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IMPACTS OF OPEN DUMPSITE LEACHATE ON SOIL ENZYMATIC ACTIVITY IN KANI-QRZHALA OPEN DUMPSITE – ERBIL CITY

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ABSTRACT:

The study was carried out to assess the effect of open dump site leachate on soil enzymes activity. Soil samples were collected in Kani-Qrzhala open dump site in Erbil city in four sites (Site1, Site2, Site3 and Site4) for different depths; surface ,30cm,60cm and 90 cm following the edge drainage pathway of leachate. The results of dehydrogenase, urease and catalase show a significant variation at significant levels ($P \leqslant 0.01$) and ($P \leqslant 0.05$) respectively. The highest rates of dehydrogenase, urease and catalase (77.69 µg TPF.g^{-1}, 454.50 µg N.g^{-1}, and 1.927µg H_2O_2.g^{-1}), were recorded at surface point in all sites, while the lowest rates of all enzymes were recorded at 90 cm respectively, this is indicating that the soil depth adversely affected enzymes activity. Using oak tree wood and walnut shell biochar by 10% as a treatment to polluted soil, significantly increased enzymes activity. Walnut shell biochar was more suitable than oak tree wood biochar to catalase and urease activity, where urease was increased by 133.61% and catalase by 63.40%, while dehydrogenase activity was increased by 95.07% after using oak tree wood biochar which was more suitable than walnut shell biochar. This was related to the feedstock and technology production of biochar that affected on biochar structure and activity, however in this study, biochar application generally had a positive effect on enzymes activity and soil depth had an adverse effect.
KEYWORDS: Soil enzyme, Biochar, Open dumped, Leachate, Soil depth.

1. INTRODUCTION

The wide generation of solid waste is one of the most significant effects of urbanization, industrialization, and population development. Solid waste discarding is one of the most serious environmental hazards in the world.(Agamuthu, 2007). Landfill leachate from (MAW) municipal solid waste disposal in landfill sites are usually identified as hazardous and strongly contaminated waste waters. Landfill leachate is formed of liquid which has come into the landfill coming from external sources, like surface drainage, rainwater, underground water, and water from underground springs, and also the liquid produced by waste decomposition, and it has percolated through the solid waste, extracting both dissolved and suspended components. Leachate is a highly polluted wastewater that exhibits considerable time and spatial variation in physical-chemical characteristics. It is also a potential source of polluting of ground, surface water and soil.Tatsi, Zouboulis, Matis, and Samaras (2003)

Biochar is a porous, carbonaceous substance produced by the thermochemical (for example; gasification pyrolysis,) and hydrothermal decomposition of organic compounds in the absence of oxygen at high temperature. This method is identical to how charcoal is made. Biochar is going to gain wide acceptance as a soil amendment because it not only mitigates climate alteration by sequestering carbon from the atmosphere into soil, but it also enhances properties of soil and soil fertility by improving microorganism's activity and moisture and nutrient content, while also increasing agricultural productivity.(Sajjad et al., 2020). Soil enzymes are essential in a variety of biochemical activities in soils, including the degradation of soil organic matters (SOM) plus other biogeochemical nutrient cycling. So those enzymes are identifying as sensing indicator elements of changes in soil functioning and have a direct relation with soil organic matter forms and also soil quality. Cellobiosidase is the enzyme which breaks down cellulose. Soil quality and also microbial respiration are influenced by dehydrogenase activity. Catalase is an enzyme that is produced by every aerobic microorganism, as well as plants and animal's cells. The large surface area of the biochar helps in the adsorption of labile substrates, which has an impact on soil enzymatic activity. Biochar's influence on soil enzymes activity is primarily determined by interrelationship of enzyme and substrate with biochar. The absorption of substrates as well as extracellular enzymes mostly to the functional groups at the surface of biochar probably enhance or inhibit enzymatic reactions.(Lammirato, Miltner, & Kaestner, 2011) .Soil enzymes activity is strongly related to improvements in soil quality, which can be used as a good indicator to sustainable soil organization and also environmental safety and stability. Across of all soil quality index, enzymes refer quickly to alterations in soil management and thus remain the best indicator of soil biological potential change.(Bandick & Dick, 1999). Solid waste, especially Municipal Solid Waste (MSW), is a major problem in the Kurdistan region's cities particularly in Erbil city, because the landfills are just dumping grounds for mixed MSW without any environmental management. Thus, the aim of this study is to determine the impact of landfill leachate on soil quality specially on soil enzymatic activity as well as to determine the effects of biochar on soil nutrients and ratio of enzymatic activity by using two different types of biochar as a treatment.

