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Microwave-Enhanced Tea Saponin-Citric Acid Composite Leaching for Remediation of Heavy Metal-Contaminated Soil in Southern Yunnan Mining Areas

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Abstract

This study investigates the removal efficiency of heavy metals (lead and copper) from heavily contaminated soils in the old mining area of southern Yunnan Province. Using microwave-enhanced composite leaching agents (tea saponin-citric acid), we conducted single-factor experiments to optimize parameters including microwave power, treatment duration, citric acid concentration, tea saponin concentration, and solid-to-liquid ratio. The optimal conditions were determined as follows: 539 W microwave power, 40-second treatment time, 0.60 mol/L citric acid concentration, 5% tea saponin concentration, and 1:25 solid-to-liquid ratio, achieving 46.86% lead removal and 40.49% copper removal. Subsequently, Plackett-Burman experiments were performed to identify factors significantly affecting lead and copper removal rates. The most efficient conditions for lead removal were 539 W microwave power, 38-second treatment time, 0.65 mol/L citric acid concentration, and 1:26 solid-to-liquid ratio, yielding 55.42% lead removal. For copper removal, the optimal conditions were 539 W microwave power, 34-second treatment time, 0.75 mol/L citric acid concentration, and 1:22 solid-to-liquid ratio, achieving 52.98% copper removal.

Keywords

Microwave Enhancement; Citric Acid; Tea Saponin; Soil Heavy Metal Pollution; Plackett-Burman Test.

1. Introduction

With the rapid socio-economic development and accelerated industrialization/ urbanization in China, heavy metal emissions from industrial and agricultural activities have increased annually, making soil heavy metal pollution a global environmental crisis[1-3]; heavy metals are non-degradable and persistent in soil, posing severe threats to human and animal health as they accumulate in soil and enter the food chain through crops, causing cancer, teratogenesis, and other serious health issues. Yunnan Province, rich in mineral resources, has suffered aggravated soil heavy metal pollution due to long-term mining and smelting, especially the lead-copper contaminated farmland in the old mining area of southern Yunnan (Lancang County, Pu'er City), which is in urgent need of remediation [4,5]. Soil heavy metal remediation has become a global research focus, and existing studies show that organic acids (e.g., citric acid) and tea saponin (a non-toxic, biodegradable biosurfactant) have effective heavy metal leaching capabilities, while auxiliary technologies such as microwave enhancement can improve leaching efficiency by accelerating heating and molecular motion, overcoming the drawbacks of traditional leaching (low efficiency, long duration); however, synthetic chelating agents like EDTA pose secondary

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pollution risks due to poor biodegradability[6]. Preliminary team research showed that EDTA has high lead removal efficiency but poor biodegradability, while citric acid is superior in copper removal and environmentally friendly, so this study builds on this to propose microwave-enhanced tea saponin-citric acid composite leaching for remediation, adopting microwave enhancement instead of traditional shaking leaching and using Plackett-Burman (PB) design to screen optimal conditions (microwave power, treatment time, citric acid concentration, tea saponin concentration, solid-liquid ratio) through single-factor experiments[7,8]. This research aims to effectively remediate the lead-copper contaminated soil in the study area, provide a research direction for soil heavy metal pollution studies, and offer theoretical guidance for leaching processes, thus supporting soil remediation in southern Yunnan mining areas [9-11].

2. Experimental Materials, Instruments and Methods

2.1. Experimental Materials

Test soil was collected from lead-copper contaminated areas around Lancang County lead mine (southern Yunnan old mining area), pretreated by 20-mesh sieving. Reagents included analytical pure hydrochloric acid, nitric acid, hydrofluoric acid, perchloric acid, caustic soda, citric acid, tea saponin, and 1000 mg/L Pb/Cu standard stock solutions (National Center for Analysis and Testing of Non-ferrous Metals and Electronic Materials); ultra-pure water was used for solution preparation.

2.2. Experimental Instruments

Main instruments: FA3204B electronic balance, Galanz P70D20P-N9 microwave oven, Zhongjia SC-3616 centrifuge, GFA-7000A flame atomic absorption spectrophotometer, KDN-08 digestor, DHG-9245A drying oven, EPED-20TJ ultra-pure water generator; conventional laboratory (centrifuge tubes, volumetric flasks, colorimetric tubes, etc.) were used.

