

Enhancement of tartaric acid modified washing solutions for lead decontamination of tropical soils

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Abstract. Tartaric acid is generally not an effective soil washing solution, hence this study focuses on enhancing its usage for soil-Pb decontamination. Three tropical soil types (sandy, clay and loamy) with different lead concentrations were subjected to single batch washing using 0.01, 0.1, 0.5 and 1 M tartaric acid with 5% and 10% KCl modification at 3% soil-pulp-density for 2, 6, 12 and 24 h washing time. The optimum washing conditions were 1 M tartaric acid at 24 h washing time, with Pb removal efficiency: sandy- 94.3%, clay-67.6% and loamy-36.8%. Modification of tartaric acid with 5% and 10% KCl brought about some degree of enhancement of Pb removal efficiency especially for clay and loamy soils. Removal efficiency for 5% KCl modification were: sandy-97.9%, clay-96.2% with 1 M tartaric acid at 24 h washing time, loamy-76.7% for 0.5 M tartaric acid. Similarly, 10% KCl modification were: sandy-96.7%, clay-97.2% for 1 M tartaric acid at 24 h, loamy-82.1% for 0.5 M tartaric acid. Removal efficiency was soil concentration dependent. Generally, removal efficiency increased with increasing tartaric acid concentrations and washing time. Tartaric acid washing is promising and recommended in events of moderate contamination and 10% KCl modification in event of high level contamination. Further study is needed on enhancing very low concentrations of tartaric acid for large scale applications.

Keywords: soil remediation; lead; tartaric acid; soil contamination.

1. Introduction

Toxic trace metals undoubtedly have continued to raise attention due to greater understanding of their toxicological importance in the environment [1-3]. Particularly, soil-Pb content has dramatically increased in recent decades and often anthropogenically derived and non-biodegradable [4-7]. In environment, toxic Pb causes several adverse effects on biota. Soils serve as final repository of Pb in environment and also major food source for most biota, therefore, contaminated soils need to be cleaned to avoid/reduce contacts between the two [8, 9]. Several methods ranging from physical, chemical and biological have been adopted for toxic Pb removal from soils [10]. Among these methods, soil washing is particularly promising due to its simplicity, viability and efficiency [11-15]. Several studies have focused on the use of washing reagents such as inorganic and organic acids, chelating agents, bio-surfactants and composites with significant effectiveness in Pb removal from soils [13, 16-19]. These reagents, however, have deleterious effects on soil ecosystem in most cases rendering the soil sterile.

Greater emphases have now been placed on the use of low molecular weight organic acids (LMWOAs) which are more biodegradable and have less secondary ecological risk, because they can be produced by plant roots or microorganisms [20, 21]. Some LMWOAs such as acetic, citric, oxalic and tartaric acids have recently been used for soil washing [3, 13, 22-24]. However, their removal efficiency is not as effective as inorganic acids or chelating agent. Hence efforts have to be made

towards achieving higher removal efficiency. Tartaric acid is one promising LMWOAs for soil washing due to its chelating characteristics [25]. It is a non-humified acid which forms naturally in soils from decaying plants exudates, animals and microbial tissues at very low concentrations [26]. However, the use of tartaric acid for soil washing has generally not proven effective particularly for removal of Pb from contaminated soils. Removal efficiency have always been below 20% [2, 9, 27-29].

This study mainly focuses on enhancing usage of tartaric acid for soil-Pb decontamination. KCl modification of tartaric acid at different concentrations and washing time is applied on three soil types with different degree of contamination to evaluate lead removal efficiency.

2. Experimental

2.1. Soil sampling and chemical analysis

Three different soil types (sandy, clay and loamy) were sampled for the washing experiment from three different locations with obvious levels of contamination. Samples were collected by scooping about 12 kg soils each using a stainless steel into plastic bags. The samples were transferred to the laboratory where it was air dried and sieved through a 4 mm mesh size sieve. The three soil types were characterized for their physical properties and lead levels. Nitrate, phosphate, sulphate and soil pH were determined using hydrometric method in a 1:1 soil to water mixture [30], while flame photometric method was used for cation exchange capacity (CEC) [30].

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Hydrometer method was used for soil mechanical properties [31], while the Walkley and Black method [32] was used for soil organic matter and organic carbon content. A 5.0 g portion each of soils was weighed into a glass beaker and digested with 50 mL portion of concentrated aqua regia (HCl and HNO₃ at ratio 3:1) mixture on a hot plate for 3 h [33] to obtain the pseudo-total lead content. The pseudo-total lead was analyzed for all soil samples using a Varian SpectraAA-600 flame atomic absorption spectrophotometer (FAAS) after calibrating with Reagecon lead standard solutions.

