of 1:10, pH 4, and a washing time of 6 h. Additionally, little effect of washing with CA on soil structure and surface morphology was observed by an X-ray diffractometer and scanning electron microscope. Wei et al. [96] used OA, CA, and TA as agents for As-contaminated soil washing, and the results showed that the removal efficiency was in the order of OA > CA > TA. This order can be regarded as more strongly acidic than CA and TA. For Cr, a kind of metal that exists in oxyanion, its mobilization ability was positively correlated with pH, and acidic conditions may immobilize Cr and reduce the removal rate. Thus, weak acids such as OA and AA have better application prospects for metallic oxyanion washing.

### 3. Combined Utilization of Washing Agents

The combined utilization of washing agents includes two application procedures: (1) a mixture of several agents for soil washing and (2) sequential washing with several agents. Informers can obtain the synergetic effect for soil washing. For example, nonionic surfactants reduce the electrostatic repulsion between the ionic surfactants and soil, so a mixture of both sides tends to have a stronger metal solubilizing ability. Lee et al. [97] reported that combined utilization of two types of surfactants can decrease the critical micelle concentration and improve washing efficiency. Zhang et al. [98] studied the Pb removal rate using a mixture of saponin and CA for washing; the results showed that the removal rate could be achieved at 56.2% for soil from a mining area, which is greater than single CA washing. Early research has revealed that EDDS facilitates the complexation interaction between saponin and HMs [99]. Cao et al. [100] attempted to probe the simultaneous removal of Pb and Cu in the soil with a mixed solution of EDDS and saponin. The mixture agent supplied the optimum removal rate, which was higher than a single application of EDDS or saponin.

Additionally, the commonly used single washing agent has limitations in the case of the simultaneous existence of As and other HMs. For example, Wei et al. [101] used EDTA\_2Na as a washing agent for Cd-Pb-As co-contaminated soil, and, compared to Cd and Pb, the removal rate for As was not significant. In the same study, the researchers found that the mixture of EDTA\_2Na and phosphoric acid has higher washing efficiency than on their own, and the removal rate for As, Cd, and Pb was 42.0%, 52.0%, and 55.6%, respectively. The limitation of the single agent used for As removal was overcome. Many studies have confirmed that mixed washing agents have application prospect for multi-metal-contaminated soils [102–104]. Mao et al. [105] figured out that an appropriate mixing of several washing agents could increase HMs' removal and inhibit the agent's residue of individual surfactants on soil, which leads to less harm to soil properties and ecology.

Another combined utilization of washing agents was sequential washing with several agents. Zhang et al. [106] conducted a sequential washing test to improve the Pb and Cu removal efficiency; an EDTA and CaCl<sub>2</sub> solution was used as a washing agent. The result suggested that sequential washings were effective in dissolving and removing HMs compared with a single washing. Yang et al. [107] conducted a simple combined solubilization and eluent drainage system to remove Cd and Cu from the soil; sequential two-stage CA–water washing removed 68.9% of total Cd and 41.4% of total Cu, and it was higher than single CA (61.4% and 31.4 for Cd and Cu, respectively). Sequential washing with CA and water successively can also decrease the CA remaining in the soil. Thus, sequential washing can apply an agent with a high HMs' removal rate but may cause environmental risks in the early stage, and then remove the washing agent injected in the early stage by the secondary washing stage. However, the combination of agents and the feasibility of application need to be further researched. Table 5 has summarized some cases of combined utilization of washing agents.

**Table 5.** The overview of application of cases of combined utilization of washing agents for the remediation of contaminated soil.

