EVALUATION OF RESPONSE SURFACE METHODOLOGY FOR CITRIC ACID DOSAGE OPTIMIZATION FOR THE REMEDIATION OF LEAD-CONTAMINATED SOILS

Dinwanbor, O. P., *Oluyemi-Ayibiowu, B. D., Falola, K. E.

Department of Civil and Environmental Engineering, The Federal University of Technology Akure, Nigeria

Correspondence
bayibiowu@yahoo.com

History
Received: 02/04/2025
Accepted: 12/05/2025
Published: 30/05/2025

https://www.futa.edu.ng

JOSTIR JOURNAL OF SCIENCE, TECHNOLOGY AND INNOVATION RESEARCH
https://www.jostir.futa.ng

ABSTRACT

Heavy metal contamination in soils poses significant risks to sustainable development and human health, necessitating effective remediation efforts. This research optimized soil washing conditions for lead removal using citric acid (CA). By varying CA concentrations, pH, and washing time, the study used a Box–Behnken Experimental Design within Response Surface Methodology (RSM) to identify optimal conditions. The result showed significant efficiency in lead removal within the first 100mM CA concentration, 150 minutes of washing time. The quadratic RSM model emerged as the best model fit out of the four (4) tested models to measure the relationships between the lead removal efficiency and the citric acid soil washing conditions. The Pareto influence analysis conducted on the model coefficients showed pH, CA concentration and the combination of both pH and CA concentration to have the highest influence on soil lead removal efficiency at influence rate of 72.24%, 7.06% and 8.51% respectively. The optimal conditions identified were a pH of 2, a washing time of 180 minutes, and a CA concentration of 64.89 mM, achieving a lead removal efficiency of 78%. This study demonstrates the effectiveness of citric acid in remediating lead-contaminated soils.

Keywords: Response Surface Methodology, Lead contamination, Box–Behnken Design, Heavy metal, Citric-acid. Optimization, Ph, Concentration

1 | Introduction

Toxic heavy metal contamination in soil represents a significant environmental challenge worldwide due to the persistent nature, concealment, toxicity, and other concerning attributes of these metals. Various anthropogenic activities, including mining, smelting, military operations, electronic manufacturing, fossil fuel consumption, waste disposal, pesticide application, and irrigation, contribute to the accumulation of heavy metals in both rural and urban soils, potentially posing risks to human health and ecosystems (Wei *et al*., 2019)

A range of in situ and ex situ remediation techniques have been developed to manage, clean, or restore soils contaminated with heavy metals. These techniques include soil flushing, surface capping, solidification, electro kinetic extraction, phytoremediation, and vitrification. Amongst these, soil washing stands out as a practical option due to its simplicity, cost-effectiveness, short processing time, and high efficiency. Soil washing utilizes a combination of physical and

https://doi.org/10.51459/jostir.2025.1.1.09

chemical processes to remove heavy metals from contaminated soil by washing it ex situ with specially formulated solutions (Zheng *et al*., 2020). The primary source of soil pollution in Nigeria stems from the mining and petrochemical industries. At mining sites, heavy metals such as copper (Cu), cadmium (Cd), lead (Pb), and zinc (Zn) are frequently detected in the soil. The "Agency for Toxic Substances and Disease Registry" has identified lead (Pb) as the second-most hazardous substance out of 275 substances in its registry, marking it as the most dangerous heavy metal found at mining locations (Abbassi *et al*., 2020). An effective strategy for remediating Pb-contaminated soil through soil washing technology hinges on the selection of an appropriate washing reagent (Guiyin *et al*., 2019). Common washing agents include mineral acids, synthetic organic chelating agents, and biosurfactants. (Guiyin *et al.*, 2019). While effective at heavy metal extraction, some agents can harm the soil environment. Mineral acids may degrade soil structure and reduce nutrient levels, which can be toxic to soil microorganisms. Organic chelating agents can also be toxic and persistent in the environment, while the high cost of biosurfactants remains a concern. To mitigate these ecological impacts, researchers are exploring greener and affordable alternatives, such as citric acid, which is less harmful to the environment, unlike the mineral acids (Soccol *et al.,* 2018). This study investigates citric acid for lead removal from contaminated soils and uses Response Surface Methodology (RSM) to establish optimal application conditions. The study innovatively employs the Box–Behnken design (BBD) to optimize lead removal efficiency from polluted soil

