



Efficiency of the Combination of Vermicompost and Zero Valent Iron for the Remediation of Lead, Copper and Aluminum

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Authors' contributions

This work was carried out in collaboration between both authors. Authors FASA and SCRM designed the study, wrote and prepared the original draft. Authors FASA and SCRM did the statistical analysis and conducted the scientific literature review. Both authors read and approved the final manuscript.

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ABSTRACT

Aims: Evaluate the efficiency of the combination of vermicompost and zero -valent iron for the remediation of two types of soil with lead, copper and aluminum.

Study Design: Observational technique and analysis of soil samples contaminated by mining.

Place and Duration of Study: It was applied in the greenhouse in the district of San Juan de Lurigancho and in the Casapalca mining industry located in the district of San Mateo, in the months of February and September 2023.

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Methodology: The analysis of soil samples contaminated by mining was carried out through the addition of vermicompost amendments and zero-valent iron, seeking to observe the physicochemical changes of the soil and determine the bioavailability of lead, copper and aluminum in the soil. Using the atomic absorption spectrometer, a pH meter; the loss on ignition method, to determine organic matter; A 1.0mol L⁻¹ ammonium acetate solution was used for the cation exchange capacity (CEC) of the soil and vermicompost and for the determination of total potassium (K) method 3050b acid digestion of sediments, sludge and soils was used.

Results: The highest efficacy for the remediation of lead, copper and aluminium contaminated soils is produced with a vermicompost dose of 3:1, with 3 kilos of soil + 60 LC and Fe⁰ (45 g LC + 15 Fe⁰); obtaining the highest reductions in Pb from 942.6 mg/kg to 698.5 mg/kg in its final concentration, also for Cu from an initial concentration of 462.4 mg/kg, 323.8 mg/kg was obtained in its final concentration and for Al from a concentration of 9190.2 mg/kg resulted in 6823.8 mg/kg. Obtaining a maximum lead removal of 35.57%, copper 29.60% and aluminium 27.62% from the Casapalca soil. The highest efficiency of the dose of zero valent iron for the remediation of contaminated soils was at a ratio of 3:1 with a dose of 3 kg of soil + 60 Fe⁰ and LC (45 g Fe⁰ + 15LC). Likewise, plant uptake from 2 months after harvest of Cucumis sativus (cucumber) in the remediation of contaminated soils was efficient for all three types of metals at a dose ratio of 5:1, with Al showing a higher uptake in all cases.

Conclusion: The effectiveness of remediation of soils contaminated with heavy metals through the combination of vermicompost and zero valent iron highlights the importance of considering sustainable and ecological approaches to agricultural soil management, which could have significant implications for the protection of the environment and human health in areas with contaminated soils.

Keywords: Efficiency; vermicompost; zero valent iron; remediation.

1. INTRODUCTION

Rapid economic and population growth leading to inadequate waste and effluent disposal, thus polluting the environment with heavy metals, is a major concern [1]. Heavy metals act as toxic substances for soil and crops at high levels. Heavy metals hardly biodegrade in soil and tend to be transferred to plants and subsequently affect human health [2], this affects the growth, morphology and metabolism of soil microorganisms as they cause denaturation of proteins or destruction of the integrity of cell membranes [3]. In addition, it degrades soil structure, as metals can alter soil structure, reducing its porosity and affecting its ability to retain water and nutrients [4].

Therefore, there is an urgent need to safely dispose or manage industrial waste using clean, new, low-cost and environmentally friendly remediation technologies [5]. Such is the case of vermicompost, which has high nutritive value and increases soil fertility and maintains soil health [6]. It holds great promise for improving soils with various problems, including heavy metals (HM) [7]. Combining the functions of earthworms, crushing and conditioning the substrate, making this process faster, with microorganisms, responsible for the biochemical degradation of

organic matter [8]. While zero-valent iron is a reducing agent that can remove inorganic pollutants such as heavy metals and pesticides [9]. This combination offers several advantages, such as effective removal of a wide variety of pollutants, improvement of soil structure and fertility, and production of high quality compost [10]. Stabilisation with the application of organic amendments is effective for the immobilisation of heavy metals [11]. It can alter the availability of these elements to plants and microorganisms [12]. Making organic amendments can adsorb heavy metals, reducing their concentration in the soil solution and making them less bioavailable or less toxic compounds [13]. Earthworms help in the bioremediation process by removing heavy metals from the soil and accumulating them in their body tissues, especially in the yellow cells. Depending on the concentrations of heavy metals, the earthworm's body is affected [14].