2.3. Experimental Methods

2.3.1. Soil Heavy Metal Determination:

1.0000 g soil was digested with HCl-HNO -HF-$HClO_4$, diluted with 1% nitric acid, and Pb/Cu content was determined by flame atomic absorption spectrophotometry.

2.3.2. Standard Curves:

Referring to HJ491-2019, 100 mg/L Pb/Cu working solutions were prepared. Series standard solutions (Pb: 0.00-10.00 mg/L; Cu: 0.00-5.00 mg/L) were used to plot curves with absorbance vs concentration (instrument conditions: Pb 283.4 nm, Cu 324.6 nm; lamp current 5.0 mA, neutral acetylene-air flame).

2.3.3. Key Formulas

Total content: $\omega=(C\times V\times n)/m_1$ (C: measured concentration; V: digestion volume; n: dilution ratio; m_1: soil mass); Removal rate: $\gamma=(C\times(V_1+V_2)\times V_3)/m_2$ (V_1: test solution volume; V_2: rinse volume; V_3: measured volume; m_2: soil mass).

2.3.4. Single-Factor Experiments

Effects of 5 factors on Pb/Cu removal were investigated (Table 1), with consistent operation: 1.0000 g soil + composite leaching agent (citric acid + tea saponin), pH=5±0.1, microwave treatment, centrifugation (3000 rpm, 20 min), supernatant dilution, and absorbance measurement (3 replicates).

2.3.5. Optimization Experiments

Based on single-factor results, a 4-factor (microwave time, citric acid concentration, tea saponin fraction, solid-liquid ratio) 2-level Plackett-Burman (PB) experiment was designed (microwave power fixed at optimal value from single-factor test). Steepest slope climbing experiment was

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conducted according to PB results to approach optimal conditions, followed by parallel validation tests to confirm the final optimal remediation parameters.

Table 1. Effects of 5 factors on Pb/Cu removal

Factor	Levels
Microwave power (W)	0, 119, 231, 385, 539, 700
Microwave time (s)	10, 20, 30, 40, 50, 60
Citric acid concentration (mol/L)	0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0
Tea saponin mass fraction (%)	0, 1, 3, 5, 7, 9, 11
Solid-liquid ratio (g:mL)	1:10, 1:15, 1:20, 1:25, 1:30, 1:35, 1:40

3. Results and Discussion

3.1. Plotting of Standard Curves

3.1.1. Plotting of Lead Standard Curve

The results of lead standard curve are shown in Table 2.

Table 2. Original Data Record of Lead Standard Curve

Volume of lead standard solution (ml)	0.00	0.50	1.00	5.00	8.00	10.00
Solution concentration of the lead standard curve: Pb (mg/L)	0.00	0.50	1.00	5.00	8.00	10.00
absorbance	0.0028	0.0283	0.0508	0.2302	0.3658	0.4608

3.1.2. Drawing of Copper Standard Curve

The results of the standard curve of copper are shown in Table 3.

Table 3. Original Data Record of Copper Standard Curve

Volume of the standard copper solution (ml)	0.00	0.10	0.50	1.00	3.00	5.00
Concentration of the copper standard curve solution: Cu (mg/L)	0.00	0.10	0.50	1.00	3.00	5.00
absorbance	0.0017	0.0131	0.0432	0.0670	0.2000	0.3206

The standard curves of Pb and Cu were plotted with the concentrations in Table 2 and 3 as the x-axis and the absorbance as the y-axis, as shown in Figure 3-1 and 3-2.

3.2. Determination of Total Lead and Copper Content in Soil

The results of the determination of total lead and copper contents in soil were shown in Table 4.

Table 4. Results of Determination of Total Content of Heavy Metals Lead and Copper in Soil

element	average absorbance	Total content (mg/g)
lead (Pb)	0.3546	9.177
copper (Cu)	0.2364	3.636

3.3. Determination of Instrument Detection Limits

3.3.1. Detection Limit of Lead Element

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Table 5. Determination Results of Lead Element Blank Value

Number of experiments	absorbance	average absorbance
1	0.0026	0.0025
2	0.0026	
3	0.0025	
4	0.0024	
5	0.0030	
6	0.0029	
7	0.0028	
8	0.0027	
9	0.0027	
10	0.0025	
11	0.0025	
12	0.0026	
13	0.0030	
14	0.0027	
15	0.0024	

The standard deviation is about 0.0003 by using the value in Table 5 into formula (3-2), and the relative detection limit of lead element is 0.0159 mg/L by using the standard deviation σ into formula.

