Effects of Washing Solution, Washing Time, and Solid-Solution Rate on the Maximum Heavy Metals Removal Efficiency

Min-Suk Kim 1, Namin Koo 2, Jeong-Gyu Kim 3,* and Sang-Hwan Lee 4

Abstract: In Korea, for heavy metal-contaminated soil, there are insufficient basic data as well as field application cases for soil washing. This study was conducted to suggest the significant factors and optimal operation conditions for the maximum heavy metal removal efficiency. Five types of washing solution [acid solution (HCl), citric acid, oxalic acid, EDTA, and CaCl2], washing time (10–360 min), and solid-solution ratio (1:2–1:100) were selected as significant operational factors. Non-observed effect concentration (NOEC) and central composite rotatable design (CCRD) were applied to derive the optimal conditions. The soil pH was slightly alkaline, and it was highly contaminated by Cd (17.34 mg kg⁻¹), Cu (307.76 mg kg⁻¹), Pb (714.78 mg kg⁻¹), and Zn (1755.47 mg kg⁻¹), complexly. For all heavy metals, CaCl2, a neutral salt, was difficult to achieve the remediation goal. On the other hand, Cd, Cu, and Pb were removed successfully from the soil by acid solution, citric acid, oxalic acid, and EDTA. For Zn, only acid solution and oxalic acid could meet the remediation goal (300 mg kg⁻¹). As the washing time increased, the heavy metal removal efficiency showed a tendency to increase overall. Especially, oxalic acid and acid solution were able to reach the highest efficiency point within 30 min, whereas citric acid and EDTA took 2 to 4 h at the longest. In the case of 1 M citric acid, through the CCRD experiment, optimal operation conditions (solid-solution ratio and washing time) could be deduced for each heavy metal. Furthermore, this series of processes can be utilized as a useful tool to find the optimal operating conditions and, at the same time, achieve the remediation goal.

Keywords: central composite rotatable design; low molecular weight organic acid; non observed effect concentration; soil remediation goal

1. Introduction

Remediation technologies for soil remediation are broad classifications and are broadly divided into three types: biological, chemical, and physical methods [1]. The biological treatment method is a method of performing soil purification based on the mechanism of bio-degradation and bio-transformation of pollutants using soil microorganisms or plants [2]. Recently, it is one of the technologies receiving a lot of attention as the demand for environmentally friendly and sustainable development increases. However, it is also true that the biological treatment method requires a lot of time and labor and has a disadvantage in efficiency due to the actual physical and chemical treatment method [3]. Chemical treatment methods include methods such as chemical immobilization, fluid extraction, and oxidation. The chemical treatment method has relative advantages in terms of treatment time and labor input and also shows a higher pollutant removal efficiency than the biological treatment method in purification efficiency [1,4]. However, the chemical treatment method has the disadvantage that the main purpose is to reduce the risk of pollutants, and it does not aim to completely remove the pollutants from the field [1].
Physical treatment methods include capping, cementitious waste forms, in-site vitrification, sorting, vapor stripping, and soil washing. Physical treatment techniques are treatment methods aimed at removing and isolating possible contaminants [5]. Similar to the chemical treatment method, it has many advantages in treatment time and efficiency but has the disadvantage of destroying the original soil function by causing a change in the biological quality of the soil [1,5].

However, the soil washing technique combined with the physicochemical treatment method can suppress the aforementioned problems through the selection of a cleaning agent and change of the treatment process and has advantages compared to other methods in treatment efficiency and cost input [6]. In fact, the US Environmental Protection Agency (US EPA) states that the soil washing method costs $80–170 per ton of contaminated soil, which is less expensive than the chemical oxidation method ($130–390/ton) or the in-site vitrification method. In addition, the treatment time shows a relatively high treatment efficiency by treating about 2–4 tons of contaminated soil per hour [4].

Soil washing is a physical and chemical method that reduces the volume of pollutants by removing pollutants with an appropriate washing solution after excavating the soil and undergoing a pretreatment process to remove large substances or soil dumps [7]. Soil washing is used as a generic term for chemical extraction and soil washing, and the USEPA used water as a solvent and chemical extraction solution with additives such as surfactants and chelating agents [7,8]. Thus, it is defined as a process for separating contaminants. That is, soil washing is a series of wet processes for removing pollutants from soil contaminated. A typical soil washing procedure consists of the following three steps: (1) chemical extraction, (2) particle separation, and (3) treatment after washing [4,8,9]. For a wide range of soil types and incoming pollutant concentrations, in some cases, remediation targets of less than 1 mg kg\(^{-1}\) can be achieved [10]. The cost for waste separation and waste volume reduction is relatively low; hence, it can be used as a closed device, allowing the release of volatiles to be controlled. Additionally, it can be used as an effective pretreatment process for biological restoration [11]. However, contaminants are not destroyed and move to the washing solution and fine soil particles, so the washing solution and fine soil particles need secondary treatment or to be treated as hazardous waste, and the sludge generated during the wastewater treatment process must be treated. In addition, it is highly dependent on chemicals, and an additional pretreatment step is required when the organic content is high [4,7,12].