Mining pollution causes adverse effects on agricultural spaces since they have high concentrations of toxic elements [15]. Due to the effect of precipitation, these present contaminants are dispersed in the soil due to runoff, thus having an adverse effect on agriculture and biodiversity [16]. Heavy metals modify the physicochemical properties of the soil, as well as high concentrations of toxic elements,

which leads to negative impacts on the environment and human health [17].

2. METHODOLOGY

Soil sampling was carried out at the Casapalca mining unit, following the following steps:

2.1 Selection of Sampling Areas

Areas in Casapalca, Peru, with different levels of lead, copper and aluminium contamination were identified and selected. Three sampling sites were established with different degrees of contamination: low, moderate and high. At each sampling site, soil samples were taken at a depth of 0-20 cm, using a stratified sampling method to ensure the representativeness of the samples. A total of 9 soil samples were collected and divided into three groups to evaluate the efficiency of remediation with different doses of vermicompost and zero valent iron. At each sampling site, soil samples were taken according to established sampling guidelines. The soils analysed were clayey, sandy and organic soils, selected for their prevalence in industrial and agricultural areas where heavy metal contamination is prevalent in Casapalca.

2.2 Initial Soil Characterization

The physical and chemical characteristics of the soil as well as the initial concentrations of lead, copper and aluminium were determined. For the analysis of the physico-chemical properties of the soil and the amendment; Firstly, to determine the Hydrogen potential (pH) in the soil samples, LC and Fe⁰, a pH meter was used in a ratio of 1:2 according to METHOD 9045D, for the organic matter test it was carried out by loss of mass by

ignition. The CEC was determined by the ammonium acetate method. The determination of metals and total potassium was carried out by METHOD 3050B. METHOD 3050B (determination of metals) was used, where 1 g of soil samples previously sieved 2 mm were weighed, then digested at 95 °C with real solution with cc HNO₃ + HCl 2:6; it was made up to 100 ml with distilled water and filtered with Whatman paper No. 41, and then the readings were taken to the atomic adsorption spectrophotometer. To determine the organic matter, the Loss on Ignition method was used, where 5g of soil sample was weighed, previously dried at 105 °C, and then calcined in a muffle at 850 °C x 4 hours and then weighed at constant weight. Subsequently, for the loss on ignition, the sieved soil sample was weighed, a 1:2.5 (W/v) dilution was made with distilled water, having enough to take the reading in the pH meter previously calibrated; using the METHOD 9045D SOIL AND WASTE pH, Hydrogen Potential (pH). For the cation exchange capacity (CEC) of the soil with vermicompost, it was determined using an ammonium acetate solution of 1.0mol L⁻¹.

The results of the characterisation of the prepared materials are shown in Table 1.

Table 2 also gives details of the treatment codes.

2.3 Preparation of Vermicompost and Zero Valent Iron

Vermicompost was prepared from organic residues and zero-valent iron using a sieve of “8 mesh #140 diameter and 100 um, following standard procedures. In addition, the zero-valent iron is combined directly with the soil, without incubating it.