2. MATERIAL AND METHOD

2.1. The properties of sampling site

Erbil landfill location is in Erbil City, Iraq, next to the Kani-Qrzhala Sub-district (as from left side of the Erbil-Mosul road). The latitude and longitude are 36°10'23"N as well as 43°35'32"E. ELS is about 15 kilometers from Erbil's city center. The landfill, that opened in 2001, includes a total area of 37 hectares. Most of the land area has been utilized. More than 1000 tons of Municipal solid wastes are transported to the site every day. The components of the buried MSW are not separated properly. In

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Erbil City, there are very few current, recognized documents about MSW characteristics.

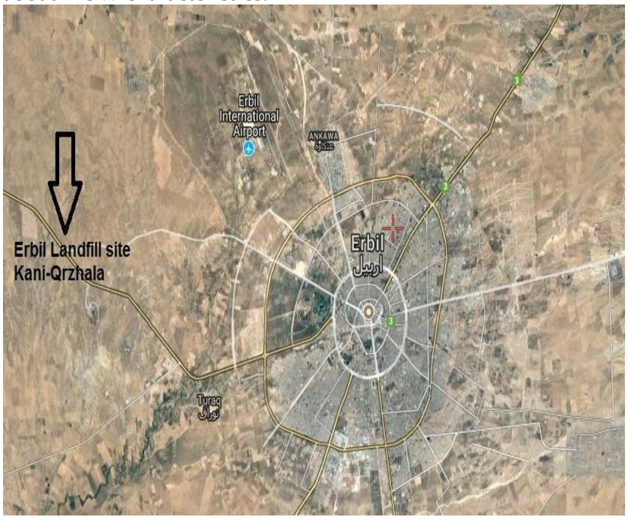

Figure.1; Kani-Qrzhala landfill site in Erbil city(Aziz & Mustafa, 2018).

2.2. Sample collection and analysis

Soil samples were collected follow the edge drainage pathway of leachate from the landfill site in Erbil city during September. Soil samples were collected from four different sites (site 1, site 2, site 3, and site 4) at surface, 30 cm 60cm, and 90 cm in Erbil city. Soil samples were air dried for 24 to 48 hours, then crushed by woody tool and sieved by 2mm sieve in laboratory.

2.3. Analysis of soil enzymes activity

Dehydrogenase was determined following methods as mentioned by (Casida Jr, Klein, & Santoro, 1964).The soil samples were treated with 2,3,5 triphenyltetrazolium chlorides (TTC) then incubated at (25 ˚C) then the absorbance of dehydrogenase activity was read by spectrophotometrically at 485 nm The value of dehydrogenase activity was expressed as µg TPFg⁻¹ dry weight soil. Urease was determined by treating one gram of soil samples with 0.25 ml toluene, 0.75 ml citrate buffer (pH,6.7) and 1 ml of 10% urea substrate solution then incubated for 3 hours at 37℃. The formation of ammonia was read by sectrophotomerically at 640 nm(Hoffmann & Teicher, 1961). The result was shown in µg N g⁻¹ dry soil. Catalase activity was determined by $KMnO_4$ titration method), one gram of soil sample was added to 5 ml of distilled water with 1 ml of %30 H_2O_2 solution, then shaken the solution 30 minutes and then added 5 ml of 1.5M of sulfuric acid. After that the solution was filtered and titrated by using (0.05M $KMnO_4$). The result was indicated in µmoll of H_2O_2 per gram soil per hour. (Wang & Zhan, 2009) and (Li, Liang, He, Hu, & Yu, 2014).