3.3.2. Detection Limit of Copper Element

Table 6. Determination results of blank value for copper element

Number of experiments	absorbance	average absorbance
1	0.0017	0.0015
2	0.0016	
3	0.0014	
4	0.0015	
5	0.0013	
6	0.0014	
7	0.0013	
8	0.0015	
9	0.0014	
10	0.0018	
11	0.0013	
12	0.0014	
13	0.0015	
14	0.0013	
15	0.0014	

The standard deviation is about 0.0002 by using the value in Table 6 in formula (3-2), and the relative detection limit of copper is 0.0046 mg/L by using the standard deviation σ in formula (3-1).

3.4. Single Factor Experiment

3.4.1. Effect of Microwave Power on Removal Rate of Heavy Metals (Lead and Copper) from Soil

The experimental results of microwave power on the removal rate of heavy metals lead and copper in soil are shown in Table 7 and Table 8.

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Table 7. Results of the experiment on the effect of microwave power on the removal rate of heavy metal lead in soil

microwave power /w	0	119	231	385	539	700
Absorbance 1	0.1680	0.1981	0.1754	0.1846	0.2657	0.2300
Absorbance 2	0.1681	0.1979	0.1756	0.1848	0.2654	0.2301
Absorbance 3	0.1682	0.1983	0.1755	0.1844	0.2651	0.2305
Average absorbance A	0.1681	0.1981	0.1755	0.1846	0.2654	0.2302
Average concentration/(mg/L)	3.602	4.262	3.765	3.965	5.741	4.967
Average lead removal rate (%)	24.52	29.01	25.63	26.99	39.09	33.83

Table 8. Experimental results of microwave power on removal rate of heavy metal copper from soil

microwave power /w	0	119	231	385	539	700
Absorbance 1	0.0290	0.0450	0.0653	0.0791	0.1196	0.0855
Absorbance 2	0.0288	0.0450	0.0649	0.0793	0.1195	0.0853
Absorbance 3	0.0286	0.0453	0.0648	0.0795	0.1197	0.0851
Average absorbance A	0.0288	0.0451	0.0650	0.0793	0.1196	0.0853
Average concentration/(mg/L)	0.355	0.613	0.927	1.153	1.790	1.248
Average removal rate of copper (%)	4.89	8.43	12.75	15.86	24.61	17.17

Microwave power affects the removal efficiency of lead in soil, with the highest efficiency (39.09%) achieved at 539 W. For copper, the removal efficiency initially increases and then decreases with rising microwave power, reaching a maximum of 24.61% at 539 W. Therefore, 539 W is determined as the optimal microwave power for removing lead and copper from soils in the old mining area of southern Yunnan.

3.4.2. Effect of Microwave Time on Removal Rate of Heavy Metals Lead and Copper from Soil

The experimental results of the effect of microwave time on the removal rate of heavy metals lead and copper in soil are shown in Table 9 and Table 10.

Table 9. Experimental results of microwave time effect on removal rate of heavy metal lead in soil

Microwave time/s	10	20	30	40	50	60
Absorbance 1	0.1593	0.2342	0.2379	0.2841	0.1853	0.1502
Absorbance 2	0.1588	0.2340	0.2377	0.2841	0.1852	0.1501
Absorbance 3	0.1589	0.2338	0.2381	0.2844	0.1854	0.1497
Average absorbance A	0.1590	0.2340	0.2379	0.2842	0.1853	0.1500
Average concentration/(mg/L)	3.402	5.051	5.136	6.154	3.980	3.204
Average lead removal rate (%)	23.15	34.38	34.96	41.88	27.10	21.82

Microwave time significantly affects the removal efficiency of lead from soil. The removal rate reaches its peak at 40 seconds, achieving 41.88%. For copper, the removal efficiency initially increases with higher microwave power but then declines, peaking at 40 seconds with a

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removal rate of 32.70%. Therefore, 40 seconds is determined as the optimal microwave time for removing lead and copper from soils in the old mining area of southern Yunnan.