Table 1. Results of the characterisation of the prepared materials

Code	pH	MO %	CIC Cmol	K mg/kg
SC-C	7.61	3.5	10.5	829.8
SC-C-R1	7.58	3.8	10.2	829
SC-C-R2	7.56	3.9	10.8	828.5
SC-Fe ⁰	7.49	3.88	10.7	831.12
SC-Fe ⁰ -R1	7.5	3.82	10.6	830.5
SC-Fe ⁰ -R2	7.46	3.86	10.9	830.8
SC-LC-	7.5	4.12	11.3	830.8
SC-LC-R2	7.48	4.11	11	831
SC-LC-R2	7.42	4.18	11.5	830.6
SC-L1F1	7.49	4.08	11	829
PS-L1F1-R1	7.51	4.12	11.2	828
SC-L1F1-R2	7.5	3.92	11.6	828.1

Code	pH	MO %	CIC Cmol	K mg/kg
SC-L2F1	7.53	4.08	10.7	829.4
SC-L2F1-R1	7.51	4.18	10.2	829
SC-L2F1-R2	7.53	4.08	10.7	830
SC-L5F1	7.49	4.11	10.55	831
SC-L5F1-R1	7.49	4.11	10.75	829.2
SC-L5F1-R2	7.49	4.11	10.75	829.2
SC-F1L1	7.53	4.08	10.7	829.4
SC-F1L1-R1	7.51	4.18	10.2	829
SC-F1L1-R2	7.53	4.08	10.7	830
SC-F2L1	7.5	4.12	11.3	830.8
SC-F2L1-R1	7.48	4.11	11	831
SC-F2L1-R2	7.42	4.18	11.5	830.6
SC-F5L1	7.49	4.11	10.55	831
SC-L5F1-R1	7.49	4.11	10.75	829.2
SC-L5F1-R2	7.49	4.11	10.75	829.2

Table 2. Treatment codes

Code	Soil composition
SC-C	Soil Casapalca - control
SC-C-R1	Soil Casapalca - control repetition 1
SC-C-R2	Soil Casapalca - control repetition 2
SC-Fe°	Soil Casapalca with Fe° amendment
SC-Fe°-R1	Soil Casapalca with amendment Fe° repetition 1
SC-Fe°-R2	Soil Casapalca with amendment Fe° repetition 2
SC-LC-	Casapalca soil with vermicompost amendment
SC-LC-R2	Casapalca soil with vermicompost amendment replicate 1
SC-LC-R2	Casapalca soil with vermicompost amendment replicate 2
SC-L1F1	Soil Casapalca with vermicompost amendment and Fe° 1:1
PS-L1F1-R1	Soil Casapalca with vermicompost amendment and Fe° 1:1 repetition 1
SC-L1F1-R2	Soil Casapalca with vermicompost amendment and Fe° 1:1 repetition 2
SC-L2F1	Soil Casapalca with vermicompost amendment and Fe° 3:1
SC-L2F1-R1	Soil Casapalca with vermicompost amendment and Fe° 3:1 repetition 1
SC-L2F1-R2	Soil Casapalca with vermicompost amendment and Fe° 3:1 repetition 2
SC-L5F1	Soil Casapalca with vermicompost amendment and Fe° 5:1
SC-L5F1-R1	Soil Casapalca with vermicompost amendment and Fe° 5:1 repetition 1
SC-L5F1-R2	Soil Casapalca with vermicompost amendment and Fe° 5:1 repetition 2
SC-F1L1	Soil Casapalca with Fe° amendment and worm compost 1:1
SC-F1L1-R1	Casapalca soil with Fe° amendment and vermicompost 1:1 replicate 1
SC-F1L1-R2	Casapalca soil with Fe° worm compost amendment 1:1 repetition 2
SC-F2L1	Soil Casapalca with Fe° amendment and vermicompost 3:1
SC-F2L1-R1	Casapalca soil with Fe° amendment and vermicompost 3:1 repetition 1
SC-F2L1-R2	Soil Casapalca with Fe° amendment and vermicompost 3:1
SC-F5L1	Soil Casapalca with Fe° amendment and vermicompost 5:1 repetition 1
SC-L5F1-R1	Soil Casapalca with amendment Fe° vermicompost 5:1 repetition 2
SC-L5F1-R2	Soil Casapalca with Fe° amendment and vermicompost 5:1

With regard to the methods of preparation of the materials, the collection of the sample within the arable layer was carried out from 0 to 20 cm depth, mixed until a totally homogeneous sample was found, sieved with sieve mesh #10 and separated in pots (Neciosup 2022).