There are more than 4600 abandoned mines in the Republic of Korea, polluting the environment over a long period of time, and heavy metal contamination of the soil is one of the important environmental issues to be resolved [13]. Because the domestic soil environment conservation law managed the total content of heavy metals extracted from aqua regia as a standard method, in order to meet the legal standards, it is essential to reduce the total concentration of heavy metal below the standard before reducing the bioavailability of heavy metals. Under these circumstances, soil washing is the main remediation technique to achieve the remediation goal. As the soil restoration work in Korea is limited to oil-contaminated sites, the response to heavy metal contamination is relatively incomplete, and the age of the soil restoration project is short, so various technologies are not applied [14]. The biggest limitation in applying the soil washing method is that there is little information about the factors affecting the performance of this method because there are few cases applied in the field to date. For the field application of the soil washing method, it is essential to review the main matters such as the type and characteristics of pollutants, equipment maintenance, soil characteristics such as the particle size of contaminated soil, residence time, solid-liquid ratio, and selection of an appropriate washing solution [1,5–7]. In particular, in Korea, there have been few comprehensive reviews of an approach to remediate soil that has been complexly polluted for a long period of time with a soil washing method. Studies have been conducted on the selection of an appropriate washing solution for single heavy metal contamination and the operating conditions of the soil washing for oil-contaminated soil on a pilot scale [15,16].
Therefore, this study was conducted to evaluate the optimal operation factors for the application of the soil washing method based on a chemometric approach. In addition, this study is to evaluate the degree and type of heavy metal contamination using actual contaminated soil and to suggest washing factors applicable to the characteristics of contaminated soil. Detailed factors to consider include the selection of a cleaning agent and application concentration and the setting of cleaning time and solid-liquid ratio. In addition, the cleaning efficiency and limiting factors for each polluted soil characteristic were evaluated by comparing the chemical distribution of heavy metals, the physical distribution of soil particles, and the cleaning efficiency.

2. Materials and Methods
2.1. Soil Sampling and Soil Analysis
Heavy metals contaminated agricultural soil was collected from the abandoned mine area near the Gahak mine in Gyeong-gi Province, Korea. Ten points of soil samples were collected using a hand auger and homogenized for a composite sample. After air dried, the soil was passed through a 2 mm sieve and stored in a polyethylene bottle until soil analysis.

Soil pH, electrical conductivity (EC), total organic carbon (TOC), exchangeable cations (Ca, K, Mg, and Na) were analyzed, followed by the Method of Soil and Plant Analysis [17]. Soil particle distribution was analyzed using the wet sieve method [18]. Aqua regia solution (HNO$_3$:HCl = 1:3) was used to determine the total concentration of heavy metals (As, Cd, Cu, Ni, Pb, and Zn) in soil followed by ISO 11466 [19]. Sequential extraction analysis was performed to find out the binding form of heavy metals in the soil. In this study, the three-step BCR (The European Community Bureau of Reference) method devised by Quevauviller et al. [20] was used. According to the BCR method, carbonates binding form was examined using 0.11 M CH$_3$COOH solution (agitation at 25 °C for 16 h). In addition, the Fe/Mn-binding form was determined using 0.1 M NH$_2$OH·HCl (pH 2) solution (agitation at 25 °C for 16 h). After that, the organic/sulfide-binding form was analyzed using H$_2$O$_2$ + 1 M NH$_4$OAc (pH 2) solution at 85 °C until all organic matter was oxidized. The last residual form was determined using the aqua regia solution. Quantification of heavy metal concentration in solution was conducted using induced plasma coupled optical emission spectrophotometry (ICP-OES, Agilent, Santa Clara, CA, USA). Certified reference material (Montana Soil SRM2711, National Institute of Standards and Technology) and blank were examined to validate the quality control.

2.2. Experiment for the Selection of Washing Solution
A washing test was performed on 4 types of heavy metals (Cd, Cu, Pb, and Zn) that exceeded legal standards among 6 types of trace elements. Acidic solutions using HCl, citric acid, oxalic acid, CaCl$_2$, and EDTA were chosen to compare the maximum washing efficiency. The washing time and solid-liquid ratio, which are the basic conditions for the washing experiment, were fixed at 30 min and 1:20, respectively, through a preliminary test. For each washing solution, the 8 types of concentrations (0, 1, 5, 10, 50, 100, 500, and 1000 mM) were used in the experiment. However, for EDTA, which has low solubility under general conditions, 100 mM was applied at the maximum concentration, and the acidic solution was divided into 12 steps (HCl 1, 3, 5 M, and pH 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5). For a detailed experiment, each solution was prepared at a target concentration using 2 g of soil, put 40 mL each in a polyethylene bottle, stirred for 30 min using a bench-top horizontal shaker, and immediately centrifuged and analyzed with ICP-OES.

2.3. Experiment for the Selection of Washing Time
Three types of washing solutions were used: citric acid (1 M), oxalic acid (1 M), and EDTA (50 mM), and the solid-liquid ratio between soil and washing solution was fixed at 1:20. Using a 50 mL centrifuge bottle, 2 g of soil was put into 40 mL of washing solution was filled and then stirred at 120 rpm using a stirrer at room temperature. The stirring time consisted of 6 steps: 10, 30, 60, 120, 240, and 360 min. After each time, centrifugation
was performed immediately, and the concentration of heavy metals in the supernatant was analyzed by ICP-OES.

2.4. Experiment for the Selection of Solid-Solution Ratio

Four types of washing solution were used: citric acid (1 M), oxalic acid (1 M), EDTA, 50 mM), and acid solution (pH 0.5), and the washing time was fixed at 360 min. The solid-solution ratio consisted of 6 steps: 1:2, 1:5, 1:10, 1:20, 1:40, and 1:100. After each solid-solution ratio, centrifugation was performed immediately, and the concentration of heavy metals in the supernatant was analyzed by ICP-OES.