2. | Materials and Method

2.1 | Materials

The study materials are as discussed:

(i) Soil

Uncontaminated soils were collected from the FUTA community. The soil was dried, crushed, and sieved through a 2mm mesh. In accordance with Zygmunt *et al*. (2020), 1.0 kg of the soil sample was spiked with 6.9 g of lead (Pb) sourced from purchased $PbCl_2$, resulting in a concentration of 1500 mg/kg. Subsequently, the contaminated soil was air-dried and stored in an airtight bag for experimental purposes. Prior to use, the concentration of Pb in the soil was measured using a flame atomic absorption spectrophotometer. A lead concentration of 735 -mg/kg and above is classified as lead-contaminated soil Zygmunt *et al*. (2020).

(ii) | Citric acid

Commercially available crystalline Citric Acid (CA) was purchased from a supplier in Ado Ekiti, Nigeria and stored in the department of civil engineering geotechnical laboratory, (located in the Federal University of Technology Akure, Nigeria) prior to use.

2.2 | Single Factor Initial Soil Washing Experiments

Single-factor experiments were conducted to investigate the impact of the individual factors, namely, citric acid concentration, pH, and washing time on lead (Pb) removal efficiency. The objective was to establish the appropriate ranges for each factor for subsequent application in the Box-Behnken Design (BBD) response surface methodology (RSM) experiments.

Batch washing experiments were performed using 100 mL acid-rinsed polycarbonate bottles, maintaining a soil-to-solution ratio of 1:10 (w/v). During each trial, 5.00 g of soil was suspended in 50 mL of washing solution. For the concentration experiments, citric acid (CA) concentrations

https://doi.org/10.51459/jostir.2025.1.1.09

ranging from 5 to 400 mM were tested. In the pH effect experiments, a fixed concentration of 100 mM CA was utilized across different pH levels (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0). To assess the impact of washing time, the soil suspensions were agitated for various intervals between 15 and 450 minutes, at 30-minute increments, using a mechanical shaker set at 180 rpm and at room temperature. In all experimental conditions, the concentration of Pb in the soil was measured with an atomic absorption spectrophotometer both before and after the washing process.

2.3 | Response Surface Methodology (RSM) Experimental Design

A three-factor, three-level Box–Behnken design (BBD) for response surface methodology (RSM) was employed to optimize the lead (Pb) removal efficiency from soil using citric acid (CA). The three factors, representing the independent variables, are the concentration of citric acid, the pH value, and the washing time. The experimental design consisted of three levels (±1 and 0). The ±1 values indicate the upper and lower boundaries for the independent variables, while the 0 represents the midpoint. The range for these independent variables was determined based on the results of preliminary single-factor batch experiments.

2.4 | Tests Methods and Specification

Tests were performed on soil samples contaminated with lead to assess their physico-chemical properties. The soil pH was measured using a digital pH meter in a suspension with a 1:2.5 (w:v) soil-to-water ratio. The content of Soil Organic Matter (SOM) was determined following the Walkley–Black titration method. The pipette method was employed to analyze soil texture. Additionally, tests for Calcium Carbonate Equivalent (CCE), Cation Exchange Capacity (CEC), and electrical conductivity (EC) were conducted. The primary test focused on measuring the concentration of lead (Pb) ions in the solution, and utilizing an atomic absorption spectrophotometer on the experimental citric acid

$$Removal\ Efficiency\ (\%) = \frac{C_L V_L}{C_o M} \times 100\% \quad (1)$$

soil washing samples. The removal efficiency of lead (Pb) was calculated using Equation 1.
where C_o (mg kg−1) and C_L (mg L^{-1}) are the content of Pb in the original contaminated soil and in the soil after washing, respectively, V_L (L) is the washing solution volume, and M (kg) is the mass of the soil.

2.5 | Response Surface Methodology (RSM) Model Development and Optimization

RSM utilizes linear, quadratic, cubic, and two-factor interaction (2FI) models to analyze the relationship between independent and response variables (Oluyemi-Ayibiowu et al., 2021). The determination of the most suitable model for the data obtained from the conducted experiment was based on its performance in tests of fit among the four models.
The optimization of the citric acid soil washing conditions and its lead removal efficiency was carried out using the desirability function (D) as shown in Equation (2) as follows;

$$D = (d_1 \times d_2 \times \cdots d_m)^{1/m} = (\prod_{i=1}^{m} d_i)^{1/m} \quad (2)$$

where m represents the total number of responses used in the optimization research and d_i represents the response's desirability. D is a function that measures how desirable (well-matched) the dependent variables are with the independent variables at a particular level. D can have a value between 0 and 1. Optimization and RSM model

https://doi.org/10.51459/jostir.2025.1.1.09

was carried out using the Design-Expert software.