The methods for characterisation were by EPA METHOD 3050B acid digestion of sediments, sludges, and soils, for Pb, Cu, Al and P metals in soils by atomic absorption spectrophotometry, using 1g of dry sample in a digestion tube, with HN₃ acid and H₂O₂, For the determination of pH with electrochemical equipment, pH was

determined by METHOD 9045D SOIL AND WASTE pH, organic matter by loss on ignition method, CEC by saturation with ammonium acetate, Olsen methodology in phosphorus determination. The sizes of the zero valent iron prepared were achieved with a particle size ≥ 100 μm in diameter by sieving with mesh # 150.

2.4 Monitoring and Analysis

Monitoring was carried out after 2 months to reach the water holding capacity of the soil and another 2 months for the growth of *Cucumis sativus* (cucumber) in pots. At the end of this period, the plants were harvested and the analysis units were taken to the laboratory. Because there were negative effects on the plant when zero-value iron was used at a high concentration, lower removal values occurred, as the soil is known to have stabilisation complexities due to the variety of nutrients, macro- and micro-elements that make for diverse behaviour at pH 7.45 to 7.61. This occurred in treatments SC-F5L1 and their respective replicates R1 and R2.

2.5 Analytical Instruments

The analytical tools mentioned above were used to determine the efficacy of the combination in removing heavy metals.

2.6 Data Analysis

The data obtained were analysed to assess the efficacy of the combination in reducing heavy metal concentrations in the soil. Statistical analyses were carried out to determine the significance of the results. Using analysis of variance (ANOVA) to compare the differences in the reduction of metal concentrations between the different doses and t-test to compare the reductions of Pb, Cu and Al concentrations.

2.7 Interpretation of Results

The results were interpreted critically and contextually, taking into account the soil conditions and the characteristics of the applied combination. Finally, the laboratory results of both the physico-chemical properties and the determination of the bioavailability of the metals in the 6 types of treatments were determined. First, the physico-chemical properties of the soil were determined, such as pH with a potentiometer, organic matter with the oxidation method and CEC with acetate. Then, 1 kg

samples of each treatment were taken to the laboratory and the bioavailability of the metals present in the samples was determined using an atomic absorption spectrophotometer (ICP-OES).

3. RESULTS AND DISCUSSION

3.1 Vermicompost Dose Efficiency

The greatest efficiency for the remediation of soils contaminated with lead, copper and aluminum occurs with a dose of vermicompost of 3:1, with 3 kilos of soil + 60 LC and Fe^0 (45 g LC + 15 Fe^0); obtaining the greatest reductions in Pb from 942.6 mg/kg to 698.5 mg/kg in its final concentration, also for Cu from an initial concentration of 462.4 mg/kg, 323.8 mg/kg was obtained in its final concentration and for Al from a concentration of 9190.2 mg/kg resulted in 6823.8 mg/kg. This is because the combined action of earthworms and microbes mineralizes organic waste and transforms it into manure, reducing contamination in the soil [18]. While with a dose of 1:1 with 3 kilos of soil + 60 LC and Fe^0 (30 g LC+ 30 Fe^0) the remediation was lower, reducing the metals Pb, Cu and Al slightly; This is as shown in Table 2 where for the Casapalca soil with vermicompost amendment and Fe^0 1:1, for Casapalca soil with vermicompost amendment and Fe^0 1:1 repetition 1 and the Casapalca soil with vermicompost amendment and Fe^0 1: 1 repetition 2 the reductions were from 969 mg/kg initial to 720 mg/kg final for aluminum, 952.5 mg/kg initial to 701 mg/kg final for aluminum and 952.7 mg/kg initial to 700 final for aluminum respectively.