Table 10. Experimental results of microwave time effect on removal rate of heavy metal copper in soil

Microwave time/s	10	20	30	40	50	60
Absorbance 1	0.0374	0.0448	0.1079	0.1571	0.0845	0.0804
Absorbance 2	0.0377	0.0447	0.1077	0.1568	0.0848	0.0800
Absorbance 3	0.0377	0.0452	0.1075	0.1568	0.0848	0.0802
Average absorbance A	0.0376	0.0449	0.1077	0.1569	0.0847	0.0802
Average concentration/(mg/L)	0.494	0.610	1.602	2.379	1.239	1.167
Average removal rate of copper (%)	6.80	8.38	22.02	32.70	17.03	16.06

3.4.3. Effect of Citric Acid Concentration on Removal Efficiency of Heavy Metals (Lead and Copper) from Soil

The results of the experiment on the effect of citric acid concentration on the removal rate of heavy metals lead and copper in soil are shown in Table 11 and Table 12.

Table 11. Experimental results of the effect of citric acid concentration on the removal rate of heavy metal lead in soil

Citric acid concentration/(mol/L)	0.0	0.05	0.1	0.2	0.4	0.6	0.8	1.0
Absorbance 1	0.0500	0.0740	0.1386	0.2079	0.2145	0.2853	0.2495	0.2085
Absorbance 2	0.0501	0.0743	0.1389	0.2074	0.2147	0.2856	0.2494	0.2087
Absorbance 3	0.0505	0.0740	0.1389	0.2078	0.2149	0.2856	0.2496	0.2083
Average absorbance A	0.0502	0.0741	0.1388	0.2077	0.2147	0.2855	0.2495	0.2085
Average concentration/(mg/L)	1.011	1.536	2.958	4.473	4.626	6.182	5.391	4.490
Average lead removal rate (%)	6.88	10.46	20.14	30.44	31.50	42.11	36.71	30.57

Table 12. Experimental results of the effect of citric acid concentration on the removal rate of heavy metal copper from soil

Citric acid concentration/(mol/L)	0.0	0.05	0.1	0.2	0.4	0.6	0.8	1.0
Absorbance 1	0.0265	0.0286	0.0438	0.0747	0.1263	0.1623	0.1570	0.1553
Absorbance 2	0.0263	0.0289	0.0442	0.0748	0.1265	0.1621	0.1578	0.1550
Absorbance 3	0.0267	0.0292	0.0437	0.0749	0.1267	0.1625	0.1577	0.1547
Average absorbance A	0.0265	0.0289	0.0439	0.0748	0.1265	0.1623	0.1575	0.1550
Average concentration/(mg/L)	0.319	0.357	0.594	1.082	1.899	2.464	2.389	2.349
Average removal rate of copper (%)	4.39	4.91	8.17	14.88	26.11	33.90	32.85	32.31

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Citric acid concentration exhibits distinct effects on the removal efficiency of heavy metals (lead and copper) from soil. For lead, the removal efficiency initially increases with higher citric acid concentrations, then stabilizes, subsequently rises with longer microwave exposure time, and finally declines with extended microwave duration. The removal rate shows significant increases from 0.0 to 0.2 mol/L, gradually stabilizes between 0.2 and 0.4 mol/L, and slowly rises from 0.4 to 0.6 mol/L, reaching a maximum of 42.11% at 0.6 mol/L. For copper, the removal efficiency first increases with microwave power under specific conditions, stabilizes after reaching a peak, and achieves 33.90% at 0.6 mol/L. Therefore, the optimal citric acid concentration for lead and copper removal in soil from the old mining area of southern Yunnan is determined to be 0.6 mol/L.

3.4.4. Effect of Tea Saponin Quality Fraction on Removal Rate of Heavy Metals Lead and Copper from Soil

The results of the experiment on the effect of the content of saponin on the removal of heavy metals lead and copper in soil are shown in Table 13 and Table 14.

