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Effect of Biochar on Soil Quality Polluted by Open Dumping Leachate in Kani-Qrzhala Area Erbil Governorate

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ABSTRACT

This study indicated landfill leachate poses serious threats to soil quality because of high content of content soluble salts, nutrient, and heavy metals. This study investigated soils collected from Erbil city landfill at four sites and depths (0-90 cm) to assess contamination levels and evaluate biochar for remediation. Results showed soil pH values between 7.40 and 7.82, indicating neutral to slightly alkaline conditions. Electrical conductivity was more high ranging from 9.79 to 20.85 ds m⁻¹, reflecting severe salinity. Organic matter content was generally low, from 1.48% at site 3 to 3.21% at site 1, below the optimum for soil fertility. Macronutrients showed high variability potassium ranged from 648.13 mg.kg⁻¹ at site 3 to 1104.67 mg.kg⁻¹ at site 1, sodium from 86.41 mg.kg⁻¹ at site 3 to 158.25 mg.kg⁻¹ at site 4 and phosphates peaked 22.52 mg.kg⁻¹ at site 2. Nitrate concentrations were also elevated 36.71-55.89 mg.kg⁻¹, indicating nutrient enrichment from waste inputs. Heavy metals extracted by EDTA confirmed contamination risks near leachate ponds. Application of walnut shell biochar and oak wood biochar at % w/w significantly reduced heavy metal bioavailability and improved soil quality, demonstrating biochars effectiveness as a remediation strategy. These results show that landfill leachate strongly degrades soil quality and soil health, while biochar serve as low cost and sustainable amendment to improve soil quality.

Key words: Landfill leachate, Soil quality, Biochar, Heavy metals, Remediation

1. Introduction

The normal operation of landfills is a source of are concerned worldwide considering the possible harm to human health and the environment. Landfills can provide a threat to many environmental aspects, including surface and groundwater, soil, as well as air, if they are incorrectly handled or negatively defended. Leachate contain a variety of pollutants, including soluble organic chemicals, inorganic contaminants, suspended particles, heavy metals, and hazardous chemicals[1]. Leachate, a byproduct of waste decomposition, frequently comprises a complex mix of harmful elements, including heavy metals, organic contaminants, and nutrients, which can significantly affect soil qualities[2].

Soil ecosystems constitute the fundamental basis for food production and are vital for achieving sustainable development goals (SDGs), hence they are considered significant resources for the environment[3]. Soil pollution from landfill leachate is a major environmental hazard, having serious consequences for land use sustainability, infrastructural stability, and groundwater quality[2]. The different components of landfill leachate affect soil behavior through a variety of processes. Heavy metals often attach to soil particles, reducing pore space and limiting water circulation. Suspended materials accumulate in pore spaces, effectively obstructing them, whereas microorganisms build biofilms and produce organic byproducts that obstruct fluid channels. Collectively, these contaminants limit soil permeability and impede efficient drainage, resulting in getting waterlogged and instability[4]. Mir, Wani [5] investigated that, These effects are more pronounced in regions near dumpsites, where soil samples frequently show lower specific gravity, maximum dry unit weight (MDUW), and strength properties than samples used for control obtained further away. In contaminated environments, increased permeability and moisture retention are common indicators of structure decomposition and chemical change of soil particles. Ibrahim, Sariyyu [6] reported in relation to landfill sites, leachate pollution has been seen to modify the geotechnical qualities of soils, such as reducing shear strength and raising compressibility and permeability, which is limiting their viability for construction. Akbari Dangarak, Motaghedi [7] reported in addition, contamination by leachate can reduce the maximum dry density and unconfined compressive strength of soils, as shown in experiments using several clay types, including both calcium and sodium. Khodary, Chihiro [8] investigated in sandy soils, leachate were found to decrease the coefficient of permeability as well as the slope of internal friction, while marginally raising the maximum dry unit weight, indicating structural alterations that may affect the stability of the soil.