2.2. Chemical washing experiment

The washing experiment was designed to improve lead removal efficiency of tartaric acid (TA) by modifying with KCL (KCl). In the experiment, 3% soil pulp density (SPD) was adopted which has been previously established to be effective [23]. A 0.3 g sandy soil was centrifuged with 10 mL (0.3 g/10 mL x 100 = 3% SPD) 0.01 M tartaric acid washing solution. They were sequentially agitated using a mechanical shaker (BOCH HY-BII Speed Governing Multipurpose Oscillator) at 172 rpm for 2, 6, 12 and 24 h. After agitation, the mixtures were centrifuged (BOSCH 80-2 centrifuge) at 2000 rpm for 35 min. The supernatants were extracted and stored for analysis. The washing step was repeated using 0.1, 0.5 and 1 M tartaric acid washing solutions. The whole washing experiment was similarly repeated for clay and loamy soils. To enhance the washing efficiency, modified solutions of 10 mL TA/5% KCl and TA/10% KCl at 1:1 ratio (TA: 0.01, 0.1, 0.5, and 1 M) were applied on each soil type for 2, 6, 12 and 24 h agitation. The supernatants were analyzed for Pb using FAAS. All analysis was performed in triplicate and the results presented as average values. Split samples were incorporated for instrument data validation. Analar grade reagents were used for the experiment. Standard deviation of the triplicate analyses performed on the extracts from the batch washing experiments was about 5%.

The percentage removal efficiency of Pb from the soils was calculated using an equation similar to the one earlier reported [23, 29, 34].

$$\text{Removal Efficiency (\%)} = \frac{C_1 \times V_1}{C_s \times M_s} \times 100$$

where C_1 and C_s are the concentrations of Pb in the supernatant (mg/L) and soil sample (mg/kg), determined using FAAS respectively. In addition, V_1 is the volume of supernatant (L) and M_s is the weight of the soil (kg) used for the washing experiment.

3. Results and discussion

3.1. Soil characteristics

Table 1 shows general characteristics of studied soils.

Table 1. General physio-chemical characteristics of studied soils

S/N	Parameter	Sandy	Loamy	Clay
1	pH value	6.17	8.18	7.79
2	Sand (%)	92.8	64.9	74.2
3	Clay (%)	1.43	12.8	25.0
4	Silt (%)	5.77	22.3	0.80

S/N	Parameter	Sandy	Loamy	Clay
5	Organic carbon (%)	1.38	5.95	4.96
6	Organic matter (%)	2.39	10.3	8.58
7	Nitrate (µg/g)	8.39	185	84.3
8	Phosphate (µg/g)	5.64	37.6	21.2
9	Sulphate (µg/g)	110	238	164
10	CEC (µhms/cm)	13.2	177	140
11	Lead (µg/g)	61.9±9.14	22,247±23.9	11,828±18.7

Soil pH values were 6.17, 8.18 and 7.79 for sandy, loamy and clay soils respectively. Soil pH is a critical factor in washing experiments, because it directly determines the mobility and solubility of metal ions, i.e. lower pH will tend to favor greater solubility of metals [35]. The soils have typical properties of sandy, loamy and clay soils in respect to mechanical properties, organic matter content, nitrate, phosphate, sulfate and cation exchange capacity [6, 23, 24]. These soil properties are generally characteristic of tropical geological environment of the Precambrian basement complex formations [36]. Sandy soil showed higher sand content (92.8%) with low organic matter (2.39%) and macro nutrient levels, has against loamy and clay soils. Porosity of the sandy soil, with slightly acidic pH, low organic matter and cation exchange capacity, will result in poor retention capacity for metals hence amenable to remediation by soil washing [37]. On the other hand, properties of loamy and clay soils may hinder easy dissolution of metals, hence modification is essential for effective washing. With increasing susceptibility of soils to trace metal contamination, these different soil properties will inadvertently influence the degree of metal removal through application of chemical soil washing techniques and therefore need to be examined. Average lead levels within the studied soils were: sandy -61.9±9.14 µg/g; loamy - 22,247±23.9 µg/g and clay -11,828±18.7 µg/g. Contamination levels were more pronounced for loamy and clay soils.