2.6 | Statistical Analysis

The Pareto statistical analysis was also conducted to calculate the percentage influence of each soil washing factor on Pb removal.

3. | Results and Discussion

3.1 | Soil Properties Experimental Result

Tests were conducted to determine the physico-chemical properties of the contaminated soil used in the study. Table 1 shows the results of the soil properties test.

Table 1 | Physico-chemical properties test of the soil sample

Characteristics	Units	Value
Pb	mg/kg	4410.12
Cu	mg/kg	60.20
Mn	mg/kg	250.00
Zn	mg/kg	115.33
Rb	mg/kg	77.66
Sand	%	30
Silt	%	33
Clay	%	37
Ph	-	7.77
EC	dSm^{-1}	0.7
SOM	%	1.01
CCE	%	20
CEC	$cmol+kg^{-1}$	17

According to Table 1, the contaminated soil is calcareous, with a calcium carbonate equivalent (CCE) of 20%, and exhibits a slightly alkaline pH of 7.77. The total lead (Pb) concentration in the soil is measured at 4410.12 mg/kg, significantly exceeding the standard levels set by FAO/WHO, which are 10 mg/kg for agricultural soils and 100 mg/kg for residential and industrial soils. Additionally, the concentration of zinc is marginally above the permissible limit for agricultural soil. The soil is primarily composed of silt and clay, leading to its classification as silty-clay.

3.2 | Single Factor Experimental Result

Figures 1a, b, and c illustrate the effects of citric acid (CA) concentration, pH, and washing time on the efficiency of lead removal from soil. As shown in Figure 1a, the Pb removal rate increased with rising CA concentrations up to 95 mM, after which there was a slight decline before increasing again at higher concentrations of 200 mM, 300 mM, and 400 mM. This trend aligns with findings reported by Yaolan *et al*. (2022), and it can be attributed to the fact that as the concentration of acid washing agents increases, greater amounts of organic acids bind with the heavy metals in the soil through chelation, resulting in the formation of heavy metal complexes. These complexes facilitate the dissolution of heavy metals, thereby enhancing washing efficiency.

Figure 1b demonstrates the impact of pH on lead removal efficiency. The Pb removal rate exhibited a sharp decrease with increasing pH, dropping from an efficiency of 78.75% at pH 2 to 24% at pH 7. This indicates that greater acidity correlates with more effective lead removal from the soil.

Figure 1c addresses the role of washing time in lead removal. Pb removal by CA surged sharply during the initial 150 minutes (from 15 to 150 minutes). Following this period, there was a slight reduction during the next hour, which was subsequently followed by a fluctuating but steady increase;

https://doi.org/10.51459/jostir.2025.1.1.09

however, this increase did not reach the peak observed during the first 150 minutes. The highest removal efficiency recorded was 77.33% at the 150-minute mark.