Washing Agents	Combined Utilization Method	Heavy Metals	Main Results	Refs
GLDA-VC, GLDA-CA	Mixture washing	Pb, Cu, Zn	The mixture of GLDA-VC removes approximately 90% of Pb and 70% of Zn, and the mixture of GLDA-AC has a greater extraction efficiency for Cu.	[108]
HCl-VC, HCl-HH, VC -EDTA_2Na	Mixture washing	Pb	HCl-VC washing has a higher Pb removal rate (98.6%) than HCl-HH (88.6%); VC- EDTA_2Na has a good performance in removing iron oxide bound Pb.	[109]
Saponin-rhamnolipid	Mixture washing	Ni, Cr, and V	Maximum removal rates were obtained as 87%, 71% and 70% for Ni, Cr, and V, respectively.	[110]
sulfuric acid-phosphoric acid	Mixture washing	As, Cu, Pb, Zn	The removal rates were 71%, 80%, 80%, and 71% for As, Cu, Pb, and Zn, respectively. The mixture agent increased the extraction efficiencies from the contaminated soils for all kinds of heavy metals.	[111]
EDTA-LMWOA (CA, TA, OA)	Mixture washing	Cu, Ni, Zn	After mixture agents washing, the heavy metals' removal rates were more than about 80% under the optimal conditions. Moreover, the soil toxicity risk caused by agent was decreased, and the residual heavy metals in soil were immobilized.	[112]
CA-surfactants (Tween 80, SDS, BCD, HAs)	Mixture washing	Cu, Zn, Pb	The removal rate of Cu, Zn, and Pb can be promoted by adding surfactant to CA. Mixture agents can absolutely decrease the ion exchange fraction, carbonates bound fraction, and Fe-Mn oxides bound fraction proportion of Cu, Zn, and Pb, and increase sulfide fraction, organic bound fraction, and residue fraction.	[35]
EDTA-CA, DTPA-CA	Sequential washing	Cd, Pb	The combined utilization of EDTA or DTPA with CA can effectively enhance the washing of Cd and Pb. After continuous three stages of soil washing with EDTA-CA, the Cd and Pb removal rate reached 63.5% and 70.3%, respectively. Removal rates of 61.4% and 72.5% were obtained for DTPA-CA.	[80]
FeCl <sub>3</sub> – CA	Mixture washing	Cd, Cu, Zn, Pb	A mixture FeCl <sub>3</sub> – CA removed 78.9% Cd, 15.8% Cu, 34.0% Zn, and 18.1% Pb from soil, respectively.	[113]
CA/Tween 80, Tween 80/CA, Tween 80-CA	Mixture washing and sequential washing	Cu	After washing with CA/Tween 80, Tween 80/CA, and mix washing, the removal efficiencies for Cu were up to 85.7%, 78.1%, and 84.4%, they were higher than washing with single Tween 80 or CA (0.1% or 76.7%).	[114]
EDDS-EDTA	Mixture washing	Cu, Zn, Pb	The combined use of EDDS-EDTA reached equivalent extraction efficiency of the target metals as EDTA, while, compared to EDTA washing alone, 50% dosage of EDTA was reduced, and with lead less risk.	[115]

Table 5. Cont.

Washing Agents	Combined Utilization Method	Heavy Metals	Main Results	Refs
Mixture chelator (CA, EDTA)–FeCl <sub>3</sub>	Mixture washing	Cd, Pb, Zn, Cu	After mixture agent washing, removal rates of Cd, Zn, Pb, and Cu were 28%, 53%, 41%, and 21%, respectively.	[116]
CA/DOC	Sequential washing	Cd	The washing efficiencies of Cd and Cu were significantly increased by using two-stage sequential washing with the sequence of CA/DOC. The potential from soil Cd was lowered by 33% from moderate to low risk, and soil nutrient contents increased.	[117]
R/R/R, R/R/S, R/S/R, R/S/S (S, saponin, R, rhamnolipids)	Sequential washing	Pb	Pb removal rate reached 64–73%, respectively, with the R-R-R, R-R-S, R-S-R and R-S-S triple sequential washing. The highest Cu removal rate was achieved 87.4%, with S/S/S sequence. Moreover, the loss of biosurfactants was below 10% after each washing.	[118]
Phosphoric acid, OA, and EDTA_2Na with different sequence order.	Sequential washing	As, Cd	Soil washing agents and their washing order has a critical effect on removal rate. Phosphoric acid/OA/EDTA_2Na sequence was identified as optimal soil washing condition for As and Cd co-contaminated soil.	[119]
Biosurfactant–HCl	Mixture washing	Cu, Pb, Zn	The removal rates of Cu, Pb, and Zn with mixture washing were 86.7%, 98.6%, and 59.1%, respectively, which were higher than washing with single biosurfactant (84.4%, 96.4%, and 57.9%).	[51]
Biosurfactant–HCl, Biosurfactant–NaOH	Mixture washing	Cu, Pb, Zn	After washing with biosurfactant–HCl, removal rates of Cu, Pb, and Zn were 75%, 75%, and 85%, respectively, and 44%, 22%, 45% removal rates for washing with biosurfactant–NaOH.	[39]
NPAM-CA	Mixture washing	Zn	The NPAM caused synergistic effects on CA during washing, leading to an increase in Zn removal by 5.0 g/L CA of 10.60%.	[120]
Phosphate–saponin	Mixture washing	As	There was an 80% removal rate of arsenic from soil when treated with a mixture of 1.5% saponin, 100 mM phosphate at a soil–solution ratio of 1:30.	[121]

Agent A/agent B, sequential washing with the order of agent B after agent A. Agent A–agent B, the mixture of Agent A and agent B is used as a washing agent.