3.2. Lead removal efficiency by tartaric acid

Tartaric acid is not known to remove Pb efficiently from soils [9, 28, 29], however, combining washing solutions with other reagents slightly improves removal efficiency [2, 27]. Variables such as tartaric acid concentration and washing time were applied on sandy, loamy and clay soils to assess impact of soil properties on Pb removal efficiency (Table 2).

Table 2. Removal efficiency of Pb ($n = 3$)

Tartaric acid conc.	Washing time (h)			
	2	6	12	24
Sandy soil				
0.01 M	0	4.90±0.58	12.7±0.85	14.5±0.72
0.1 M	0	6.07±0.46	26.0±0.67	55.4±1.79
0.5 M	0	12.6±0.71	58.8±0.25	89.1±1.65
1 M	0	18.2±0.98	67.1±0.66	94.3±1.13
Clay soil				
0.01 M	3.03±0.09	5.73±0.33	7.71±0.37	9.69±0.46
0.1 M	5.78±0.14	7.89±0.23	12.9±0.85	15.2±1.36
0.5 M	23.4±0.16	24.6±0.56	46.6±0.65	46.4±0.63
1 M	26.6±0.43	33.7±0.35	66.73±0.27	67.6±0.95

Tartaric acid conc.	Washing time (h)			
	2	6	12	24
Loamy soil				
0.01 M	5.33±0.13	5.36±0.15	9.13±0.38	8.45±0.52
0.1 M	4.00±0.02	8.63±0.15	14.6±0.45	14.0±0.31
0.5 M	20.1±0.65	18.7±0.39	29.9±0.78	29.3±0.91
1 M	16.0±0.73	29.7±0.43	35.0±0.34	36.8±1.97

*n = number of extractions

Concentration of tartaric acid and washing time played significant roles on the amount of Pb removed from sandy soil. For instance, 0.5 M and 1 M tartaric acid washing solutions removed 58.8% and 67.1% Pb respectively in 12 h, and 55.4% (for 0.1 M), 89.1% (for 0.5 M) and 94.3% (for 1 M) in 24 h washing. It thus appears that high concentration of TA at longer washing time results in higher degree of Pb removal from sandy soils. The relatively low Pb level (61.9±9.14 µg/g), pH (6.17), organic matter content (2.39%), cation exchange capacity (13.2 µhms/cm) and finally porous nature of the sandy soil have significantly contributed to enhanced Pb removal. For clay soil, tartaric acid concentration and washing time play little role on Pb removal efficiency. Only for 1 M tartaric acid solution, a removal efficiency of 66.7% at 12 h and 67.6% at 24 h washing time was reported. The concentration and time factor played no role for loamy soil with just about 30% Pb removal for 1 M tartaric acid solution at 12 and 24 h washing time, compared to sandy and clay soils. Complex matrix of the loamy soil property coupled with high Pb content (22,247 µg/g) and pH (8.18) could explain the rather low Pb removal. Buffering effect of alkaline soil on weak organic acid like tartaric acid is known to affect solubilization of metals from soils [1, 9, 38].

3.3. Lead removal efficiency by modified tartaric acid

Tables 3 and 4 shows Pb removal efficiency using tartaric acid solution modified with 5% and 10% KCl at different concentrations and washing time.

Table 3. Removal efficiency of Pb using 5% KCl modification (n = 3)

Tartaric acid conc.	Washing time (h)			
	2	6	12	24
Sandy soil				
0.01 M	15.6±0.25	28.6±0.63	48.4±0.37	74.3±3.87
0.1 M	19.6±0.37	37.7±0.85	55.8±1.29	81.8±4.01
0.5 M	27.2±0.16	41.0±1.20	64.6±2.14	92.9±3.86
1 M	36.2±1.47	56.4±1.16	70.7±2.27	97.9±1.36
Clay soil				
0.01 M	3.99±0.08	6.36±0.91	11.4±0.89	18.3±0.42
0.1 M	37.3±1.28	39.6±1.26	67.6±1.96	80.0±2.92
0.5 M	47.1±2.58	48.9±1.10	72.4±1.35	85.5±2.86
1 M	51.8±2.21	55.5±1.57	84.0±2.06	96.2±3.46
Loamy soil				
0.01 M	8.37±0.50	9.02±0.95	13.4±0.27	16.6±0.86
0.1 M	14.4±0.42	12.5±0.41	28.1±1.08	38.7±1.54
0.5 M	36.5±1.83	46.9±1.30	70.9±3.83	76.7±3.00
1 M	23.0±1.31	24.8±1.26	54.6±1.65	63.8±1.91