During the recent decade, several studies have been concentrated on assessing the potential of new creative materials to be applied to the increase of the shear properties of granular soils, with the analysis of its impacted parameters[9]. Biochar is an organic material derived through the thermal decomposition of the organic biomass, although active carbon could be produced by processing biomass in addition to other carbonaceous compounds, such as charcoal[10]. Sørmo, Lade [11] investigated using biochars sorbents made from wood and sewage sludge to stabilize PFAS-contaminated soil. According to their research, using waste-based biochars sorbents to clean up polluted soil can improve future waste management processes since it better embodies the concepts of reducing waste and reuse. The aim of this study to determine impacts of landfill leachate on soil, and determine the rate of heavy metals in soil. Using biochars as soil remediation to decrease or immobilize of heavy metal rates and improve soil property.

2. Material and method

2.1 Study area (sampling site)

Erbil landfill is situated in Erbil City, Iraq, close to the Kani-Qrzhalah Town area on the left side of the main Erbil-Mosul Road. It was officially opened in 2001, and its proximity from Erbil's city center is nearly 15 km. The total area of the landfill is 37 ha. The majority of the space has been utilized, in (2017) the site received nearly 2000 tons of mixed municipal solid waste per day. (Information's based on ELS administrative staff).

2.2 Sample collection

Soil samples collected at four sites in the Erbil city (kani-Qrzhalah) landfill area follow the leachate ponds, which took samples at surface, 30 cm, 60 cm, and 90cm. After sampling soil air dried by 48 hours after that used wood to crushed samples and sieved by (2 mm sieve).

2.3 Analysis's of soil chemical parameters

Analyzed soil chemical parameters (pH, electrical conductivity, organic matter, calcium carbonate, potassium, sodium, calcium, magnesium) and measured the activity of three soil enzymes (dehydrogenase, urease and catalase). For analysis pH and electrical conductivity used (pH meter and EC meter) in lab after samples air dried and sieved by 2mm sieve. Organic matter was determined using walkly black method. Calcium carbonate (NaOH titrimetric method) Calcium and magnesium by (EDTA titrimetric method) Na⁺ and K⁺ by (flame photometric method)[12]

2.4 Determination of heavy metals

Soil samples extracted by using EDTA method to determine available heavy metal in soil. 5g of air dried soil was taken into conical flask 250 ml, then added 100 ml of (0.05 M EDTA) solution placed in shaker about one hour. After shaking process filtered sample by using filter paper No.1[13].

2.5 Statistical analyzing

The SPSS software application (version 25), was used to conduct the statistical analysis of the data. The design of experimental was ANOVA with three replications. Duncan multiple range was used to comparison between sites, depths and treatments. The significant level was set at $p < 0.05$. [14]

2.6. Biochar treatment

The polluted soil samples by leachate were remediate by using walnut shell biochar and Oak tree biochar. Oak biochar produced by oak wood. Walnut shell biochar was produced by collecting the shells of walnut and sundried for 24 hours then crushed the shells. Biochar was produced in lablotary under limited oxygen in covered crucibles in an incinerator heating for 3 hours at temperature (400 °C-600 °C). [15],[16]. Biochar was mixed well with soil by 10% biochar, and incubated samples for four weeks at 25 °C. [17].

Table 1. Some of physical and chemical characteristics of soil samples

Parameters	Site 1	Site 2	Site 3	Site 4
pH	7.538	7.408	7.825	7.658
EC (dS.m ⁻¹)	9.790	15.604	12.727	20.859
CaCO ₃ %	13.766	17.125	9.951	13.796
O.M %	3.211	3.046	1.479	3.008
Ca (mg.kg ⁻¹)	6.581	15.077	5.192	15.881
Mg (mg.kg ⁻¹)	14.804	18.305	23.970	17.782
K (mg.kg ⁻¹)	1104.67	833.76	648.13	822.55
Na (mg.kg ⁻¹)	122.333	94.916	86.416	158.250
PO ₄ (mg.kg ⁻¹)	0.970	22.529	8.917	21.089
NO ₃ (mg.kg ⁻¹)	36.710	55.895	48.202	52.920

