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Properties of Recycled Nanomaterials and Their Effect on Biological Activity and Yield of Canola in Degraded Soils

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Abstract: Recycling waste, such as rice straw and water treatment residuals, is important to reduce harmful effects on the environment and to improve canola yield and soil quality in degraded soils. Nanotechnology for the production of nanomaterials from biochar and water treatment residues will be a future revolution for improving soil quality and increasing canola yield in degraded soil. Therefore, this study aims to identify the properties of some recycled nanomaterials, such as nanobiochar (nB) and nanowater treatment residue (nWTR), and their effect on the biological activity and productivity of canola in degraded soils. The results showed that the nWTR and nB contain many functional groups and minerals, and they also have high negative zeta potential. The addition of the studied soil amendments significantly improved microbial biomass carbon (MBC) and biological activity, which played a major role in increasing canola yield. The highest dehydrogenase (DHA) and catalase (CLA) activity was found in nWTR-treated soil at 50 mg kg^{-1}, with increases of 32.8% and 566.7% compared to the control, respectively. The addition of nB greatly improved the growth of canola plants in the soil. This was evident from the increase in the weight of seeds, the weight of 1000 grains, the number of pods per plant, and the highest increase was for nB added at the rate of 250 mg per kg^{-1} soil. The addition of 50 mg kg^{-1} of nWTR gave the best results in seed yield by 150.64% compared to the control. These results indicate that recycled nWTR and nB are some of the best waste recycling treatments, in addition to good soil health, in increasing soil biology and canola yield in degraded soils. In the future, research on recycled nanomaterials should examine the residual effect they have on yield, soil quality, and soil fauna in the long term.

Keywords: soil amendments; nanobiochar; functional groups; surface area; zeta potential

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1. Introduction

Soil contamination with heavy metals and organic pollutants in the areas surrounding factories has become one of the most challenging health and environmental sustainability issues due to its toxicity, stability, bioaccumulation and non-biodegradability [1]. In the same area of the current study, Al-Shall [2] showed that the Kafr El-Zayat area (Egypt) received atmospheric emissions from neighboring factories. The quantitiy of heavy metals in this area was very high, exceeding the permissible limit. Farmers in Egypt burn rice straw, which causes a black cloud over the Middle Delta governorates, and the burning process is one of the ways to get rid of it. This leads to the loss of organic matter and nutrients. Therefore, recycling rice straw in the form of biochar is one of the alternatives to its burning, as it can be used as a soil amendment to immobilize pollutants. It is also of increasing importance in many applications, particularly in its nano-sized form, because of its distinctive properties [3]. The application of nanomaterials in agriculture has become very important recently due to the increasing population and depletion of resources. Nanomaterials less than 100 nm in diameter have a large surface area, highly porous surface, and numerous active adsorption sites, compared to the same materials that are larger in size [4]. Recently, nanomaterials have been used in agriculture to increase crop yields and adsorb toxic substances such as heavy metals and pesticides [5]. Husein and Siddiq [6] found that the use of nanoparticles as nanofertilizers and insecticides in degraded soils improved yields, reduced excessive use of chemical fertilizers, and increased the vital capacity of the soil.