2.4. Biochar treatment

The polluted soil samples by leachate were remediated by using walnut shell biochar and Oak tree biochar. Oak biochar was 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 400℃-600℃,(Igalavithana et al., 2017),(Zahed, Salehi, Madadi, & Hejabi, 2021).Biochar was mixed well with soil by 10% biochar, and incubated samples for four weeks at 25℃.(X. Zhang et al., 2013).

2.5. Calculation of percentage and enzymes activity rate:

1.The increasing percentage rate of enzymes activity after treatment was estimated by using this equation:
Percent increase= [(new value – original value)/original value] *100

2. Calculation of catalase activity rate = [($KMnO_4$ ml) *(N)*(0.071) *(1000)]/grams of samples used
*Were N:(Normality of the standardized potassium permanganate)

3. Calculation of dehydrogenase activity(DHA) = (TPF(concentration)*V)/Wt.
V= the volume of solution added to the soil sample, Wt.= the weight of your sample used

2.6. Statistical analysis

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 compare sites, depths and treatments. The significant level was set at $p<0.01$, and $p<0.05$.(H. L. Harter, 1960)

2. RESULTS AND DISCUSSION

Data indicated in Table (1) show the effect of landfill leachate on soil enzymes activity (dehydrogenase µg $TPF.g^{-1}$, catalase µg $H_2O_2.g^{-1}$ and urease µg $N.g^{-1}$) at four different sites (site 1, site2, site3, and site4) in Kani-Qrzhala landfill area Erbil city. The results of dehydrogenase and urease indicated significant variation at ($P\leqslant0.01$), While the results of catalase activity showed significant variation at ($P\leqslant0.05$), wherears no significant differences were shown in the results between Site 1 and Site 2. The maximum value 64.04 µg $TPF.g^{-1}$,393.82 µg $N.g^{-1}$ of dehydrogenase and urease were recorded at site4, while the catalase maximum value was 1.828 µg $H_2O_2.g^{-1}$) at site2. The minimum values 45.57 µg $TPF.g^{-1}$, 1.401 µg $H_2O_2.g^{-1}$, of dehydrogenase and catalase were recorded at site3 and minimum value of urease was 245.93 µg $N.g^{-1}$ at site2. This variation among sites of dehydrogenases, urease and catalase concentration and the activity rate may be due to the amount, period of time, leachate components absorbed by the soil. According to many studies sometimes maybe the landfill leachate enhance soil enzymes activity which related to the activity of microorganisms , these results are agreement with those reported by Shailaja, Srinivas, and Rao (2021). However, maybe leachate consists many harmful substances such as heavy metals inorganic materials which have adverse effects on soil property and damage to planting. The results indicated in table (1 and 2) show that the leachate had not adverse effects on soil enzymes activity.

Table .1 The means of soil enzymes activity of different sites

Sites	Dehydrogenase µg $TPF.g^{-1}$	Urease µg $N.g^{-1}$	Catalase µg $H_2O_2.g^{-1}$
Site 1	47.54^{c}	273.68^{c}	1.766^{a}
Site 2	55.42^{b}	245.93^{d}	1.828^{a}
Site 3	45.57^{d}	354.35^{b}	1.401^{c}
Site 4	64.04^{a}	393.82^{a}	1.559^{b}

Table (2) shows the effect of soil depth on soil enzymes activity, in which the depths adversely affected enzymes activity. The results show that the enzymes activity decreased with increasing soil depth. The higher rate of dehydrogenase, urease and catalase activity were 77.69 µg $TPF.g^{-1}$, 454.50 µg $N.g^{-1}$ and 1.927 µg $H_2O_2.g^{-1}$ observed at surface, while the lowest activity rate of them recorded at 90 cm about 31.60 µg $TPF.g^{-1}$, 180.08 µg $N.g^{-1}$ and 1.32 µg $H_2O_2.g^{-1}$). These results may be due to activity of microorganisms and oxygen content which decrease with the soil depth and may be due to the organic matter content. The same result was obtained by Avazpoor et al. (2019). The Leachate drainage or absorption of leachate in soil may decrease with increasing soil depths that is also may be one of the effects of decreasing soil enzymes activity, because leachate contains some organic materials and microorganisms which generally enhance the enzymes activity.