2.5. CCRD Experiment for Simultaneous Evaluation of Washing Time and Solid-Solution Ratio

As an additional experiment for evaluating washing conditions, analysis was performed through central composite rotatable design (CCRD), which is a type of response surface methodology (RSM) to simultaneously evaluate the solid-solution ratio and washing time. As the washing solution, 1 M citric acid, which showed the optimum removal efficiency for the experimental soil, was chosen. The experimental model contained two factors (n = 2) and five levels in the CCRD, which were determined as follows: $2^n (2^2 = 4, \text{cube point}) + 2n (2 \times 2, \text{star point}) + 4 (\text{central point})$ (Table 1). Through the multiple regression, the following response $Y$ (maximum washing efficiency) could be calculated as the second-order polynomial model:

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_{12}x_1x_2 + \beta_{11}x_1^2 + \beta_{22}x_2^2$$  \hspace{1cm} (1)

where, $\beta_0$, $\beta_1$, $\beta_2$, $\beta_{12}$, $\beta_{11}$, and $\beta_{22}$ are the intercept, the linear coefficient for $x_1$, the linear coefficient for $x_2$, the interaction coefficient, the quadratic coefficient for $x_1^2$, and the quadratic coefficient for $x_2^2$, respectively, and $x_1$ and $x_2$ are the coded independent variables (solid-solution ratio and washing time, respectively).

**Table 1.** Experimental set-up in the central composite rotatable design.

| Code | Actual Level |
|------|--------------|
|      | SSR          | Washing Time | SSR          | Washing Time |
| Cube | −1 −1        | 1:20         | 120          |
|      | −1 1         | 1:20         | 240          |
|      | 1 −1         | 1:40         | 120          |
|      | 1 1          | 1:40         | 240          |
| Star | 2 0          | 1:50         | 180          |
|      | −2 0         | 1:10         | 180          |
|      | 0 −2         | 1:30         | 60           |
|      | 0 2          | 1:30         | 300          |
|      | 0 0          | 1:30         | 180          |
|      | 0 0          | 1:30         | 180          |
|      | 0 0          | 1:30         | 180          |

$^1$ Solid-solution ratio. $^2$ The unit of washing time is minute.

2.6. Statistical Analysis

All experiments were performed in 3 replicates. Statistical analysis of each experimental result was performed using statistical software, SAS 9.4. In the washing solution selection experiment, 3-parameter sigmoidal logistic model was used, and the significant difference in the maximum washing efficiency at each washing solution (citric acid, oxalic acid, CaCl$_2$-1 M, EDTA-100 mM) was determined by Dunnet’s test. Through this, the NOEC (non-observed effect concentration) value was calculated to confirm the concentration of the lowest washing solution concentration in which the amount of heavy metal removal did not show a statistically significant difference compared to maximum washing solution
concentration. In addition, the lowest washing time and solid-liquid ratio, which could meet the maximum washing efficiency, were analyzed through the same statistical analysis.

3. Results and Discussion
3.1. Soil Properties and Heavy Metal Contamination

Soil pH, EC, and TOC were 8.37 ± 0.05, 8.73 ± 0.11 ms m⁻¹, and 9.99 ± 0.48 g kg⁻¹, respectively. Exchangeable cation concentration of Ca, K, Mg, and Na were 2.66 ± 0.05 g kg⁻¹, 79 ± 7 mg kg⁻¹, 20 ± 0.46 mg kg⁻¹, and 25 ± 1.5 mg kg⁻¹, respectively. The Ca content in the basic cation that can act as a limiting factor for heavy metal desorption along with pH was higher than other cations [20]. Since Ca has a major effect on the buffering capacity of the soil, it may be a factor that can inhibit the washing efficiency in the soil washing process [21]. The concentration of heavy metals (Cd, Cu, Ni, Pb, and Zn) and metalloid (As) were 17.34 ± 0.43 mg kg⁻¹, 307.76 ± 11.65 mg kg⁻¹, 18.65 ± 1.14 mg kg⁻¹, 714.78 ± 16.28 mg kg⁻¹, 1755.47 ± 18.32 mg kg⁻¹, and 11.47 ± 0.42 mg kg⁻¹, respectively. According to the Soil Environmental Conservation Act of Korea, considering that the study area is agricultural land, the concerned levels are 4, 150, 100, 200, 300, and 25 mg kg⁻¹ for Cd, Cu, Ni, Pb, Zn, and As, respectively. It indicated that experimental soil was highly contaminated by Cd, Cu, Pb, and Zn, simultaneously, and the regulation level could be a goal of soil remediation and could allow for greater flexibility for site uses in the future [22]. Cultivation of food crops on heavy metal contaminated agricultural soil has a human health risk via dietary intake of contaminated crops; hence, the research on the reduction in the concentration of heavy metal and its availability in soil has been studied continuously [23,24].

Figure 1 showed the binding fraction of each heavy metal in soil assessed using the BCR sequential extraction method. In general, the earlier the extraction step among the results of the sequential extraction method means that it can be extracted relatively easily by a specific solution. In the case of Cd and Zn, the exchangeable fraction occupied more than 40%, which can be considered a high-risk state due to high mobility and bioavailability in the soil environment [25]. In the case of Cu and Pb, the sum of the fraction of carbonate binding and metal oxide binding was 75.3% and 91.5%, respectively, which is assumed to be able to be significantly removed by acid-based washing solution [26].

![Figure 1. Binding fraction (%) of heavy metals in soil assessed by BCR method.](image-url)

3.2. Comparison of Heavy Metal Removal Efficiency According to the Type of Washing Solution

The total concentration of Cd was 17.34 mg kg⁻¹. To meet the remediation goal, 4 mg kg⁻¹, about 77% of the total concentration should be decreased (Figure 2). For Cd, the maximum removal efficiency of washing solutions were 86.8%, 67.0%, 64.5%, 47.5%, and
15.6% for acid solution (HCl 3 M), citric acid (100 mM), EDTA (100 mM), oxalic acid (1 M), and CaCl$_2$ (100 mM), respectively (Figure 2). NOEC showed the lowest concentration of EDTA at 50 mM and citric acid and oxalic acid at 100 mM and 1 M, respectively. The remediation goal was found to be satisfied only in the acid solution at pH$_{eq}$ 5.7.