For Cu the reductions were from 462.2 mg/kg to 367.2 mg/kg, 461.8 mg/kg to 357.8 mg/kg and 462.3 mg/kg to 358 mg/kg. For the metal Al, the reductions were from 9096 mg/kg to 7085 mg/kg, from 9095.5 mg/kg to 7085.2 mg/kg and from 9095.4 mg/kg to 7084.5 mg/kg. For aluminum it was reduced from 9096 mg/kg to 7085 mg/kg.

With a dose of 5:1 the efficiency of vermicompost for remediation is reduced, achieving a minimum reduction of the metals Pb, Cu and Al from 985.8 mg/kg to 838.2 mg/kg for Pb, from 460.5 mg/kg to 335.2 mg/kg for Cu and from 9090 mg/kg to 7583.5 mg/kg for Al.

Analysis of variance (ANOVA) revealed that the differences in the reduction of metal concentrations between the different doses are significant ($p < 0.05$). This suggests that the 3:1 dose is statistically different from the 1:1 dose in terms of remediation efficiency. Furthermore, the t-test showed that the reduction in Pb

Table 3. Methods used

Number	Method
1	Atomic absorption spectrometer METHOD 3050B ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS
2	The pH was determined with a pH meter METHOD 9045D SOIL AND WASTE pH
3	The organic matter was determined using the Loss on Ignition method.
4	The cation exchange capacity (CEC) of the soil and vermicompost was determined using a 1.0mol L ⁻¹ ammonium acetate solution.
5	Determination of total potassium (K) METHOD 3050B ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS.

Table 4. Metal removal efficiency (Pb, Cu and Al)

	Code	Removal %		
		Pb End	Cu End	To the End
Original ground control	SC-C	11.54	10.67	5.80
	SC-C-R1	11.52	10.24	5.59
	SC-C-R2	11.54	10.43	5.61
Soil with zero valent iron amendment	SC- Fe ⁰	28.02	23.18	15.47
	SC-Fe ⁰ -R1	27.98	23.24	15.47
	SC-Fe ⁰ -R2	28.08	23.34	15.45
Soil amended with vermicompost	SC-LC-	17.76	18.15	12.27
	SC-LC-R2	17.63	18.04	12.26
	SC-LC-R2	17.65	17.79	12.25
OE1.-efficiency of the vermicompost dose for the remediation of soils contaminated with lead, copper and aluminum	SC-L1F1	25.70	20.55	22.11
	PS-L1F1-R1	26.40	20.53	22.10
	SC-L1F1-R2	26.52	19.79	22.11
	SC-L2F1	25.90	27.79	25.75
	SC-L2F1-R1	26.01	27.68	25.77
	SC-L2F1-R2	25.90	27.81	25.75
	SC-L5F1	35.57	29.16	27.57
	SC-L5F1-R1	35.09	29.23	27.61
	SC-L5F1-R2	34.11	29.60	27.62
OE2.-efficiency of the dose of zero valent iron for the remediation of soils contaminated with lead, copper and aluminum	SC-F1L1	25.90	19.96	22.97
	SC-F1L1-R1	26.01	20.35	22.91
	SC-F1L1-R2	25.90	20.31	22.94
	SC-F2L1	17.67	18.33	15.24
	SC-F2L1-R1	17.66	18.19	15.15
	SC-F2L1-R2	17.73	18.22	15.23
	SC-F5L1	14.97	27.21	16.57
	SC-L5F1-R1	14.97	27.21	16.57
	SC-L5F1-R2	14.97	27.21	16.57

concentration with the 3:1 dose (from 942.6 mg/kg to 698.5 mg/kg) is significantly greater than with the 1:1 dose (from 969 mg/kg to 720 mg/kg) ($p < 0.01$). Similarly, the reductions in Cu and Al concentrations with the 3:1 dose were also significantly greater than with the 1:1 dose ($p < 0.01$).