2.7. CCME soil quality index (SoQI)

The CCME (Canadian Council of Ministers of the Environment), soil quality index is an additional tool tends to focus more on determining the relative risk through comparing pollutant concentration levels with the suitable soil quality guidelines. The SoQI index for contaminated sites was developed by using three factors, which are F1(scope), F2 (Frequency), and F3 (Amplitude) [18].

$$F_1 = \frac{\text{Number of failed contaminants}}{\text{Total number of contaminants}} * 100 \dots (3.2)$$

$$F_2 = \frac{\text{Number of failed tests}}{\text{Total number of tests}} * 100 \dots \dots \dots (3.3)$$

$$Excursion_1 = \frac{Failed\ Test\ Value}{Guideline} - 1 \dots \dots \dots (3.4)$$

-For the cases in which the test value must not fall below the guideline:

$$Excursion_2 = \frac{Guideline}{Failed\ Test\ Value} - 1 \dots \dots \dots (3.5)$$

$$ase = \frac{\sum_{i=1}^n excursion}{\# of failed tests} \dots \dots \dots (3.6)$$

$$F_3 = \frac{ase}{0.01 ase + 0.01} \dots \dots \dots (3.7)$$

$$SoQI = 100 - \frac{\sqrt{F1^2 + F2^2 + F3^2}}{1.732} \dots \dots \dots (3.8)$$

Table 2. concern levels of soil quality index

Site Classes or Level of concern	Soil Ranking Categories of the SoQI
Very low	90-100
Low	70-90
Medium	50-70
High	30-50
Very high	0-30

3. Result and discussion

3.1. Physicochemical properties

The analysis of soil samples collected from the studied landfill sites revealed significant variations in physicochemical parameters, as shown in table (3) soil pH values ranged from 7.408 at site 2 to 7.825 at site 1, indicating that the soils are generally neutral to slightly alkaline. This may be influence nutrient solubility in landfill. Electrical conductivity (EC) values varied considerably among the sites, with the lowest value at site 2 (15.604 ds.m⁻¹) and the highest value at site 4 (20.869 ds.m⁻¹), these values are markedly above the acceptable range, this reflecting high salinity. The elevated EC may be attributed to the accumulation of soluble salts as well as inorganic pollutants in landfill leachates, which can adversely affect soil quality and environmental soil health. Calcium carbonate (CaCO₃) concentration ranged from 9.951 % at site 3 to 317.125 % at site 2, these ranges suggest a moderate to high presence of carbonate minerals, possibly derived from landfill debris and construction materials. Organic matter (OM) content was relatively low across the sites, ranging from (1.479 mg.kg⁻¹) at site 3 to (3.211 mg.kg⁻¹) at site 1 which below the optimal levels required to sustain soil fertility. This indicated that landfill may have contributed to the degradation of organic matter through enhanced microbial decomposition. Macronutrient concentrations also showed considerable variation. Calcium(Ca) ranged from (6.581 mg.mk⁻¹) at site 1 to (15.881 mg.kg⁻¹) at site 4, while magnesium (Mg) concentrations were highest value at site 3 (23.970 mg.kg⁻¹) and lowest value at site 1 (14.802 mg.kg⁻¹). Potassium (K) exhibited extremely high values, particularly at site 1 (1104.675 mg.kg⁻¹) and lowest value (648.133 mg.kg⁻¹) at site 3, suggesting contamination from agricultural wastes rich in K- fertilizers and organic residues disposed in the landfill. Sodium (Na) concentration were also elevated with the maximum recorded at site (158.250 mg.kg⁻¹) and the minimum at site 2 (86.416 mg.kg⁻¹), high sodium levels are consistent with the presence of soluble salts in landfill leachates, leading to increased salinity and sodality hazards in the soil, This results and explanation supported by those results reported by [19] who mentioned that soluble salts from landfills, such as K and Na had a significant impact on the soil, resulting in increasing. phosphorus (PO₄⁻³) concentration ranged from (22.529 mg.kg⁻¹) at site 2 to (0.970 mg.kg⁻¹) at site 1, reflect

variability in nutrient enrichment due to decomposition of organic wastes, fertilizer and plant residues. Nitrate (NO_3) ranges were high ranging from ($55.895 \text{ mg.kg}^{-1}$) at site 2 to ($36.710 \text{ mg.kg}^{-1}$) at site 1, exceeding the acceptable range for unpolluted soils. These elevated nitrate levels suggest heavy contamination from chemical fertilizer, animal manures, as well as sewage inputs in landfill leachate.