The total concentration of Cu was 307.76 mg kg$^{-1}$. To meet the remediation goal, 150 mg kg$^{-1}$, about 51% of the total concentration should be decreased (Figure 3). For Cu, the maximum removal efficiency of washing solutions were 91.6%, 75.8%, 53.8%, 52.8%, and 0.5% for acid solution (3 M), oxalic acid (100 mM), citric acid (100 mM), EDTA (100 mM), and CaCl$_2$ (100 mM), respectively (Figure 3). NOEC showed the lowest concentration of oxalic acid at 10 mM and EDTA and citric acid at 50 mM and 100 mM, respectively. The remediation goal was found to be satisfied in the acid solution at pH$_{eq}$ 0.5, EDTA at 4.4 mM, citric acid at 11.1 mM, and oxalic acid at 5.6 mM, respectively.

The total concentration of Pb was 714.78 mg kg$^{-1}$. To meet the remediation goal, 200 mg kg$^{-1}$, about 72% of the total concentration should be decreased (Figure 4). For Pb, the maximum removal efficiency of washing solutions were 100%, 81.0%, 62.1%, and 3.1% for acid solution (3 M), EDTA (100 mM), citric acid (1 M), and oxalic acid (1 M), respectively (Figure 4). NOEC showed the lowest concentration of EDTA at 50 mM and oxalic acid and citric acid at 500 mM and 1 M, respectively. The remediation goal was found to be satisfied only in the acid solution at pH$_{eq}$ 0.5 and EDTA at 3.4 mM, respectively.

Figure 2. The effect of the washing solution and its concentration on Cd removal efficiency. Red dotted line indicates the minimum removal efficiency of heavy metals to meet the legal standards (4 mg kg$^{-1}$ for Cd).
The total concentration of Zn was 1755.47 mg kg\(^{-1}\). To meet the remediation goal, 300 mg kg\(^{-1}\), about 83% of the total concentration should be decreased (Figure 5). For Zn, the maximum removal efficiency of washing solutions were 91.5, 64.1%, 56.7%, and 30.4% for acid solution (3 M), oxalic acid (1 M), citric acid (100 mM), and EDTA (100 mM), respectively (Figure 5). NOEC showed the lowest concentration of EDTA at 50 mM and oxalic acid and citric acid at 1 M and 100 mM, respectively. The remediation goal was found to be satisfied only in the acid solution at \(\text{pH}_{\text{eq}}\) 0.6.

The main mechanism of washing and removal of heavy metals in the soil can be explained by the increase in the mobility of the heavy metals due to the decrease in pH and the formation of ligand complexes by the heavy metals and chelating agents [6,9,27]. The acidic solution (pH adjustment by HCl) used in this study to wash and remove heavy metals, chelating agents such as organic acids (citric acid, oxalic acid, EDTA), and neutral salts (CaCl\(_2\)) are also major heavy metal desorption agents based on the above two mechanisms. Qin et al. [28] attempted to remove Cd from soil using various types of low-molecular-weight organic acids (LMOWAs). As a result, although there was a large difference in pH depending on the type of organic acid after washing, the actual Cd removal rate showed a greater difference according to the difference in the formation coefficient of the ligand complex of the organic acid rather than the change in pH. In the case of Cu, citric acid has higher complex formation coefficients (metal-ligand complex constant, citric acid 6.1–18.0, and oxalic acid 4.5–8.9) with Cu. Therefore, it is judged that
the high removal efficiency of oxalic acid was exhibited due to the synergistic effect of the low complex formation coefficient of oxalic acid compared to citric acid and the low pH by oxalic acid [29]. In the case of Pb, the effect of organic acid (CA and OA) on Pb removal is lower than the acid solution and EDTA. Unlike other heavy metals, the complex formation constant of Pb and oxalate is high, but the solubility ($K_{sp}$) is $2.74 \times 10^{-11}$, which is lower than that of other heavy metals–oxalate complexes due to precipitation and re-adsorption [30]. Among the heavy metals studied, the removal efficiency of Zn in the soil was least affected by pH, so the removal efficiency was lower in the organic acid solution compared to the acid solution [31].

![Figure 4](image-url)  
**Figure 4.** The effect of the washing solution and its concentration on Pb removal efficiency. Red dotted line indicates the minimum removal efficiency of heavy metals to meet the legal standards (200 mg kg$^{-1}$ for Pb).

### 3.3. Comparison of Heavy Metal Removal Efficiency According to Washing Time

Except for the acid solution, which had very high and fast removal efficiency, and CaCl$_2$, which had the lowest removal efficiency, the heavy metal removal efficiency according to the washing time was evaluated for the remaining three types of washing solution (Figure 6). Gzar and Gatea [32] reported that HCl solution could easily remove Cd, Pb, and Ni within 1 h. In particular, the equilibrium was reached within 1 h in most cases regardless of the concentration of HCl. Lee et al. [33] tested four types of extraction solution and revealed that the heavy metal removal efficiency is the highest in HCl solution rather than citric acid, EDTA, and CaCl$_2$. In addition, the removal equilibrium was reached within
30 min. In the 1 M citric acid, the equilibrium time of Cu was 120 min, indicating that desorption reached equilibrium the fastest, and it was evaluated that the washing reaction reached equilibrium in all other heavy metals at 240 min. In the 1 M oxalic acid, it was investigated that Cd and Pb reached equilibrium at 30 min, and Cu and Zn reached equilibrium at 60 min. In the EDTA (50 mM), Cd and Pb were reached at the same equilibration time of 120 min, and the remaining two metals reached equilibrium at 240 min.