Table 13. Experimental results of the effect of saponin content on the removal rate of heavy metal lead from soil

Tea saponin content (%)	0	1	3	5	7	9	11
Absorbance 1	0.1652	0.2087	0.2651	0.2995	0.2875	0.2812	0.2752
Absorbance 2	0.1650	0.2086	0.2654	0.2997	0.2878	0.2810	0.2751
Absorbance 3	0.1648	0.2082	0.2651	0.2999	0.2875	0.2808	0.2747
Average absorbance A	0.1650	0.2085	0.2652	0.2997	0.2876	0.2810	0.2750
Average concentration/(mg/L)	3.534	4.490	5.736	6.495	6.229	6.054	5.952
Average lead removal rate (%)	24.07	30.56	39.05	44.23	42.40	41.41	40.53

Table 14. Experimental results of the effect of saponin content on the removal rate of heavy metal copper from soil

Tea saponin content (%)	0	1	3	5	7	9	11
Absorbance 1	0.0303	0.0619	0.1499	0.1759	0.1690	0.1609	0.1552
Absorbance 2	0.0304	0.0616	0.1498	0.1758	0.1689	0.1610	0.1551
Absorbance 3	0.0308	0.0616	0.1494	0.1760	0.1688	0.1608	0.1547
Average absorbance A	0.0305	0.0617	0.1497	0.1759	0.1689	0.1609	0.1550
Average concentration/(mg/L)	0.382	0.879	2.265	2.679	2.569	2.442	2.349
Average removal rate of copper (%)	5.26	12.03	31.15	36.85	35.32	33.57	32.31

The removal efficiency of tea saponin on soil heavy metal lead first increases with increasing concentration, then gradually decreases before stabilizing. The maximum removal rate of 44.23% is achieved at 5% tea saponin concentration. For soil heavy metal copper, the removal efficiency initially rises with increasing concentration, reaches a peak, then declines before stabilizing, with the highest removal rate of 36.85% at 5% tea saponin concentration. Therefore, the optimal tea saponin concentration for removing lead and copper in the old mining area of southern Yunnan is determined to be 5%.

3.4.5. Effect of Solid-to-Liquid Ratio on Removal Efficiency of Heavy Metals (Lead and Copper) from Soil

The results of the experiment on the effect of solid-liquid ratio on the removal of heavy metals Pb and Cu in soil are shown in Table 15 and Table 16.

Table 15. Experimental results of the effect of solid-liquid ratio on the removal rate of heavy metal lead in soil

solid-to-liquid ratio	1:10	1:15	1:20	1:25	1:30	1:35	1:40
Absorbance 1	0.3770	0.2089	0.3336	0.3175	0.1899	0.1745	0.0858
Absorbance 2	0.3772	0.2086	0.3336	0.3176	0.1897	0.1744	0.0861
Absorbance 3	0.3774	0.2086	0.3333	0.3174	0.1898	0.1752	0.0861
Average absorbance A	0.3772	0.2087	0.3335	0.3175	0.1898	0.1747	0.0860
Average concentration/(mg/L)	8.198	4.495	7.237	6.886	4.079	3.747	1.798
Average lead removal rate (%)	22.33	18.36	39.42	46.86	33.32	35.71	19.57

Table 16. Experimental results of the effect of solid-liquid ratio on the removal rate of heavy metal copper from soil

solid-to-liquid ratio	1:10	1:15	1:20	1:25	1:30	1:35	1:40
Absorbance 1	0.0831	0.1303	0.1540	0.1553	0.0937	0.0880	0.0395
Absorbance 2	0.0829	0.1305	0.1544	0.1556	0.0938	0.0879	0.0392
Absorbance 3	0.0827	0.1307	0.1545	0.1556	0.0942	0.0878	0.0398
Average absorbance A	0.0829	0.1305	0.1543	0.1555	0.0939	0.0879	0.0395
Average concentration/(mg/L)	1.210	1.962	2.338	2.357	1.384	1.289	0.524
Average removal rate of copper (%)	8.32	20.24	32.15	40.49	28.54	31.01	14.42

The removal efficiency of lead from soil heavy metals exhibits an "irregular" variation pattern with increasing solid-to-liquid ratio (S/L ratio). Initially decreasing with higher S/L ratios, the efficiency first increases, then decreases again after reaching its peak. The optimal removal efficiency of lead (46.86%) is achieved at a S/L ratio of 1:25. For copper, the removal efficiency initially rises sharply with increasing tea saponin concentration, then declines before gradually increasing again, followed by a sharp drop. The best removal efficiency (40.49%) is also observed at a S/L ratio of 1:25. Therefore, the optimal S/L ratio for removing lead and copper from soil heavy metals in the old mining area of southern Yunnan is determined to be 1:25.