Table 3. Some of physicochemical properties of the soils at studied Sites.

Parameters	Site 1	Site 2	Site 3	Site 4
pH	7.583 ^b	7.408 ^c	7.825^a	7.658 ^b
EC (dS.m^{-1})	9.790 ^d	15.604 ^b	11.210 ^c	20.859^a
CaCO_3 %	13.766 ^{ab}	17.125^a	9.951 ^b	13.796 ^{ab}
OM (mg.kg^{-1})	3.211^a	3.046 ^{ab}	1.479 ^c	3.008 ^{ab}
Ca (mg.kg^{-1})	6.581 ^b	15.077 ^a	5.192 ^b	15.881^a
Mg (mg.kg^{-1})	14.802 ^c	18.305 ^b	23.970^a	17.782 ^b
K (mg.kg^{-1})	1104.675^a	833.766 ^b	648.133 ^c	822.558 ^b
Na (mg.kg^{-1})	122.333 ^b	94.91 ^c	86.416 ^c	158.250^a
PO_4 (mg.kg^{-1})	0.970 ^c	22.529^a	8.917 ^b	21.089 ^a
NO_3 (mg.kg^{-1})	36.710 ^c	55.895^a	48.202 ^b	52.920 ^a

*The different letter means significant difference at ($p \leq 0.05$), while the same letter means there is no significant difference.

3.2. Heavy metal concentration in soil

Data present in table (4) indicated that landfill leachate significantly affected at ($p \leq 0.05$) on heavy metal concentration in the soils studied sites. Highest value for lead, cadmium, and nickel were $105.200 \text{ mg.kg}^{-1}$ at Site1, 3.592 mg.kg^{-1} at Site2, and $467.136 \text{ mg.kg}^{-1}$ at Site3, recorded respectively. While lowest value for lead, cadmium, and nickel were $30.400 \text{ mg.kg}^{-1}$ at Site4, 2.538 mg.kg^{-1} at Site1, $10.260 \text{ mg.kg}^{-1}$ at Site1, recorded respectively. These values indicated significant contamination, particularly in site1, which may be likely the most directly impacted by leachate seepage. High Pb levels suggest anthropogenic inputs from municipal solid waste, industrial residues, and vehicular emissions commonly disposed of in landfills. As well as highest concentration of Cd was at site 2 may reflect leachate percolation or accumulation in soil. High Ni concentration was among site 3 compared to other sites, this level may be possibly linked to disposal of Ni rich industrial waste or batteries in the landfill, high level of Ni posing risks to both soil productivity and ecological health these finding similar to [20] reported the correlation study's results demonstrated a significant connection between toxins and the decrease in their concentration as one's distance from the landfill increased. As a result, this study recommends adopting cell systems with strong technical and scientific methodologies to treat leaching and gasses that harm the environment in and near sanitary landfills. [21] heavy metals such as lead (Pb), iron (Fe), Cadmium (Cd), manganese (Mn), Nickel (Ni) copper (Cu), Zink (Zn) and chromium (Cr), (Zn) were identified in high concentrations in the soil close to the site; however, the contamination level is not serious based on the checked pollution indices, such as pollution index (PI) .

Table 4. Heavy metal concentration in soil at the studies sites

Sites	Pb (mg.kg ⁻¹)	Cd (mg.kg ⁻¹)	Ni (mg.kg ⁻¹)
Site 1	105.200 ^a	2.538 ^{abcd}	10.260 ^b
Site 2	79.200 ^b	3.592 ^a	12.916 ^b
Site 3	47.680 ^c	3.218 ^{ab}	467.136 ^a
Site 4	30.400 ^d	2.884 ^{abc}	10.574 ^b

*The different letter means significant difference at ($p \leq 0.05$), while the same letter means there