Based on the equilibration time, it is judged that the washing reaction reaches equilibrium at the fastest time in the 1 M oxalic acid treatment. However, when actually comparing the removal efficiency, the removal efficiency of the other heavy metals except for Cu (81%) was significantly lower than that of citric acid and EDTA. It was predicted that Cd could only be removed at 70% and 79% levels, respectively, compared to the two treatment groups, and Zn was also evaluated to be only 87% higher than citric acid. In addition, in the case of Pb, the removal efficiency was less than 50% (47% compared to citric acid, 49% compared to EDTA), so it is judged that it is necessary to consider the removal efficiency as well as the reaction equilibrium time. Meeting the remediation goal was observed only for Cu and Pb. It was predicted that Cu took less than 1 min in the citric acid and oxalic acid, respectively, and it is expected that it will take about 10.7 min longer in the EDTA than citric acid and oxalic acid. It was evaluated that Pb required 68.4 min for citric acid and 50.0 min for EDTA, respectively.

Figure 5. The effect of the washing solution and its concentration on Zn removal efficiency. Red dotted line indicates the minimum removal efficiency of heavy metals to meet the legal standards (300 mg kg\(^{-1}\) for Zn).
Figure 6. The effect of the washing time on heavy metals removal efficiency by 1 M citric acid (a), 1 M oxalic acid (b), and 50 mM EDTA (c). Red dotted line indicates the minimum removal efficiency of heavy metals to meet the legal standards.
The rapid extraction at the beginning of agitation confirmed in this experiment can be viewed as a result of the presence of metals in the soil. In the case of general soil, it takes a long time to remove heavy metals because the fraction of residual form is high, resulting in the fact that the dissolution and movement of metals into the extractants are limited [33]. On the other hand, it can be seen that heavy metals were extracted and removed in a relatively short period of time in the soil of the abandoned mine area, as there are many carbonate bonds and Fe/Mn–oxide bonds, which have weak bonding with soil components. In this study, it can be seen that the residual fraction is all less than 20% for four types of heavy metals except Ni, which is not highly contaminated (Figure 1).

3.4. Comparison of Heavy Metal Removal Efficiency According to Solid-Solution Ratio

The soil-solution ratio has been known as a key factor controlling the sorption and desorption of metal on soil [34]. In this study, except for CaCl$_2$, which had the lowest removal efficiency, the heavy metal removal efficiency according to the solid-solution ratio was evaluated for the remaining four types of washing solution (Figures 7 and 8). In 1 M citric acid, the removal efficiency of Cd, Cu, and Zn reached equilibrium at all solid-solution ratios, respectively, and only in the case of Pb, the reaction reached equilibrium at a 1:20 ratio. The maximum removal efficiency at each equilibrium solid-solution ratio was 84%, 80%, 89%, and 93% for Cd, Cu, Pb, and Zn, respectively. In the oxalic acid (1 M), all heavy metals were found to be reached at the maximum removal efficiency at 1:100 ratio, and the amount of heavy metal removal at 1:100 ratio was Cd 88%, Cu 92%, Pb 74%, and Zn 96%. That is, except for Pb, all heavy metals exhibited higher removal efficiency than citric acid. In the EDTA, the reaction of the remaining three heavy metals except for Zn reached equilibrium at 1:10 and Zn reached equilibrium at 1:20. However, the amount of heavy metal removal was relatively low compared to the rest of the washing solutions, showing 64% Cd, 72% Cu, 81% Pb, and 58% Zn. In the acid solution (pH 0.5), it was analyzed that all heavy metals reached equilibrium at the 1:5 treatment ratio and that the reaction reached equilibrium at the lowest solid-solution ratio among all solutions applied to the soil. In particular, the acid solution showed the highest treatment efficiency as all of the maximum removal efficiency was over 90% despite the low solid-solution ratio. Achieving the remediation goal was observed in all treatments except for the EDTA. Citric acid satisfied all criteria at a treatment ratio of 1:2 or higher in all treatment groups except for Cd (1:10), and oxalic acid satisfied the criteria at 1:100 or higher in all treatment groups except for Cu (1:20). In the acidic solution with the highest treatment efficiency, all heavy metals satisfied the criteria at 1:5 or higher, but EDTA was found to satisfy the criteria at 1:5 and 1:10 solid-solution ratio only for Cu and Pb, respectively. Lee and Park [35] examined citric acid, EDTA, and oxalic acid as a washing solution and reported that the removal efficiency showed a tendency to increase as the solid-solution ratio increased.

![Figure 7](image_url)

**Figure 7.** The effect of the solid-solution ratio on the heavy metal removal efficiency by 1 M citric acid (a), 1 M oxalic acid (b). An asterisk indicates significant difference from maximum removal efficiency.
Figure 6. The effect of the washing time on heavy metals removal efficiency by 1 M citric acid (a), 1 M oxalic acid (b), and 50 mM EDTA (c). Red dotted line indicates the minimum removal efficiency of heavy metals to meet the legal standards.

Figure 7. The effect of the solid-solution ratio on the heavy metal removal efficiency by 1 M citric acid (a), 1 M oxalic acid (b). An asterisk indicates significant difference from maximum removal efficiency.

Figure 8. The effect of the solid-solution ratio on the heavy metal removal efficiency by pH 0.5 acid solution (a), 50 mM EDTA (b). Asterisk indicates significant difference from maximum removal efficiency. Red dotted line indicates the minimum removal efficiency of heavy metals to meet the legal standards.

3.5. Simultaneous Evaluation of Washing Time and Solid-Solution Ratio in Heavy Metal Removal Efficiency

So far, the effect of the type of washing solution, washing time, and the solid-solution ratio was evaluated through batch-type experiments. Additionally, other ions interacted with the washing solution, and the interaction depended on metal forms, ion affinity and surfactant structure [39]. Among them, the optimum washing time and solid-solution ratio, which represent the maximum amount of heavy metal removal, were calculated through CCRD arrangement for the washing time and solid-solution ratio, which were determined to have a complex effect on heavy metal removal (Table 2). Through the multiple regression and predictive second-order polynomial equation, a model equation representing the maximum $r^2$ for each heavy metal was calculated (Table 3). In addition, the results are presented as 2D-contour and 3D-mesh plots, and the optimum solid-solution ratio and washing time, which indicate the maximum removal efficiency of each heavy metal, were suggested using the maximum value option in the solver method (Figures 9 and 10).