Table.2 Effect of soil depth on enzymes activity

Depth	Dehydrogenase µg TPF.g^{-1}	Urease µg N.g^{-1}	Catalase µg H_2O_2.g^{-1}
Surface	77.69^{a}	454.50^{a}	1.927^{a}
30 cm	60.23^{b}	378.64^{b}	1.788^{b}
60 cm	42.95^{c}	248.56^{c}	1.513^{c}
90 cm	31.60^{d}	186.08^{d}	1.326^{d}

The results in Table (3) shows that the application of biochar significantly affected the soil enzymes activity. Dehydrogenase activity increased after applying walnut shell biochar (T_1) and oak tree wood biochar(T_2), by 85.65% and 95.07% for T_1 and T_2 respectively. These results indicated that the T_2 (oak tree wood biochar) was more effective on dehydrogenase activity. These results are similar to those obtained by L. Zhang, Xiang, Jing, and Zhang (2019) and Beheshti, Etesami, and Alikhani (2018) were reported that the application of biochar increased microbial biomass and intracellular which is due to improvement dehydrogenase activity. Urease activity increased by133.61% after using walnut shell biochar and 99.40% after using oak tree wood biochar. The main factor affected urease activity was N cycle ,which is the important to this enzymes activity, this is reported by J. Harter et al. (2014).Catalase activity increased by 63.40% after using walnut shell biochar and 45.13% after using Oak tree wood biochar respectively. According to Tabatabai (1994) indicated that biochar amendment greatly assisted to increase soil microbe oxidative capacity here because microbes oxidative-reductase metabolic is driven by catalase activity and is connected to the metabolism activity of aerobic soil microorganisms. Oladele (2019) reported that the biochar application due to involvingP,N,C cycling which manage the dynamics and fluxes of soil nutrients and improve the enzymes activity in soil.

Table.3 Effect of biochar on soil enzymes activity

Treatment	Dehydrogenase µg TPF.g^{-1}	Urease µg N.g^{-1}	Catalase µg H_2O_2.g^{-1}
T_0	33.51^{c}	178.39^{c}	1.203^{c}
T_1	60.55^{b}	416.74^{a}	1.964^{a}
T_2	65.37^{a}	355.71^{b}	1.746^{b}

Note: control (T0), walnut shell biochar(T1), Oak tree wood biochar(T2)].

Data stated in Table (4) show the effect of biochar on soil enzymes (dehydrogenase, urease, and catalase) activity, at four different sites in Kani-Qrzhala landfill area Erbil City. The highest activity rate (42.50 µg TPF.g^{-1}, 278.35 µg N.g^{-1}) of dehydrogenase and urease activity was recorded at site 4 that received Oak tree wood biochar and walnut shell biochar respectively, while catalase highest rate (1.378 µg H_2O_2.g^{-1}) was at Site1 which was treated by walnut shell biochar(T1). The biochar application had significant effects on enzymes activity at four sites. Dehydrogenase activity increased more by T_2 than T_1 for all sites except site (1) T_1 was more effective than T_2. This is may be due to the soil property ,biochar component, moisture, temperature, aeration rate, which reported by Zheng et al. (2018),and Wojewódzki, Lemanowicz, Debska, and Haddad (2022). Urease and catalase result indicated that the T_1 biochar was more effective than T_2 on their activity at all sites except for urease activity at Site 3 which increased more by T_2 and catalase activity at site 2 increased more by T_2. This is may be due to many physical and chemical prosperities of soil and biochar which positively or negatively affected on enzymes activity.Zahed et al. (2021) reported that biochar quality and their activity to remediation affected by some factors such as the feedstock property, pyrolysis temperature during biochar production, which affected the composition structure of biochar. pyrolysis temperature it's the main factor to changing biochar characteristics.