3.3. CCME soil quality index (SoQI)

Data in table 5 indicated that landfill leachate significantly affected soil quality index across four studied sites ranged between (40.55 to 42.18) which placed within 30-50 ranking and high level concern according to Canadian Council of Ministers of the Environment (CCME) guidelines. This indicates clear degradation of soil quality under the influence of landfill leachate. These results demonstrate that landfill leachate stress a considerable negative impact on soil quality, primarily due to migration of heavy metals such as Pb, Cd and Ni as well as high organic pollutants. Higher SoQI observed at site 2 indicated that may be spatial variability in leachate infiltration. These results consist with [22] reported the evident from the statistics that the leachate promoted and fostered the deterioration of soil quality. Given the analysis of the correlations between the SQI models, the relationship between the SQI models and wheat yield, and the sensitivity index values, the IQI calculated by MDS was the best model among the various SQI models used in this study for determining soil quality

Table 5. Effect of landfill leachate on CCME soil quality index (SoQI)

Sites	SoQI Index	Soil Ranking Categories of the SoQI	Level of Concern
Site 1	40.55	30- 50	High
Site 2	41.77	30-50, to 50-70	High to Medium
Site 3	42.18	30-50	High
Site 4	41.33	30-50	High

3.3. Effect of biochars on soil properties

The application of biochars significantly influenced the physicochemical properties of the studied site soils as indicated in table (6) improvement several soil chemical parameters. Soil pH increased from 7.61 at T0 (before treatment) to 8.251 at T1 and with slight increasing at T2 demonstrating the liming effect of biochars due to its alkaline nature and abundance of basic cations, such increases in pH value have been widely but to more stability of soil chemical reactions, these finding similar to [23] results, who reported in their study after wheat straw biochars remediation, after incubation of 30 days of biochars and soil, results showed soil organic matter, and soil pH increased. At 12% dosage, od biochars soil pH enhanced by (1.8 units), as well as SOM enhanced by (8.5 folds), therefore with adding of wheat straw biochars enhance soil quality.[24] reported that pH and calcium carbonate were higher in soils mixed with biochars than the control soil. Electrical conductivity conductivity decreased steadily from (14.745 dS.m⁻¹) at T0 to (11.031 dS.m⁻¹) at T2 indicating that biochars reduced high concentration of soluble salts in the soil solution, this result agreements with [25] who reported that adding biochars to the soil under salinity stress significantly reduced electrical conductivity and the amount of soluble Sodium ions as well as Cl. In addition, application of biochars improved the soil capacity to exchange cations, soil organic matter, humid, total nitrogen, nitrogen and phosphorus components in the soil, suggesting biochars enhanced the soil properties [26] reported biochars

improved soil fertility and reduced electrical conductivity in soil. Nutrients dynamics improvement following biochars addition calcium carbonate (CaCO_3) values increased from 13.660 % at T₀ to 72.779 % at T₁ and 16.619 % at T₂ the substantial rise in CaCO_3 at T₁ suggest a strong interaction between biochars and soil carbonate more than T₂ this may be related to the biochars properties. Organic matter content improved substantially, from (2.686 mg.kg⁻¹) at T₀ to (4.244 mg.kg⁻¹) at T₂ this reflects both addition of stable carbon from biochars and the stimulation of microbial activity leading to improve soil structure, aeration, and nutrient retention. Increasing organic matter is a major benefit of biochars application as it enhances long term soil fertility and soil quality.

Table 6. Effect of biochars on physicochemical properties of the studied soils.