#### 4. The Effect of Washing Conditions

The main factors affecting the leaching effect of heavy metals include the concentration of agents, the washing time, the soil/liquid ratio, and pH. Generally, the higher the concentration of the agent, the longer the washing time, and a higher liquid/solid ratio caused a more efficient washing rate. The high soil/liquid ratio may have an efficient washing rate, but it determines the amount of washing agent and the washing wastewater output. A low ratio leads to an insufficient washing rate. Generally, for inorganic washing agents, the appropriate soil/liquid ratio is 1:5 to 1:10, while the soil/liquid ratio for bio-surfactants is about 1:40 (Table 2). However, an excessively low soil/liquid ratio will lead to the production of more wastewater output and need a higher energy input. In general, a low soil/liquid ratio may lead to a higher washing rate, but it is not linearly related. For example, the efficiency does not increase continuously with the prolongation of the washing time when the optimal washing time was achieved. Moreover, with the leaching of active-form HMs, the dissolution of residues will consume a large amount of the washing agent, leading to more stability. pH values affect the ability of a washing agent to extract HMs by altering the ion concentrations in the liquid phase, adsorption and desorption processes, and ion exchange behavior, as well as the re-adsorption mechanisms associated with newly formed metal–chelates [122]. In addition, as discussed in Section 2.1.2, acid solutions are a kind of efficient washing agent. Generally, HMs are more easily desorbed from soil particle surfaces at lower pH values. However, not all of the research followed the rule. For example, a strongly acidic environment weakened the electrostatic adsorption by reducing the strength of the electrostatic and enhanced soil washing. A high Eh environment enhances washing by influencing HMs' chemical forms [123]. Contact time is one of the critical parameters that affect the washing process. The reaction equilibrium time for different leaching agents and pollutants in soil differs. The washing time of HMs is generally between 0.5 and 24 h. Researchers have suggested several mathematical models for the simulation of HMs' kinetic release by soil washing [124].

Therefore, the determination of optimal conditions is extremely important for elution technology. Before the field scale washing is carried out, it is advisable to carry out lab-scale experiments to obtain the best washing conditions, and the engineering application should be carried out under optimal conditions, which can achieve a higher pollutant removal rate with lower agent consumption and engineering cost.

#### 5. The Application of Soil Washing in Pilot Field Studies

The application of soil washing for remediation at a field scale in European and American countries is relatively reliable, and it is available on a commercial scale. The 2007 Annual Status Reports database revealed that soil washing had been implemented at only two Superfund sites, and several cases had failed in the framework of the Superfund program [8]. Soil washing was carried out in a Cd production base in Oregon, USA. The washing reduced the Cd content in the soil from 5 g/L to 50 mg/L [125]. In Winlow Township, New Jersey, USA, soil washing was used to remediate a site with 4 hm<sup>2</sup> of polluted soil. In that site, all Cu, Ni, and Cr contents in the soil exceeded 10 g/kg, while, after washing, Cu, Ni, and Cr contents were reduced to 110, 25, and 73 mg/kg, respectively [126]. However, soil washing has a shorter history in China. It mainly focuses on the selection of washing agents, the optimization of washing conditions, and the improvement in washing efficiency. From 1970, some field scale applications were carried out in China. For example, the farmland of Silong Town in Baiyin City, China, was contaminated by sewage irrigation, and the land was abandoned for farming. Soil washing was used for soil remediation, and, after that, the contamination was eliminated. Chemical washing was also used in Dongdagou Base, which reduced contamination to an acceptable level [127]. Several implemented soil washing cases on a field scale are listed in Table 6 [128].