Although the washing condition is (types of solution, time, and solid-solution ratio) the same, the removal efficiency of each heavy metal is significantly different. This is because the behavior characteristics in soil are different for each type of heavy metal. Wydro et al. [36] reported that the uptake of heavy metal from soil to lawn grasses was conducted more easily as follows: Cd > Cu > Zn > Ni > Pb. This result was found to be affected by the type of heavy metals bound to the soil assessed by sequential extraction. For example, the behavior of Cu has been influenced by metal oxides and interactions with other elements, resulting in changes in Cu-binding fractions [37].

It goes without saying that the greater the amount of washing solution compared to the soil, the greater the amount of removal efficiency [33]. However, the amount of heavy metals removed by the volume of washing solution decreases [38]. In addition, due to the problem of cost, it is important to find the optimal ratio.
Table 2. Removal amount by heavy metals according to treatment code.

| Code | SSR | Washing Time | Cd       | Cu       | Pb       | Zn       |
|------|-----|--------------|----------|----------|----------|----------|
| −1   | −1  | 12.4 ± 0.5   | 189.2 ± 8.6 | 575.9 ± 30.9 | 1254.6 ± 57.9 |
| −1   | 1   | 12.6 ± 0.7   | 196.3 ± 9.6 | 595.8 ± 24.4 | 1351.7 ± 47.2 |
| 1    | −1  | 12.5 ± 0.2   | 185.1 ± 3.7 | 591.4 ± 17.6 | 1248.5 ± 20.9 |
| 1    | 1   | 13.1 ± 0.9   | 197.1 ± 14.9 | 620.8 ± 51.6 | 1360.0 ± 104.6 |
| 2    | 0   | 12.7 ± 1.0   | 187.6 ± 16.4 | 580.4 ± 52.2 | 1288.2 ± 109.3 |
| −2   | 0   | 13.5 ± 0.9   | 209.9 ± 19.6 | 602.5 ± 52.3 | 1354.9 ± 121.1 |
| 0    | −2  | 12.1 ± 0.3   | 178.6 ± 2.4  | 537.9 ± 5.7  | 1097.1 ± 17.8 |
| 0    | 2   | 12.5 ± 0.6   | 188.1 ± 10.4 | 574.0 ± 28.7 | 1274.5 ± 98.7 |
| 0    | 0   | 12.5 ± 0.8   | 184.4 ± 14.4 | 559.0 ± 63.8 | 1205.2 ± 125.9 |
| 0    | 0   | 13.4 ± 0.5   | 203.1 ± 8.2  | 631.6 ± 32.9 | 1348.8 ± 31.9 |
| 0    | 0   | 13.5 ± 0.7   | 202.5 ± 10.8 | 641.5 ± 42.4 | 1345.5 ± 66.6 |
| 0    | 0   | 13.0 ± 0.8   | 196.1 ± 12.6 | 619.4 ± 41.1 | 1334.8 ± 89.1 |

1 Solid-solution ratio.

Table 3. The model equation for the evaluation of the maximum heavy metal removal efficiency (RE).

| Model 1 | \( r^2 \) | \( \text{adj.-}r^2 \) | Cd \( \text{RE(\%)} = 74.7 - 1.94x_1 + 1.14x_2 - 1.81x_1^2 - 0.68x_2^2 + 0.03x_1x_2 \) |
|---------|------------|------------------|------------------------------------------------|
| Cu      | 0.479      | 0.317            | \( \text{RE(\%)} = 74.5 - 2.93x_1 + 1.67x_2 - 1.62x_1^2 - 0.84x_2^2 + 0.38x_1x_2 \) |
| Pb      | 0.443      | 0.269            | \( \text{RE(\%)} = 84.2 - 1.86x_1 + 2.02x_2 - 2.78x_1^2 - 1.25x_2^2 + 0.29x_1x_2 \) |
| Zn      | 0.498      | 0.341            | \( \text{RE(\%)} = 76.6 - 2.23x_1 + 3.35x_2 - 1.87x_1^2 - 1.22x_2^2 + 0.63x_1x_2 \) |

1 \( x_1 \) and \( x_2 \) means coded solid-solution ratio and coded washing time, respectively.

Figure 9. The effect of the solid-solution ratio and washing time on heavy metal removal efficiency using 1 M citric acid through CCRD using 2D contour plot.
Figure 10. The effect of the solid-solution ratio and washing time on heavy metal removal efficiency using 1 M citric acid through CCRD using 3D mesh plot.