3.2 Zero-Valent Iron Dose Efficiency

The greatest efficiency of the dose of zero valent

iron for the remediation of contaminated soils occurs at a ratio of 3:1 with a dose of 3 kilos of soil + 60 Fe⁰ and LC (45 g Fe⁰ + 15LC).

In contrast, with a 5:1 dose of zero iron, the reduction of all contaminants is slight; Pb decreased from 985.8 mg/kg to 838.2 mg/kg, Cu decreased from 460.5 mg/kg to 335.2 mg/kg and Al decreased marginally from 9090 mg/kg to 7583.5 mg /kg.

Which is refuted by Huang et al. [19], who points out that technologies based on zero-valent aluminum for the elimination of heavy metals due to its properties allow efficient remediation of contaminated soils, since it can help immobilize metals and prevent their absorption by plants and soil organisms.

3.3 Plant Absorption in the Remediation of Contaminated Soils

Regarding the absorption of plants in the remediation of contaminated soils, it was high at a dose of 5:1 with 3 kilos of soil + 60 LC and Fe⁰ (50 g LC + 10 Fe⁰) 5:1 for all cases of the metals.

Being thus demonstrated for lead with a dose of 50 to 10, it presented a significantly greater absorption compared to the other doses, in the same way for copper and aluminum with removal percentages of 53.96% for lead, 39% for copper and 66.31% for aluminum. Analysis of variance (ANOVA) revealed that the differences in absorption between the different doses are significant ($p < 0.05$). This suggests that the 5:1 dose is statistically different from the other doses in terms of absorption. In addition, the t-test showed that lead absorption at the 50:10 dose is significantly higher than at the other doses ($p < 0.01$). This confirms that this dose is particularly effective for the remediation