Table 4. Removal efficiency of Pb using 10% KCl modification (n = 3)

Tartaric acid conc.	Washing time (h)			
	2	6	12	24
Sandy soil				
0.01 M	19.7±1.91	43.1±1.31	62.3±2.12	80.1±0.61

Tartaric acid conc.	Washing time (h)			
	2	6	12	24
0.1 M	27.2±1.00	38.3±1.63	68.8±2.25	87.5±1.15
0.5 M	30.1±1.86	56.6±2.36	78.4±0.85	93.2±2.86
1 M	42.3±2.43	68.0±2.10	87.3±6.11	96.7±2.80
Clay soil				
0.01 M	5.81±0.34	8.42±0.53	12.5±0.15	14.0±0.21
0.1 M	40.5±1.14	58.6±1.81	65.8±1.27	70.9±2.24
0.5 M	46.2±1.07	63.1±2.93	75.5±3.13	86.9±3.21
1 M	62.3±1.63	72.1±2.55	83.4±4.25	97.2±2.11
Loamy soil				
0.01 M	9.20±0.04	10.7±0.42	20.5±0.02	25.0±0.30
0.1 M	20.8±0.26	21.0±0.17	32.1±0.05	47.6±0.75
0.5 M	47.1±0.24	59.9±1.92	80.6±3.51	82.1±3.58
1 M	33.4±0.87	39.8±1.77	66.2±0.42	65.9±1.29

Modified 5% KCl/TA and 10% KCl/TA washing solutions apparently enhanced removal efficiency of Pb across the four concentrations and washing time for sandy soils compared to tartaric acid washings solution alone. The enhancement was achieved mostly for 12 and 24 h washing time for all concentrations. 0.5 M and 1 M tartaric acid solutions can efficiently remove Pb from relatively uncontaminated sandy soils, as shown in Table 1, but these high concentrations could have uncertain effect on the soil ecosystem. Modification of lower concentration of 0.01 M tartaric acid solution which is more soil friendly, as shown in Figure 1, could enhance Pb removal of up to 74.3% and 80.1% at 24 h washing. Proportional increase in removal efficiency could be achieved with increasing washing time.

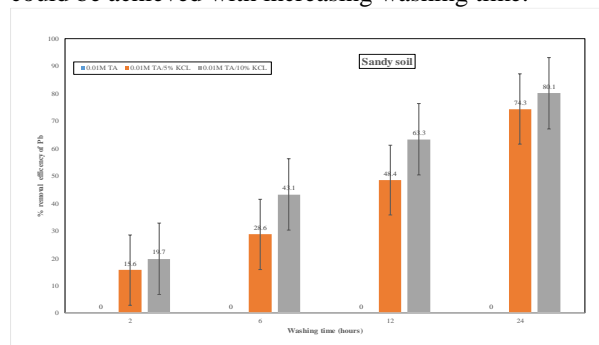


Figure 1. Removal efficiency of Pb in modified and unmodified 0.01 M TA washing solution

For clay soils, 5% KCl modification of 0.5 M and 1 M tartaric acid solutions recorded significant enhanced removal efficiency across all washing time, attaining 96.2% for a concentration of 1 M at 24 h. The least removal efficiency was observed for 0.01 M while for 0.1 M attained over 60% for 12 and 24 h washing time. The high Pb level in clay soils, its complex matrix of organic macro nutrients and low concentration of KCl may account for the much needed high concentration tartaric acid for effective Pb removal. With 10% KCl modification, 97.2% removal efficiency obtain with 1 M tartaric acid solution at 24 h. The 0.1 M and 0.5 M tartaric acid solutions also attained enhanced removal efficiency of over: 40% for 2 h, > 50% for 6 h, > 60% for 12 h and > 70% for 12 h washing.