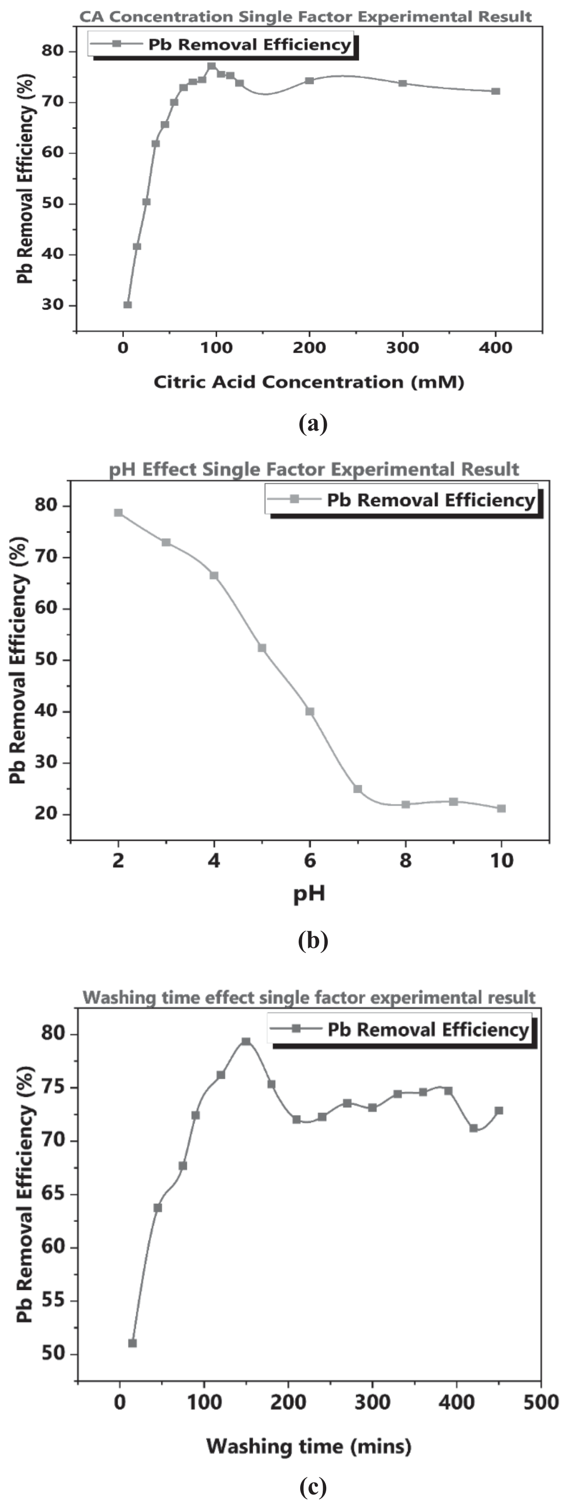

Figure 1 | Effects of (a) CA concentration (b) pH and (c) washing time on lead removal from soil

3.3 | Box–Behnken Experimental Design Result

Table 2 shows the range of values of the independent variables selected for the BBD experimental design based on the single factor experimental results. The values and variables were inputted into the Box–Behnken Design module of the Design Expert Software to determine the number of experiment (runs) at different soil washing conditions within the limit set by the range of the variables. The variables (soil washing conditions) included pH at a limit of 2 - 6, soil washing time at a limit of 75 mins – 180 mins, and CA concentrations of 35 mM-105 mM.

Table 2: Box–Behnken Design Experimental Designs Set-up

3.4 | Response Surface Methodology Model Result

Response Surface Methodology employs linear, quadratic, cubic, and Two Factorial Interactions (2FI) models to assess the relationship between independent variables and response variables. Table 3 presents the outcomes of the four models applied to the specified parameters for the lead (Pb) removal efficiency response variable, along with their respective performance evaluation indices. Among these models, the quadratic model exhibited the lowest p-value and the smallest difference between the adjusted R^2 and predicted R^2 values. A lower p-value indicates greater significance of the model, while a smaller difference between the adjusted R^2 and predicted R^2 signifies a better fit. In this instance, the quadratic model outperformed the others, with a difference of just 0.1124. The quadratic RSM regression model for soil washing parameters related to lead removal from soil using citric acid is expressed in Equation 3 as:

Pb Removal Efficiency = 67.92 – (10.78 × pH) +

https://doi.org/10.51459/jostir.2025.1.1.09

Table 2 | Box–Behnken Design Experimental Designs Set-up

Independent Variables	Symbols	Values		
		Low	Medium	High
pH	A	2	4	6
Washing time (mins)	B	75	127.5	180
CA concentration (Mm)	C	35	70	105

Table 3 | Model Choice Fit Performance for the Response Variable

Source	Sequential p-value	Adjusted R²	Predicted R²	
Linear	0.0885	0.8848	0.7225	
2FI	0.1325	0.9124	0.7729	
Quadratic	0.0246	0.9646	0.8522	**Suggested**
Cubic	0.2985	0.9836	0.6100	

(2.43 × washing time) + (3.37 × CA concentration) – (0.3659 × pH × washing time) + (3.70 × pH × CA concentration) – (0.0462 × washing time × CA concentration) – (3.45 × pH^2) + (0.0446 × washing $time^2$)– (1.29 × CA $concentration^2$) (3)

3.5 | Pareto Influence Analysis Result

Pareto analysis was used for the calculation of percentage influence of each factor on Pb removal. It measures the contribution of each model coefficients against the collective. Figure 2 illustrates the results of the Pareto analysis. According to this analysis, pH (72.24%) emerged as the most influential parameter in this process. The two pH variables, along with CA concentration (7.06%) and the interaction between CA concentration and pH (8.51%), had the most significant impacts on the removal efficiency. Collectively, these three factors accounted for 87.81% of the total influences on lead (Pb) removal.