In conclusion, the removal efficiency of lead and copper in the soil of the southern Yunnan mining area is the best under the conditions of microwave power 539 w, microwave time 40s, citric acid concentration 0.60 mol/L, the mass fraction of tea saponin 5%, solid-liquid ratio 1:25, the removal rate of lead reaches 46.86% and the removal rate of copper reaches 40.49%.

3.5. Plackett-Burman test

Based on the single-factor experiment described above, we investigated four factors: microwave duration, citric acid concentration, tea saponin mass fraction, and solid-liquid ratio. Each factor was tested at two levels (high and low), with the high level being 1.25 times the low level. The response variable was the removal rate of heavy metals (lead and copper) from soil. A Plackett-

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Burman experiment was designed with four factors and two levels. Each experiment was repeated three times, and the removal rates of lead and copper were calculated as the average of the three replicates. The factors and corresponding values in the PB experiment design are shown in Table 17.

Table 17. Factors and Levels of the Plackett-Burman Experimental Design

horizontal	A: Microwave time/s	B: Citric acid concentration (mol/L)	C: Tea saponin mass percentage (%)	D: solid-to-liquid ratio
+1	40	0.75	6.25	1:25
-1	32	0.60	5	1:20

The Plackett-Burman experiment was designed according to Table 15, with experiments conducted under various rinsing conditions. The results are presented in Table 18.

Table 18. Plackett-Burman Test Design and Results

number	A: Microwave time/s	B: Citric acid concentration (mol/L)	C: Tea saponin mass percentage (%)	D: solid-to-liquid ratio	Average lead removal rate/%	Average removal rate of copper/%
1	1	1	-1	1	49.16	46.20
2	-1	1	1	-1	52.06	49.19
3	1	-1	1	1	48.84	46.82
4	-1	1	-1	1	52.39	50.19
5	-1	-1	1	-1	48.04	48.16
6	-1	-1	-1	1	49.87	47.26
7	1	-1	-1	-1	48.27	46.36
8	1	1	-1	-1	49.86	47.75
9	1	1	1	-1	48.73	47.57
10	-1	1	1	1	51.60	49.10
11	1	-1	1	1	48.39	46.67
12	-1	-1	-1	-1	49.87	49.57

The study aimed to evaluate the removal efficiency of heavy metals (lead and copper) by processing experimental data with Design-Expert.V8.0.6.1 software, with the significance of each factor analyzed as shown in Tables 19 and 20.

Table 19. Analysis of Variance for Factor Levels (Lead Removal Rate)

parameter	quadratic sum	free degree	mean square	F	Prob>F	conspicuousness
model	19.78	4	4.95	6.70	0.0152	significant
A: Microwave time/s	9.33	1	9.33	12.64	0.0093	
B: Citric acid concentration (mol/L)	9.22	1	9.22	12.50	0.0095	
C: Tea saponin mass percentage (%)	0.26	1	0.26	0.35	0.5728	
D: Liquid-to-solid ratio	0.97	1	0.97	1.32	0.2882	
Lack of Fit	5.06	6	0.84	8.34	0.2591	
residual	0.10	1	0.10			
calibration sum	24.95	11				
R^2=0.7929						
Regression equation: Y=47.96-0.88A+0.88B-0.15C+0.29D						

Table 20. Analysis of Variance for Factor Levels (Copper Removal Rate)

parameter	quadratic sum	free degree	mean square	F	Prob>F	conspicuousness
model	14.89	4	3.72	5.43	0.0261	significant
A: Microwave time/s	12.20	1	12.20	17.79	0.0039	
B: Citric acid concentration (mol/L)	2.22	1	2.22	3.24	0.1151	
C: Tea saponin mass percentage (%)	2.700E-003	1	2.700E-003	3.937E-003	0.9517	
D: Liquid-to-solid ratio	0.46	1	0.46	0.68	0.4348	
Lack of Fit	4.79	6	0.80	70.94	0.0906	
residual	0.011	1	0.011			
calibration sum	19.69	11				
R^2=0.7562 Regression equation: Y=47.90-1.01A+0.43B+0.015C-0.20D						

3.6. Design of the Steepest Slope Climbing Experiment

Based on the results of the PB experiment, the most steep gradient of the positive and negative effect of the factors that significantly affect the removal rate of heavy metals lead and copper in soil was designed. The effect analysis diagrams of the removal rate of heavy metals lead and copper in soil are shown in Figure 3-8 and Figure 3-9.