Data in Table (5) describe the effect of biochar on enzymatic activity at different soil depths. The results showed that both of biochars (T_1 and T_2) had a positive effect on soil enzymes activity, which significantly improved soil enzymes activity at all deep points of soil (surface, 30 cm, 60 cm, and 90cm). This indicates that the biochar application increases the enzymatic activity at all soil depth. This increase of enzyme activity at all soil depth may be related to the increase of the soil organic matter which directly supply the nutrients and energy for soil organisms. Increasing of soil enzymes activity beneficial to bioremdiation of pollutant in soil this agreement with the results obtained by Sebiomo, Banjo, Ade-Ogunnowo, and Fagbemi (2017) investigated in their study that dehydrogenase and urease enzymes could be used as soil indicator and could help in bioremediation of contaminated soil

. **Table.4 Effect of biochar on enzymes activity at different site**

Sites	**Treatment**	**Dehydrogenase µg TPF.g^{-1}**	**Urease µg N.g^{-1}**	**Catalase µg H_2O_2.g^{-1}**
Site 1	T_0	25.38^{c}	142.85^{ef}	1.321^{e}
	T_1	60.08^{ab}	376.30^{abc}	2.358^{a}
	T_2	57.17^{ab}	301.91^{bcd}	1.620^{cde}
Site 2	T_0	38.41^{bc}	95.41^{f}	1.378^{ce}
	T_1	58.02^{ab}	389.50^{abc}	1.865^{bc}
	T_2	69.84^{a}	252.90^{cde}	2.240^{ab}
Site 3	T_0	27.75^{c}	196.96^{def}	0.887^{f}
	T_1	49.57^{abc}	408.00^{ab}	1.780^{cd}
	T_2	59.38^{ab}	458.10^{a}	1.537^{cde}
Site 4	T_0	42.50^{bc}	278.35^{d-e}	1.225^{ef}
	T_1	74.54^{a}	493.16^{a}	1.854^{bc}
	T_2	75.08^{a}	409.96^{ab}	1.598^{cde}

Note: control (T0), walnut shell biochar(T1), Oak tree wood biochar(T2)].

Table.5 Effect of biochar on enzyme activity at different soil depths

Depth	Treatment	Dehydrogenase µg TPF.g^{-1}	Urease µg N.g^{-1}	Catalase
Surface	T_0	54.38^{c}	271.55^{cd}	1.517^{c}
	T_1	85.82^{a}	557.80^{a}	2.257^{a}
	T_2	92.88^{a}	534.16^{ab}	2.007^{ab}
30 cm	T_0	39.08^{de}	198.96^{de}	1.508^{c}
	T_1	71.29^{b}	497.50^{ab}	2.075^{ab}
	T_2	70.60^{b}	439.46^{b}	1.780^{bc}
60 cm	T_0	22.54^{f}	134.13^{e}	1.004^{d}
	T_1	53.09^{cd}	341.33^{c}	1.769^{bc}
	T_2	53.24^{cd}	270.23^{cd}	1.767^{bc}
90 cm	T_0	18.05^{f}	108.93^{e}	0.782^{d}
	T_1	32.00^{ef}	270.33^{de}	1.757^{bc}
	T_2	44.75^{cde}	179.00^{de}	1.440^{c}

Note: control (T0), walnut shell biochar(T1), Oak tree wood biochar(T2)]

4. CONCLUSION

The study was generally focused on the impact of landfill leachate, soil depths, and biochar on soil enzymes activity. The results show that the leachate had not negative impacts on soil enzymes activity because the leachate contains many organic or nutrient substance and microorganisms which enhance the activity of soil enzymes. Soil depth adversely affected enzymes activity, activity was decreased with increasing soil depths related to available nutrients, microorganism, moisture, aeration rate in soil layers. In this study used two types of biochar at the same concentration, oak tree wood and walnut shell biochar to determine effect of biochar on enzymes activity. Urease and catalase activity increased more by walnut shell biochar than the oak tree wood biochar, however dehydrogenase activity increased more after using oak tree wood biochar than the walnut shell. The results indicated that biochars application had a positive effect on enzymes activity.

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