First, Cd was predicted to show the maximum removal efficiency at the solid-solution ratio of 1:24.7 (coded value: $-0.53$) and washing time 230.1 min (coded value: 0.83) when washing with 1 M citric acid. The amount of Cd removal under the predicted conditions was 75.7%. Looking at the results of setting the washing conditions in the previous three steps, the maximum removal efficiency was 59.7% at 1 M citric acid, 1:20 solid-solution ratio, and 30 min of washing time in the first step for selecting a washing solution. When the second-step washing time was set, the maximum removal efficiency was 70.1% at 1 M citric acid, a solid-solution ratio of 1:20, and a washing time of 240 min. Finally, in the solid-solution ratio selection step, it was analyzed that the maximum removal efficiency was 80.0% at 1 M citric acid, washing time 360 min, and solid-solution ratio 1:10. It is thought that it would be difficult to directly compare the overall results because each condition is slightly different, but there was no significant difference between the results of the actual CCRD arrangement and the results of the solid-solution ratio selection stage, which showed the maximum removal efficiency among the three-stage analysis results. The CCRD, which is one of the response surface methodologies, has been known to efficiently minimize and simplify the number of experimental steps and their scale [40]. Therefore, in the case of Cd, it is judged that the decision-making process of washing conditions through the three-step evaluation method contains meaningful results to some extent. Copper was predicted to represent the maximum removal efficiency (77.1%) at the solid-solution ratio of 1:21.9 (coded value: $-0.81$) and washing time 228.8 min (coded value: 0.81). In the case of Pb, it was predicted to show the maximum removal efficiency (85.3%) at the solid-solution ratio of 1:26.2 (coded value: $-0.38$) and washing time 256.4 min (coded value: 1.27). The maximum removal efficiency of Zn was 79.2%, with the solid-solution ratio at 1:26.2 (coded value: $-0.38$) and the washing time at 256.4 min (coded value: 1.27). Similar to Cd, it was confirmed that Cu, Pb, and Zn did not show a significant difference from the maximum removal efficiency of the three-step procedure.
Phasukarratchai [39] also utilized the CCRD method to optimize Cd and Zn removal from contaminated soil using anionic surfactants. They controlled solution concentration, solution soil ratio and agitation speed, and they also considered the cost of chemicals required for the soil remediation.

4. Conclusions

Soil washing is the constant current topic related to the contamination of soils with heavy metals and their remediation. In this study, we evaluated the optimal parameters influencing maximum heavy metal removal efficiency to meet the legal regulation level at the same time. This study dealt with the effect of type of washing solution, washing time, and solid-solution ratio. It is judged that it will have great meaning as data for future field application and prior research by setting major factors as basic data for applying the washing method to the soil in the agricultural land around the mine contaminated with multiple heavy metals and completing analysis by level for all conditions. The application of the interpretable model and NOEC concept in the washing solution selection process is a new attempt in the soil washing condition setting experiment, and it is thought that it can be used as a new evaluation tool when a wide range of heavy metal-contaminated soil data is accumulated in the future. In addition, the applicability of the CCRD batch experiment in setting the solid-solution ratio and washing time, which is a major influence factor for soil washing and is evaluated as the most important factor in the design of actual site facilities, is expected to lead to the minimization and simplification of the experimental steps. Further studies on soils of various characteristics to expand the scope of application should be continuously performed.

Author Contributions:

Conceptualization, N.K.; methodology, S.-H.L.; writing—original draft preparation, M.-S.K.; writing—review and editing, J.-G.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Mine Reclamation Incorporation (MIRECO) and partly supported by Korea University Grant and OJEong Resilience Institute.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Juwarkar, A.A.; Singh, S.K.; Mudhoo, A. A comprehensive overview of elements in bioremediation. Rev. Environ. Sci. Biotechnol. 2010, 9, 215–288. [CrossRef]
2. White, C.G.; Lee, D.J. Enzyme technology and biological remediation. Enzym. Microb. Technol. 2006, 38, 291–316. [CrossRef]
3. Kim, S.H.; Song, S.K.; Suh, J.H. Field test assessment of biological recovering agent for treating oil contaminated soil. Kor. Soc. Biotechnol. Bioeng. 2010, 25, 73–78.
4. Hamby, D.M. Site remediation techniques supporting environmental restoration activities—A review. Sci. Total Environ. 1996, 191, 203–224. [CrossRef]
5. Dhaliwal, S.S.; Singh, J.; Taneja, P.K.; Mandal, A. Remediation techniques for removal of heavy metals from the soil contaminated through different sources: A review. Environ. Sci. Pollut. Res. 2020, 27, 1319–1333. [CrossRef]
6. Gusiathin, Z.M.; Klimiuk, E. Metal (Cu, Cd and Zn) removal and stabilization during multiple soil washing by saponin. Chemosphere 2012, 86, 383–391. [CrossRef] [PubMed]
7. Dermont, G.; Bergeron, M.; Mercier, G.; Richer-Lafêche, M. Soil washing for metal removal: A review of physical/chemical technologies and field application. J. Hazard. Mater. 2008, 152, 1–31. [CrossRef]
8. USEPA. Contaminants and Remedial Options at Selected Metal Contaminated Sites; EPA/540.R-95/512; Office of Research and Development: Washington, DC, USA, 1995.
9. Shen, Z.; Hou, D.; Zhao, B.; Xu, W.; Ok, Y.S.; Bolan, N.S.; Alessi, D.S. Stability of heavy metals in soil washing residue with and without biochar addition under accelerated ageing. *Sci. Total Environ.* 2018, 619–620, 185–193. [CrossRef]

10. Arwidsson, Z.; Elgh-Dalgren, K.; von Kronhelm, T.; Sjöberg, R.; Allard, B.; van Hees, P. Remediation of heavy metal contaminated soil washing residues with amino polycarboxylic acids. *J. Hazard. Mater.* 2010, 173, 697–704. [CrossRef]

11. Riser-Roberts, E. *Remediation of Petroleum Contaminated Soils: Biological, Physical, and Chemical Processes*; CRC Press: Boca Raton, FL, USA, 2020.

12. Abumaizar, R.; Khan, L.I. Laboratory investigation of heavy metal removal by soil washing. *J. Air Waste Manag. Assoc.* 1996, 46, 765–768. [CrossRef]

13. Kim, M.S.; Lee, S.H.; Kim, J.G. Assessment of fraction and mobility of arsenic in soil near the mine waste dam. *Sustainability* 2020, 12, 1480. [CrossRef]

14. Kim, Y.W. Case of investigation and design of environment remediation of oil-contaminated soil/groundwater. *Geoenviron. Eng.* 2001, 2, 10–19.

15. Chang, Y.Y.; Shin, J.Y.; Hwang, K.Y. Development of a pilot scale soil washing process. *Kor. Soc. Soil Groundw. Environ.* 1998, 3, 55–62.