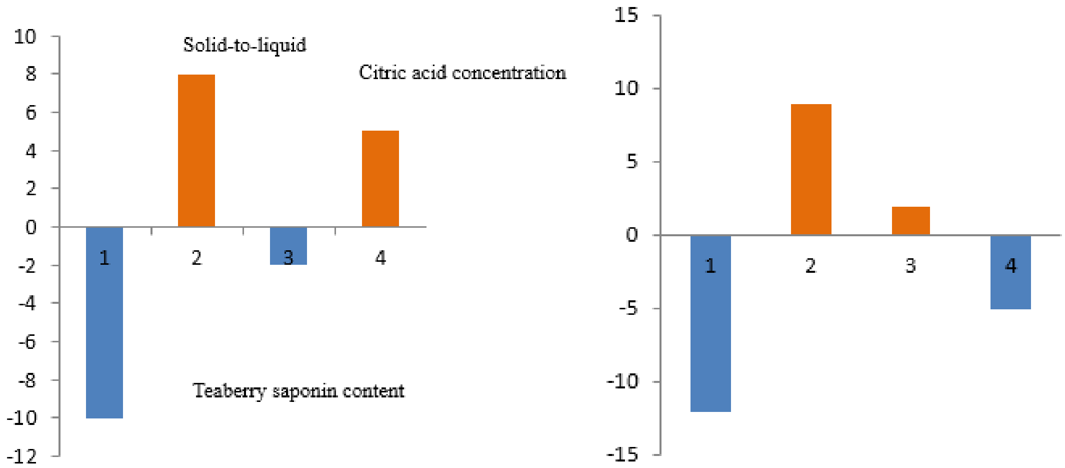

Figure 1. Lead removal efficiency effect analysis diagram

Table 21. (Lead Removal Rate) Steep Slope Experiment Design and Results

Experiment ID	Microwave time/s	Citric acid concentration/(mol/L)	Tea saponin content/%	solid-to-liquid ratio	Lead removal rate/%
1	38	0.65	4	1:26	55.43
2	36	0.70	3	1:27	53.05
3	34	0.75	2	1:28	52.19
4	32	0.80	1	1:29	53.48
5	30	0.85	0.5	1:30	50.57

As shown in Figure 1, among the four factors affecting soil heavy metal lead removal efficiency, microwave duration and tea saponin concentration exhibit negative effects, while citric acid concentration and solid-liquid ratio demonstrate positive effects. Similarly, Figure 3-11 reveals that microwave duration and solid-liquid ratio negatively influence soil heavy metal copper removal efficiency, whereas citric acid concentration and tea saponin concentration positively affect it. Consequently, the most rigorous experimental design and corresponding results are presented in Tables 21 and 22.

Table 22. (Copper Removal Rate) Steep Slope Experiment Design and Results

Experiment ID	Microwave time/s	Citric acid concentration/(mol/L)	Tea saponin content/%	solid-to-liquid ratio	Lead removal rate/%
1	38	0.65	6	1:24	50.22
2	36	0.70	7	1:23	49.96
3	34	0.75	8	1:22	52.98
4	32	0.80	9	1:21	52.29
5	30	0.85	10	1:20	48.30

As shown in Table 21 (most steep slope test results), the maximum lead removal efficiency of 55.42% was achieved under the following conditions: microwave power of 539 W, microwave duration of 38s, citric acid concentration of 0.65 mol/L, tea saponin mass fraction of 5%, and solid-to-liquid ratio of 1:26. Table 22 indicates that the optimal copper removal performance (52.98%) was obtained at the following parameters: microwave power of 539 W, microwave duration of 34s, citric acid concentration of 0.75 mol/L, tea saponin mass fraction of 8%, and solid-to-liquid ratio of 1:22.