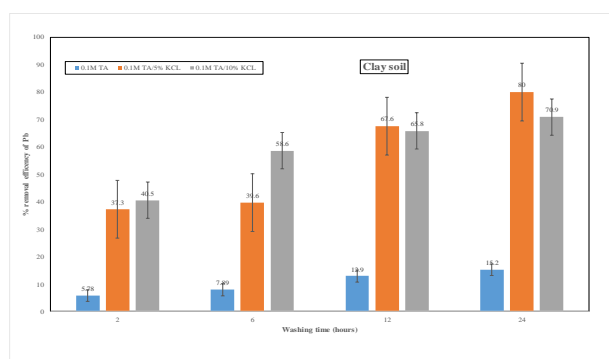


Figure 2. Removal efficiency of Pb in modified and unmodified 0.1 M TA washing solution

From Figure 2, the weak unmodified 0.1 M TA washing solution is significantly enhanced with addition of 5% and 10% KCl modification and washing time. As much as for other soils, loamy soils recorded the least enhanced removal efficiency when modifying TA with 5% and 10% KCl (Tables 3 and 4). 5% and 10% KCl modified 0.5 and 1 M tartaric acid solutions also showed enhancement especially for 12 and 24 h washing time. The highest attainable Pb removal efficiency is 76.7% for 5% KCl and 82.1% for 10% KCl at 24 h washing. The loamy soils had highest Pb level of 22,247 $\mu\text{g/g}$ which explains why modified 0.5 M and 1 M tartaric acid solutions had relatively low removal efficiency compared to clay and sandy soils.

Figure 3 shows the enhancement of 0.5 M tartaric acid solution with respect to washing time. Longer washing time favored greater removal efficiency.

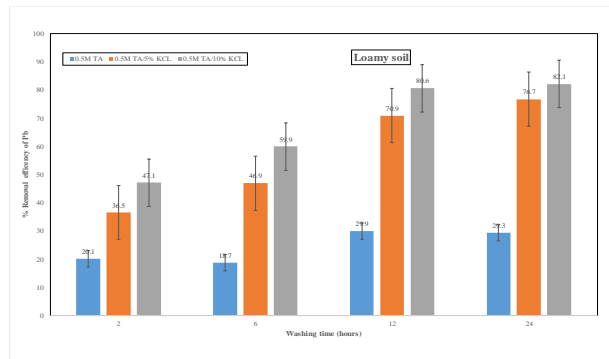


Figure 3. Removal efficiency of Pb in modified and unmodified 0.5 M TA washing solution

The relationship between Pb removal efficiency and tartaric acid concentrations for the three soil types observed for 5% KCl modification was also observed for 10% KCl modification (Tables 3 and 4). However, 10% KCl modifications were more efficient in removing Pb from the soils. The high salt concentration of 10% KCl washing solution substantially enhances the displacement of Pb from the soil crystalline lattice hence, responsible for enhancing Pb removal efficiency of 10% KCl TA washing solutions. Differences between lead and potassium in the activity series might explain a possible extraction mechanism, which involves initial dissolution of Pb pool from soils, and subsequently exchange with high concentration potassium cations from the KCl solutions. For the soils examined in this study, the effect of modification had negligible impact on Pb removal efficiency for 0.01 M tartaric acid

solution particularly in clay and loamy soils. These could well be attributed to high Pb levels and buffering capacity of those soils. In addition, increased washing time associated with elevated tartaric acid concentrations will eventually deplete buffering capacity of soils and under the present soil conditions (Table 1) concentration dependent solubilization of Pb will be achieved, since organic acids are known to decrease soil pH and form soluble complexes with trace metals [1]. In the washing experiment, Pb was removed from the soils with the following efficiency: 1 M > 0.5 M > 0.1 M > 0.01 M TA with respect to increasing washing time, exception being 0.5 M modified tartaric acid for loamy soil.

4. Conclusion

From the batch experiment study, tartaric acid has relatively weak removal efficiency of Pb particular from highly contaminated clay and loamy soils. However, for uncontaminated sandy soils, removal efficiency is as high as 94.3% for 1 M tartaric acid washing solution at 24 h washing time which is very efficient. Generally, removal efficiency was observed to increase with increasing concentrations in most cases and also with increasing washing time. Modifications of the various concentrations of tartaric acid with 5% and 10% KCl significantly enhanced Pb removal efficiency of 60-90%, especially for 12 and 24 h washing time. Concentrations most significantly enhanced were 0.01 M, 0.1 M, 0.5 M and 1 M for sandy, 0.1 M, 0.5 M and 1 M for clay, and 0.5 M and 1 M for loamy soils. Removal efficiency was in the following order: 1 M > 0.5 M > 0.1 M > 0.01 M tartaric acid solution. Tartaric acid washing is promising and recommended in events of moderate contamination and 10% KCl modification in event of high level contamination. Further study is needed on enhancing very low concentrations of tartaric acid for large scale applications.

Conflict of interest

The author declares no conflict of interest.

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