**Table 6.** Some field applications of soil washing technologies.

No.	Soil Field Site and Location	Year	Pollutant
1	Abandoned small arms firing ranges, USA	1990	Pb
2	Smelting plant site, USA.	1991	Pb
3	Battery manufacturing site, USA.	1995	Pb
4	Wood preserving site, UAS.	1990	Cu, Cr, As
5	Citric acid factory, Wuxi City, China.	2008	Cu, Zn, Pb
6	Electroplating factory, Wuxi City, China.	2011	Cr, Cu, Ni, Pb, Zn
7	Polluted farmland, Baiyin City, China.	2011	Cd, As, Pb, Hg
8	Polluted farmland, Zhuzhou City, China.	2012	Cd, Pb
9	Dye factory, Wuhan City, China.	2012	Pb, Hg, Cd, Cr
10	Cr-contaminated soil, Xiyang City, China.	2013	Cr
11	Cr slag storage site, Shijiazhuang City, China.	2014	Cr
12	Industrial site, Hengnan City, China.	2014	All kinds of HMs.
13	Polluted farmland, Qingyuan City, China.	2015	Cu, Cd, As
14	Steel plant site, Guangzhou City, China	2015	Cd, Cr, Cu, Ni, Pb, Zn, As
15	Chemical plant site, Haibei City, China	2016	Cr

## 6. Conclusions

In the manuscript, the review summarized the fundamental aspects of using washing agents for the remediation of contaminated soil. Inorganic acids and salt solutions have high removal rates of HMs, but they may cause severe damage to soil structure. The use of synthetic surfactants and chelators are generally often limited by economy cost and residual risk. Accordingly, biosurfactants, HAs, and LMWOA are suggested washing agents. A massive and cost-effective production is critical to promoting the extensive use of biosurfactants and HAs. Moreover, the combined utilization of several washing agents is necessary for the selected site to obtain a higher washing efficiency, but the combined utilization methods need to be investigated.

## 7. Future Prospects and Recommendations

- (1) For the in situ soil washing technology, the blank seepage area caused by the heterogeneity and anisotropy of the soil structure should be considered in practical application. For the ectopic soil washing technology, the transformation of research results should be strengthened in practical application, the washing efficiency should be improved, and the leaching equipment with low cost and broad applicability should be developed.
- (2) The development of low-cost green washing agents should be promoted. They do not affect soil fertility, do not damage the original structure and physical and chemical properties of the soil, do not cause secondary pollution to the environment, and the eluent should be easily available.
- (3) The combination of multiple soil remediation technologies is an inevitable trend in dealing with complex contaminated sites. Soil washing technology can be combined with other soil remediation technologies to further improve and be popularized through the soil remediation demonstration project for contaminated sites.
- (4) The development of washing eluents' recovery, regeneration, and reuse needs to be achieved. Soil washing technology would produce a large amount of eluent, which may cause secondary pollution if the eluent is not treated effectively. Moreover, HMs in eluent are an important resource, and the extraction of HMs follows the concept of sustainable development.
- (5) Currently, most of the research focuses on screening eluents' conditions. The intensified research on the washing mechanisms may be more conducive to apply washing technology.

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## Abbreviations

The following abbreviations were used in this manuscript:

AA	Acetic acid
Ammonyx KP	Oleyl dimethyl benzyl ammonium chloride
AOT	Bis(2-ethylhexyl) sulfosuccinate sodium
APG	alkyl polyglucoside
BCD	beta-cyclodextrin crystalline
Brij-35	Poly(oxyethylene)23 dodecyl ether
CA	Citric acid
CATB	Cetyltrimethylammonium bromide
DDAC	Didecyl dimethyl ammonium chloride
DOC	dissolved organic carbon which
DPC	Dodecylpyridinium chloride
EDTA	Ethylenediaminetetraacetic acid
EDDS	Ethylenediamine- <i>N,N'</i> -disuccinic acid
GLDA	Glutamate <i>N,N</i> -diacetic acid
HAs	Humic acids
HH	Hydroxylamine hydrochloride
HTAB	Hexadecyl trimethyl ammonium bromide
IDS	Tetrasodium iminodisuccinate
LED3A	Sodium <i>N</i> -lauroyl ethylenediamine triacetate
LMWOA	Low-molecular-weight organic acids
MGDA	Methyl glycine diacetic acid
NPAM	Nonionic polyacrylamide
NTA	Nitrilotriacetic acid
OA	Oxalic acid
PFOA	Perfluorooctanoic acid
TA	Tartaric acid
Texapon-40	Sodium lauryl ether sulfate
SDBS	Sodium dodecyl benzene sulfonate
SDHS	Sodium dihexyl sulfosuccinate
SDS	Sodium dodecyl sulphate
SLES	Sodium laureth sulfate
Spolapon AOS 146	Linear sodium alkene sulfonates and hydroxyalkanesulfonates (C12–C16)
Triton X-100	Polyethylene glycol octyl phenyl ether
Tween 80	Polyoxyethylene sorbitan monooleate
VC	ascorbic acid

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