3.7. Verification Experiment

To validate the accuracy of the predicted values, the experimental results and predicted values for lead and copper removal rates, based on the optimal conditions obtained from the aforementioned PB experiment, are presented in Table 23.

Table 23. Verification of Experimental Results and Predicted Values

	Microwave time/s	Citric acid concentration/(mol/L)	Tea saponin content (%)	solid-to-liquid ratio	Prediction value (removal rate/%)	Validation value (removal rate/%)
lead	32	0.75	5	1:25	51.95	51.91
copper	32	0.75	6.25	1:20	49.55	49.50

The optimal conditions for lead removal were determined as follows: microwave power of 539 W, microwave duration of 32s, citric acid concentration of 0.75 mol/L, tea saponin mass fraction of 5%, and solid-liquid ratio of 1:20. After conducting three replicate experiments, the verified average removal rate of lead was 51.91%, while the predicted value was 51.95%. The two values showed minimal deviation and remained consistent. For copper removal, the optimal conditions were set at the same parameters (539 W microwave power, 32s microwave duration, 0.75 mol/L citric acid, 6.25% tea saponin mass fraction, and 1:25 solid-liquid ratio). Three replicate experiments yielded a verified average removal rate of 49.50% for copper, with the predicted value being 49.55%. The verified and predicted values demonstrated negligible differences and maintained consistency. These results indicate that the selected model effectively predicts the removal efficiency of heavy metals (lead and copper) from soil under actual conditions.

3.8. Comparison of Results from Single Factor Experiments, Plackett-Burman Experiments, and Steepest Ascent Experiments

The results of single factor experiment, Plackett-Burman experiment and steepest climb experiment are compared in Table 24.

Table 24. Comparison of Single Factor Experiment, Plackett-Burman Experiment, and Steepest Ascent Experiment

Experiment name	optimum condition	Lead removal rate/%	Copper removal rate/%
experiment of single factor	Microwave power: 539 W, microwave time: 40s, citric acid concentration: 0.60 mol/L, tea saponin mass fraction: 5%, solid-to-liquid ratio: 1:25	46.85	40.49
PB Experiments	Microwave power: 539 W, microwave time: 32s, citric acid concentration: 0.75 mol/L, tea saponin mass fraction: 5%, solid-to-liquid ratio: 1:25	52.39	50.19
most steep climb experiment	Lead: microwave power 539 W, microwave time 38s, citric acid concentration 0.60 mol/L, tea saponin mass fraction 4%, solid-liquid ratio 1:26 Copper: microwave power 539 W, microwave time 34s, citric acid concentration 0.75 mol/L, tea saponin mass fraction 8%, solid-liquid ratio 1:22	55.43	52.98

4. Conclusion

This study focused on heavily lead and copper contaminated soil from the old mining area in Lancang, southern Yunnan, adopting microwave enhancement technology combined with a tea saponin-citric acid composite leaching agent for remediation; through single-factor experiments, Plackett-Burman (PB) experiments and the steepest slope test, the optimal conditions for heavy metal removal were determined, achieving a lead removal rate of 55.43% under conditions of 539 W microwave power, 38 s duration, 0.65 mol/L citric acid concentration and 1:26 solid-liquid ratio, and a copper removal rate of 52.98% under 539 W microwave power, 34 s duration, 0.75 mol/L citric acid concentration and 1:22 solid-liquid ratio. This study has certain innovations: it innovatively combines microwave enhancement technology with a tea saponin-citric acid composite leaching agent, uses PB experiments to screen optimal leaching conditions, fills the gap in the application of PB method in the screening of leaching agents for lead and copper contaminated soil, explores the application of organic acids and tea saponin composite system in multi-heavy metal contaminated soil remediation, and effectively overcomes the shortcomings of traditional shaking leaching such as long time and low efficiency by virtue of microwave's promotion of catalyst heating and organic matter Brownian motion. The research provides a direction and theoretical guidance for the remediation of severe heavy metal pollution in old mining areas of southern Yunnan and future soil heavy metal pollution research. It should be noted that due to limited time and class hours, the experiment has shortcomings such as unstable microwave temperature control and possible uneven heating, which need to be optimized in subsequent research.

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