16. Lee, M.; Chung, S.Y.; Kang, D.; Choi, S.; Kim, M. Surfactant enhanced in-situ soil flushing pilot test for the soil and groundwater remediation in an oil contaminated site. *Kor. Soc. Soil Groundw. Environ.* 2002, 7, 77–86.

17. National Institute of Agricultural Science and Technology. *Method of Soil and Plant Analysis*; Rural Development Administration: Suwon, Korea, 2008.

18. Robertson, J.; Thomas, C.J.; Caddy, B.; Lewis, A.J.M. Particle size analysis of soils—A comparison of dry and wet sieving techniques. *Forensic Sci. Int.* 1994, 24, 209–217. [CrossRef]

19. ISO. *Soil Quality—Extraction of Trace Element Soluble in Aqua Regia*; ISO 11466; International Organization for Standardization: Geneva, Switzerland, 1995.

20. Moghal, A.A.B.; Al-Shamrani, M.A.A.; Zahid, W.M. Heavy metal desorption studies on the artificially contaminated AL-QATIF soil. *Int. J. Geomat.* 2015, 8, 1323–1327.

21. Kim, C.; Lee, Y.; Ong, S.K. Factors affecting EDTA extraction of lead from lead-contaminated soils. *Chemosphere* 2003, 51, 845–853. [CrossRef]

22. Li, X.N.; Jiao, W.T.; Xiao, R.B.; Chen, W.P.; Chang, A.C. Soil pollution and site remediation policies in China: A Review. *Environ. Res.* 2015, 23, 263–274. [CrossRef]

23. Lim, H.S.; Lee, J.S.; Chon, H.T.; Sager, M. Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au-Ag mine in Korea. *J. Geochem. Explor.* 2008, 96, 223–230. [CrossRef]

24. Liu, X.; Song, Q.; Tang, Y.; Li, W.; Xu, J.; Wu, J.; Wang, F.; Brookes, P.C. Human health risk assessment of heavy metals in soil-vegetables system: A multi-median analysis. *Sci. Total Environ.* 2013, 463–464, 530–540. [CrossRef]

25. Ngole, V.M. Using soil heavy metal enrichment and mobility factors to determine potential uptake by vegetables. *Plant Soil Environ.* 2011, 57, 75–80. [CrossRef]

26. Ko, I.; Lee, C.H.; Lee, K.P.; Lee, S.W.; Kim, K.W. Remediation of soil contaminated with arsenic, zinc, and nickel by pilot-scale soil washing. *Environ. Prog.* 2005, 23, 39–48. [CrossRef]

27. Zou, Z.; Qiu, R.; Zhang, W.; Dong, H.; Zhao, Z.; Zhang, T.; Wei, X.; Cai, X. The study of operating variables in soil washing with EDTA. *Environ. Pollut.* 2009, 157, 229–236. [CrossRef]

28. Qin, F.; Shan, X.Q.; Wei, B. Effect of low-molecular-weight organic acids and residence time on desorption of Cu, Cd, and Pb from soils. *Chemosphere* 2004, 57, 253–263. [CrossRef]

29. Yuan, S.; Xi, Z.; Jiang, Y.; Wan, J.; Wu, C.; Zheng, Z.; Lu, X. Desorption of copper and cadmium from soils enhanced by organic acids. *Chemosphere* 2007, 68, 1289–1297. [CrossRef]

30. Elliott, H.A.; Herzeg, L.M. Oxalate extraction of Pb and Zn from polluted soils: Solubility limitations. *Sediment Contam.* 1999, 8, 105–116. [CrossRef]

31. McBride, M.B. *Environmental Soil Chemistry*; Oxford Press: New York, NY, USA, 1994.

32. Gzar, H.A.; Gatea, I.M. Extraction of heavy metals from contaminated soils using EDTA and HCl. *J. Eng.* 2015, 21, 45–61.

33. Lee, S.H.; Kim, E.Y.; Seo, S.K.; Kim, K.B.; Kim, J.H.; Lee, J.K. Remediation of heavy metal contamination in OBOD site with soil washing: Selection of extractants. *J. Kor. Soil. Sci. Groundwat. Eng.* 2008, 13, 44–53.

34. Du, Y.J.; Hayashi, S.; Xu, Y.F. Some factors controlling the adsorption of potassium ions on clayey soils. *Appl. Clay Sci.* 2004, 27, 209–213. [CrossRef]

35. Lee, J.H.; Park, K.S. Comparison of soil washing for heavy metal contaminated shooting range soil using various extracts. *Econ. Environ. Geol.* 2010, 42, 123–136.

36. Wydro, U.; Jabłoń ska-Trypuć, A.; Hawrylik, E.; Butarewicz, A.; Rodziewicz, J.; Janczukowicz, W.; Wolejko, E. Heavy metals behavior in soil/plant system after sewage sludge application. *Energies* 2021, 14, 1584. [CrossRef]

37. Wei, B.; Yang, L. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchem.* J. 2010, 94, 99–107. [CrossRef]

38. Cline, S.R.; Reed, B.E. Lead removal from soils via bench-scale soil washing techniques. *J. Environ. Eng.* 1995, 121, 700–705. [CrossRef]
39. Assawithalerd, M.; Phasukarratchai, N. Optimization of cadmium and zinc removal from contaminated soil by surfactants using mixture design and central composite rotatable design. *Water Air Soil Pollut.* 2020, 231, 1–12. [CrossRef]

40. Koo, N.; Kim, M.S.; Hyun, S.; Kim, J.G. Effects of the incorporation of phosphorus and iron into arsenic-spiked artificial soils on root growth of lettuce using response surface methodology. *Commum. Soil Sci. Plant Anal.* 2013, 44, 1259–1271. [CrossRef]