A similar analysis conducted by Zahra *et a*l. (2020) on the removal of zinc heavy metal from soil using tartaric acid also indicated that pH played a critical role in heavy metal removal, underscoring the importance of the washing agent's pH when using acid as a means of removal. However, unlike citric acid, where the combination of pH and acid concentration had the most significant effect following pH, Zahra *et al.*, (2020) found that for tartaric acid, the tartaric acid concentration was the primary factor influencing the removal efficiency.

3.6 | Optimization Analysis and Result

Table 4 presents the optimization goals established for each variable involved in the optimization

https://doi.org/10.51459/jostir.2025.1.1.09

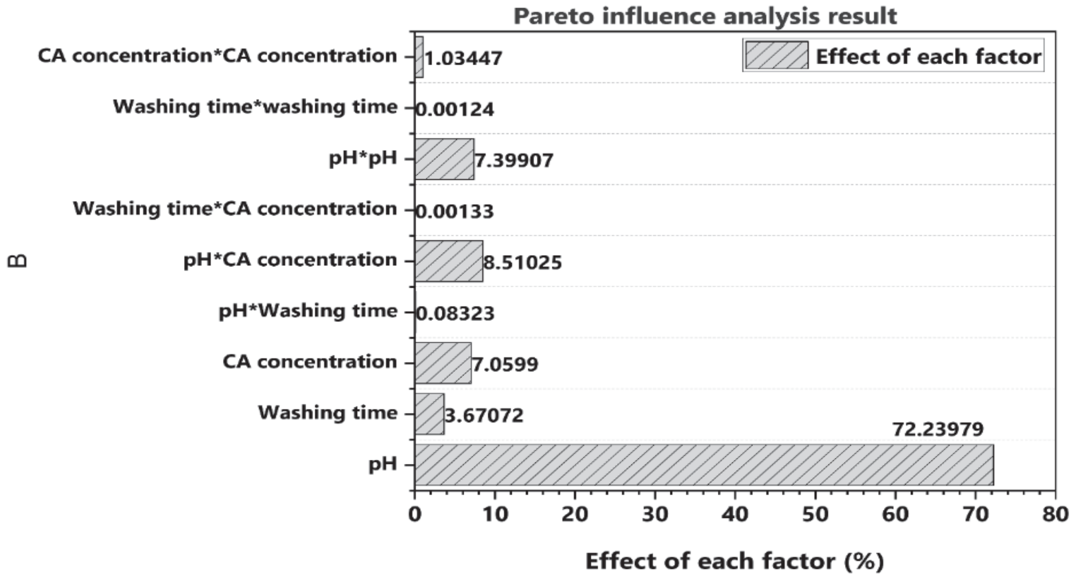

Figure 2 | Pareto graphic analysis to determine the effectiveness of each variable on the Lead removal efficiency

analysis. The independent variables were confined to the ranges utilized in the BBD experimental designs pertinent to this study. The response variables were aimed to maximize, as higher values correlate with improved soil cleanliness from lead contamination. All variables were considered equally important in terms of their significance and preference.

Through the application of this desirability function and the establishment of pre-selected objectives for each factor, the optimized specific value for the response (Pb removal efficiency) was determined, with results illustrated in Figure 3. A total of fifty-nine (59) potential solutions were generated, from which the optimal variable composition was selected. Figure 3 displays the optimum solution via a desirability ramp plot, indicating a pH of 2, a washing time of 180 minutes, and a CA concentration of 64.89 mM, which together achieve a maximum lead removal efficiency of 78%.