Parameters	T ₀	T ₁	T ₂
pH	7.618 ^c	8.251 ^a	8.050 ^b
EC (dS.m ⁻¹)	14.745 ^a	12.050 ^b	11.031 ^b
CaCO ₃ %	13.660 ^b	72.779 ^a	16.619 ^b
O.M (mg.kg ⁻¹)	2.686 ^c	3.341 ^b	4.244 ^a
Ca (mg.kg ⁻¹)	10.683 ^c	27.707 ^b	34.987 ^a
Mg (mg.kg ⁻¹)	18.715 ^a	11.952 ^b	8.971 ^c
K (mg.kg ⁻¹)	852.28 ^a	767.647 ^b	604.241 ^c
Na (mg.kg ⁻¹)	115.479 ^a	22.375 ^b	51.916 ^b

*The different letter means significant difference at ($p \leq 0.05$), while the same letter means there is no significant difference

3.4. Effect of Biochars on heavy metals concentration

Figure 1 indicated that the application of biochars significantly reduced Pb concentration in soil contamination compared to the control treatment. This this reduction may be attributed the immobilization of Pb through adsorption by the large surface area and function groups (-OH, -COOH) of biochars, which decreased its mobility. Similar finding was reported by [27] The biochars-cement combination performed admirably in treating highly concentrated Pb²⁺ polluted soil, with leaching concentrations reducing dramatically with increasing biochars levels and falling below the Chinese hazardous waste identification level. Overall, using a biochars-cement composite curing agent to solidify heavy metal-contaminated soil appears to be a good subgrade infill strategy.

Figure 2 show that Cd concentration also decreased with biochars applications. Although to a less than Pb range decreasing if compared. This indicates that the stabilization mechanisms differ between these metals. Cd is highly mobile in soil, however biochars adsorbs Cd mainly through cation exchange with Ca⁺² and K⁺ present in biochars structure. These results consistent with [28] The findings of the pot trials showed that they immobilized soil Cd and Pb while decreasing tomato plant Cd and Pb uptake. These findings demonstrate that the enrichment of particular taxa caused by biochars amendment is linked to the repair of soil contaminated with heavy metals.

Figure 3 show that biochars as well as contributed to the reduction of Ni concentration in soil, although the effect was more pronounced compared to Pb and Cd. This may be related to ion exchange, ash, surface area, pH value carbon content of biochars properties which directly influence by feedstock and pyrolysis temperature this results agreement with those results reported by [29], who used four different pyrolysis's temperature to produce biochars, the results shows that the higher pyrolysis had a highest increasing rate of calcium carbonate in soil. overall, the results confirm that biochars is an effective amendment for mitigating heavy metals Pb, Cd, and Ni contamination in soil.

Figure 4 indicated that significantly soil quality index improved after additional both of biochars to contaminate soil compared to control T0. Before treatment the lowest SoQI (32.05), indicating reduced soil functionality likely due to contamination and poor nutrient status. In contrast, soils treated with biochars T1 and T2 exhibited higher SoQI values of 36.57 and 36.59 respectively which improved soil health. These results observed increase in SoQI under both biochars treatments T1 and T2 may be attributed to the adsorptive capacity, porosity, and alkalinity of biochars which collectively reduce heavy metal mobility, enhance nutrient retention, and improve soil structure. Although both biochars types yielded similar improvements, the marginally higher value in T2 by 36.59 suggest that biochars feedstock and pyrolysis condition may influence remediation efficiency. The close similarity in SoQI values between T1 and T2 suggest that both biochars types are effective in mitigating soil degradation caused by landfill leachate or similar contaminants. Previous studies have shown that while biochar feedstock influence chemical composition, the general remediation mechanisms, immobilization of heavy metals, pH regulation and organic matter enrichment are consistent across biochar [30].