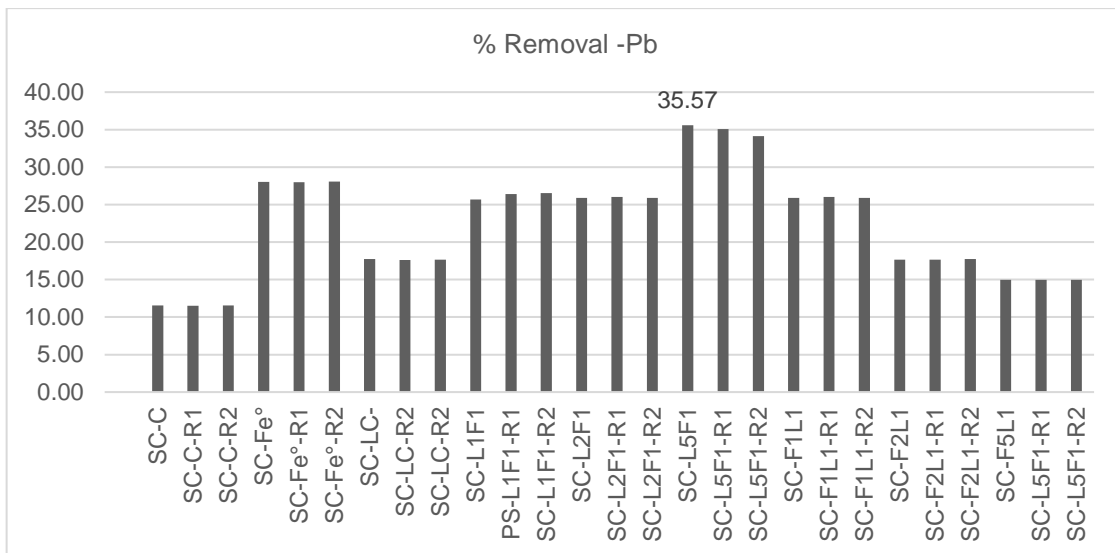


Fig. 1. Lead removal

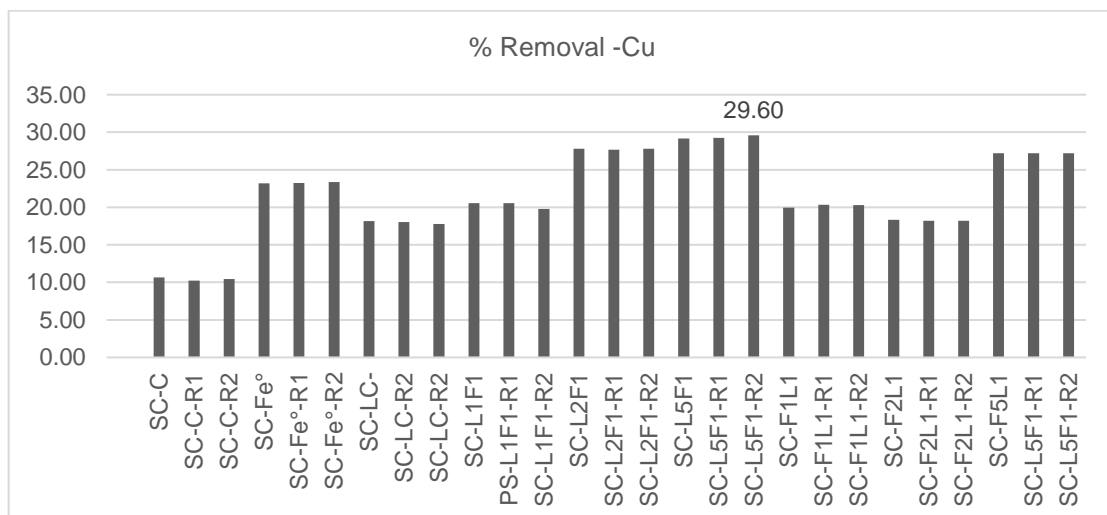


Fig. 2. Copper removal

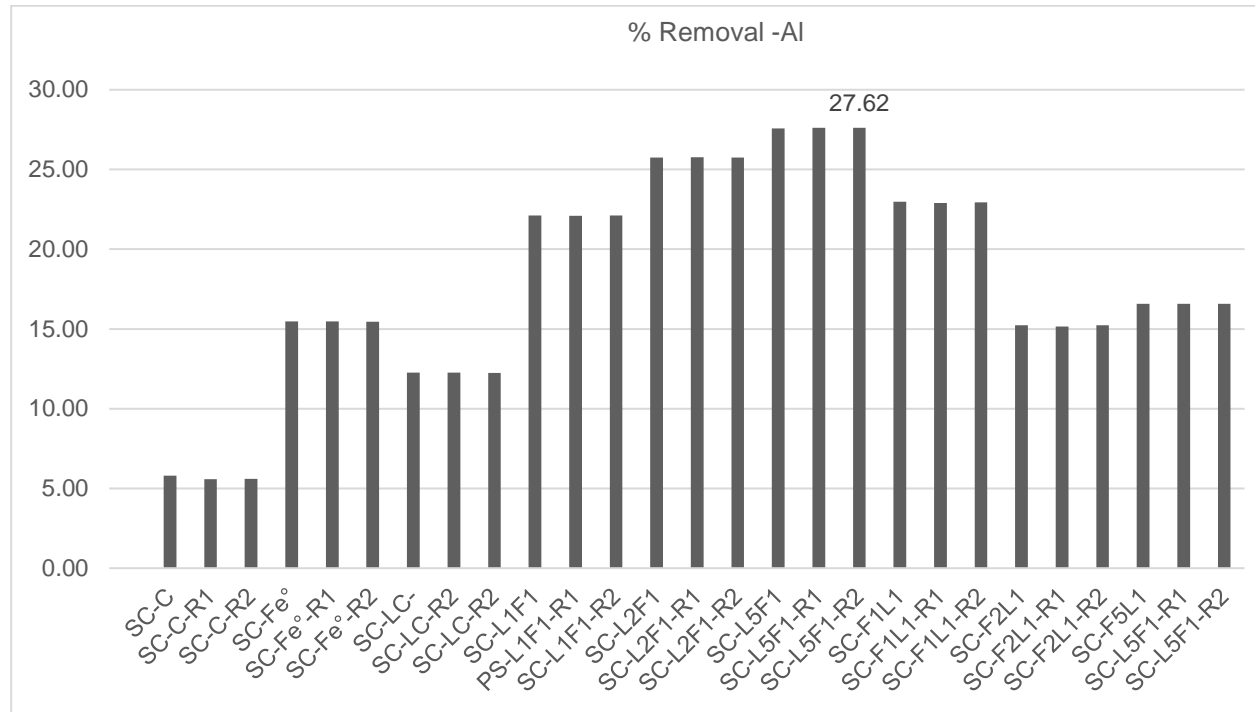


Fig. 3. Aluminum removal

of lead-contaminated soils. Such a result being supported by Atiyeh et al. [20], who explains that the efficiency of vermicompost is attributed to its ability to improve plant growth by enriching the soil with nutrients and organic compounds; since, in their study, the interaction between humic acids and the decomposition processes of organic waste resulted in an improvement in the soil structure and the availability of essential nutrients for plants.

Although the study provides promising results on the effectiveness of contaminated soil remediation techniques, there are some limitations that need to be considered when interpreting the results and assessing their applicability in real-life scenarios. One of the main limitations is the potential variability of soil types. The study focused on a specific soil type, which may limit the generalisability of the results to other soil types. Soil composition and structure can vary significantly depending on factors such as geology, climate and vegetation, which may affect the effectiveness of remediation techniques. Therefore, it is important to consider soil variability when applying remediation techniques in real-life scenarios.

4. CONCLUSION

The application of vermicompost is efficient in the different types of doses applied, but for greater removal it should be applied at a ratio of 3:1 (3 kilos of soil + 60 LC and Fe^o (45 g LC + 15 Fe^o)). Likewise, the efficiency of the dose of zero valent iron for the remediation of soils contaminated with lead, copper and aluminum is ideal in conditions of 3 kilos of soil + 60 Fe^o and LC (45 g Fe^o + 15LC) 2:1.

A promising area for future research is the study of the long-term effects of remediation treatments on soil health. While the current study provided promising results on the efficacy of remediation techniques, it is important to assess how these treatments affect soil health in the long term. This could include assessing soil structure, microbial biodiversity, water quality and the ability of the soil to support vegetation. Another