4. | CONCLUSIONS

The following conclusions were made from the

Table 4 | The Individual Variables Optimization Goals

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
pH	is in range	2	6	1	1	3
Washing time	is in range	75	180	1	1	3
CA concentration	is in range	35	105	1	1	3
Pb removal efficiency	maximize	45.128	79.658	1	1	3

https://doi.org/10.51459/jostir.2025.1.1.09

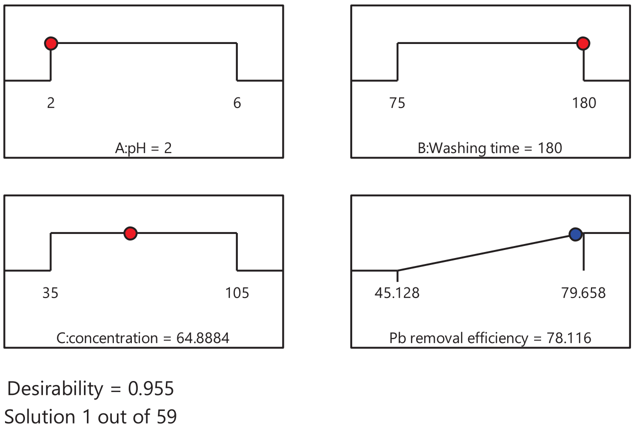

Figure 3 | Desirability ramp results for lead removal optimization from soil

study:

- The removal of lead from soil through washing with citric acid improves with increasing CA concentration, washing time and at strong acidity
- The relationship between the lead removal efficiency and the CA soil washing conditions was given mathematically as: Pb Removal Efficiency = 67.92 – (10.78 × pH) + (2.43 × washing time) + (3.37 × CA concentration) – (0.3659 × pH × washing time) + (3.70 × pH × CA concentration) – (0.0462 × washing time × CA concentration) – (3.45 × pH^2) + (0.0446 × washing time^2) – (1.29 × CA concentration^2)
- The Pareto influence analysis showed pH (72.24%) was the most effective parameter in the lead removal efficiency. Both pH variables, CA concentration (7.06%) and interaction between CA concentration and pH (8.51%) has the most effects on the removal efficiency.
- The desirability analysis showed that pH of 2, washing time of 180 minutes and CA concentration of 64.89 mM as the optimum soil washing conditions that yielded the maximum lead removal efficiency of 78%.

5. | RECOMMENDATIONS

A pH of 2, citric acid concentration of 64.89mM and washing time of 180minutes is recommended for soil remediation in lead contaminated mining sites.

Reference

Abbassi, F., Ahmad, F., Gulzar, S., Belhadj, T., Karrech, A., and Choi, H. S. (2020). Design of T-shaped tube hydroforming using finite element and artificial neural network modeling. *Journal of Mechanical Science and Technology, 34*, 1129-1138.

Guiyin, W., Shirong, Z., Ting, L., Xiaoxun, X., Qinmei, Z., Yue, C. and Yun, L. (2019). Application of response surface methodology for the optimization of lead removal from contaminated soil using chelants. *RSC Advance, 5*, 58010-58018.

Oluyemi-Ayibiowu Bamitale Dorcas (2021). Investigating the Strength Properties of Concrete containing Construction & Demolition Waste Using Response Surface Methodology Techniques (RSM). *European Journal of Applied Sciences*, 9(6), 629-645.

Soccol, C. R., Vandenberghe, L. P., Rodrigues, C., and Pandey, A. (2018). A new perspective for citric acid production and application. *Food Technology Biotechnology, 44*(2), 141-149

Wei, J., Duan, M., and Li, Y. (2019). Concentration and pollution assessment of heavy metals within surface sediments of the Raohe Basin, China. *Scientific Reports, 9*, 1-7.

Yaolan, N., Wei, H., Taming, S., Kun, D., and

https://doi.org/10.51459/jostir.2025.1.1.09

Dunqu, W. (2022). Response Surface Methodology for the Optimization of Zn-Contaminated Soil Remediation by Soil Washing with Water-Soluble Chitosan. *ACS Omega, 7*, 41929-41936.

Zahra, S. A.-A., Hossein, P., & Farrokh, A. (2020). Application of response surface methodology for optimization of zinc elimination from a polluted soil using tartaric acid. *Adsorption Science & Technology, 38*(3-4), 79-83.

Zheng, X. J., Chen, M., Wang, J. F., Li, F. G., Liu, Y., and Liu, Y. C. (2020). Ecological Risk Assessment of Heavy Metals in the Vicinity of Tungsten Mining Areas, Southern Jiangxi Province. *Soil Sediment Contaminants International Journal, 29*, 665-679.

Zygmunt, M. G., Dorota, K., and Barbara, K. (2020). New-Generation Washing Agents in Remediation of Metal-Polluted Soils and Methods for Washing Effluent Treatment: A Review. (MDPI, Ed.) *International Journal of Environmental Research and Public Health, 17*, 1-19.

https://doi.org/10.51459/jostir.2025.1.1.09