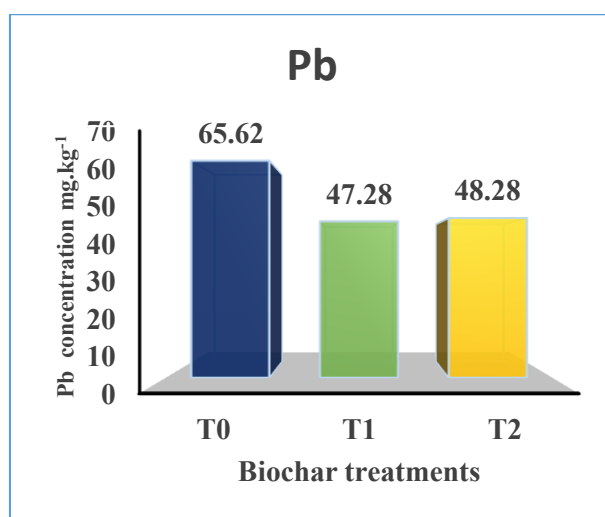


Fig. 1. Effect of biochars on Pb concentration

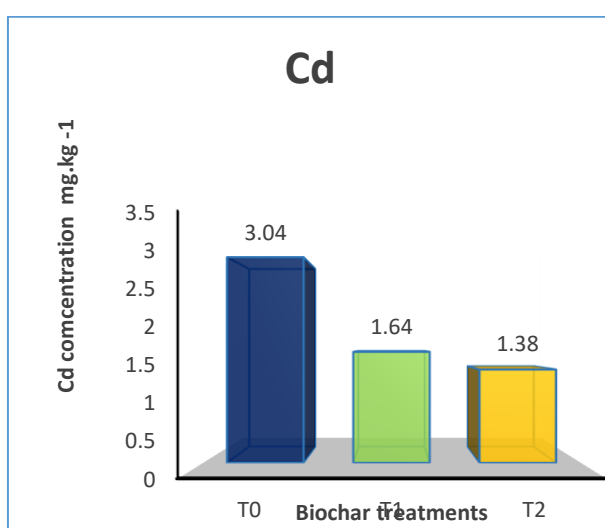


Fig. 2. Effect of biochar on Cd concentration

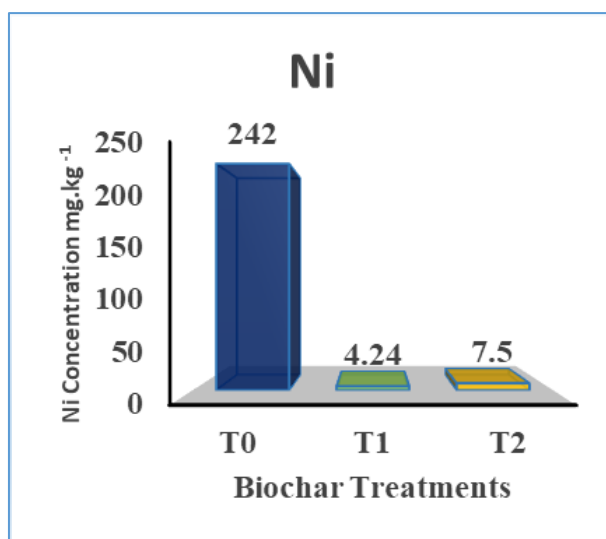


Fig. 3. Effect of biochar on Ni concentration

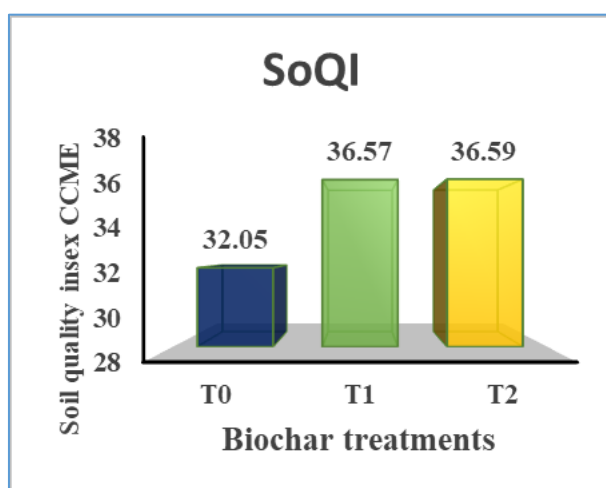


Fig. 4. Effect of biochar on CCME SoQI Index

Conclusion

This study demonstrated that landfill leachate had strongly negative impact on soil health, leading to high level of salinity, nutrient imbalance, as well as heavy metal contamination. Such alterations threaten both agricultural productivity of walnut shell and oak wood biochar proved to be an effective remediation measure, enhancing soil structure, reducing contaminant mobility, and supporting soil retention soil quality. The results indicated that biochar not only offers a low cost and eco friendly solution for leachate contaminated soil, while as well as contributes to sustainable waste management and enhance climate or status of agriculture.

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