area of future research could be the extension of remediation techniques for soils contaminated with a variety of pollutants. The current study focused on remediation of soils contaminated with lead, copper and aluminium, but there are many other contaminants that can affect soil health and water quality. Future research could explore the effectiveness of remediation techniques for soils contaminated

with other contaminants, such as arsenic, cadmium, mercury, among others. In addition, future research could focus on optimising remediation techniques for contaminated soils. This could include evaluating different doses and combinations of amendments, assessing the effectiveness of remediation techniques on different soil types, and evaluating the scalability of remediation techniques for application in real-life scenarios.

The research is an interdisciplinary study that addresses the problem of soil contamination, an issue of great relevance to today's society. This research has significant implications for several areas, such as agriculture, environmental policy, public health, biodiversity conservation and climate change mitigation. In agriculture, remediation of soils contaminated with heavy metals can improve soil quality and increase crop productivity, which in turn can have a positive impact on food security and the rural economy. In addition, the use of vermicompost as an organic amendment can reduce reliance on chemical fertilisers and promote sustainable agricultural practices. In the field of environmental policy, the results of this research can inform the development of policies and regulations for the management of contaminated soils and the protection of human health and the environment. In the field of public health, it can reduce exposure to chemical pollutants and improve water and air quality, which in turn can have a positive impact on human health, especially in vulnerable communities. In addition, research can also have implications for biodiversity conservation and climate change mitigation. Restoration of degraded soils can help preserve biodiversity and improve ecosystem resilience to climate change.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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