Biochar is an organic matter that is rich in carbon. It is produced by pyrolysis of biomass in an oxygen-limited environment, and it is used as a soil amendment to improve soil fertility and increase soil health. Reducing biochar to nano-size improves its properties to include high surface area, high porosity, increased surface functional groups, and surface-active sites. This, in turn, leads to increased adsorption of pollutants, enhanced nutrient retention, and consequently increases crop yield [7]. Oleszczuk et al. [8] and Zhou et al. [9] found that nanobiochar can be used to adsorb pollutants from different environmental media due to its smaller pore size and large surface area. Yue et al. [10] showed that a biochar nanoparticle was able to reduce cadmium (Cd^{2+}) uptake and phytotoxicity in rice plants because it induces oxidative stress in them. Nanoparticles (NPs) derived from biochar can have a profound impact on important plant processes responsible for increasing plant growth and productivity. Various types of nanobiochar on seed germination and seedling development in different plants were evaluated by Zhang et al. [11,12]. The activity of dehydrogenase is one of the most important activities in assessing soil condition and organic matter stability in biochar-amended soils because dehydrogenases are intracellular enzymes, and therefore they are related to microorganisms [13]. Nanobiochar has larger surface area, smaller particle size, higher negative zeta potential, and greater diversity in crystal forms than biochar. Thus, nanobiochar binds to soil nutrients and microelements easily to become a highly efficient fertilizer [14,15]. Nanobiochar is superior to bulk biochar in aggregate stability due to its speed and ease of movement in the root zone, its entry into pores and contact with roots, and its binding to clay minerals in the formation of microaggregates [16]. Zhang et al. [17] showed that the use of nanobiochar improved the growth and productivity of wheat crops significantly.

Water treatment residue (WTR) is a byproduct produced by drinking water plants in sedimentation ponds after adding alum to settling suspended matter and clay. The production of WTR from water treatment plants amounts to several million tons of sludge in most parts of the world annually [18]. In Egypt, more than 100 million tons are produced per year through drinking water treatment plants [19]. Previous studies have shown that water treatment residue (alum sludge) can be used as a soil amendment to manage P mobility and adsorption in salt-affected soils [20,21], and in some heavy metals and dyes [22].

Canola is a new oil seed crop in Egypt and many other countries and it is now grown on large areas. Canola cultivation in Egypt may provide an opportunity to overcome some of the local deficits in the production of edible vegetable oils. In recent decades, the canola plant has become a highly productive crop of agro-economic importance throughout the world, where it is used as fodder, food, and for fuel purposes [23]. The use of nitrogen and organic fertilizers increased the yield of canola seed under challenging conditions such as salinity and contamination by heavy metals. Mahmoud et al. [3] showed that canola yield increased, and soil properties were improved by adding WTR and compost, either alone or in combination. The seed yield of canola plants showed a significant increase with increasing nitrogen from zero to 100 kg ha^{-1} with the addition of 50 ton ha^{-1} compost. However, the increase of nitrogen above 100 kg ha^{-1} had no significant effect on canola seed yield [24]. Recycled nanomaterials are currently undergoing many studies. Nevertheless, to date there are still significant knowledge gaps that it is desirable to address. Research into recycled nanomaterials and techniques for their effective implementation is under sustainable development. However, interest in recycled nanomaterials as a multifaceted solution that addresses agricultural, environmental, and health problems, is growing at an accelerating pace both nationally and internationally. The novelty of this study is that the use of recycled nanomaterials to improve canola yield and biological activity in degraded soils. The study is based on the following hypotheses:

Hypothesis 1. *Knowing the spectral and chemical properties of recycled nanomaterials.*

Hypothesis 2. *Recycled nanomaterials at different rates have the potential to contribute to increased enzymatic and microbial activity and increased canola yield in degraded soils through water and nutrient retention and reduced toxicity from heavy elements, thereby reducing required amounts of agricultural inputs.*

2. Materials and Methods

2.1. Studied Area

Ten surface samples from 0–20 cm depth were collected from the Kafr El-Zayat area (30°40′ N Latitude, 30°43′ E Longitude) Gharbia Governorate, Egypt. The soil is classified as *Vertic Torrifluvents* (Entisols order) which has originated from fluvial deposits. The samples were mixed with each other thoroughly so they became homogeneous. The main source of pollution in the studied area is the reception of emissions laden with heavy metals from neighboring factories, such as a pesticide processing plant, another a super phosphate industry, and a salt and soap company. The average concentrations of Ni, Pb, Co, Cd, and Cr in the studied soil were 1051.20, 164.23, 26.60, 0.60, and 51.00 mg kg^{-1}, respectively, which is higher than the acceptable limits set by USEPA [25] for agricultural soil. Physical and chemical analyses of the studied soil are shown in Table 1.

Table 1. Characteristics of soil, rice straw biochar (nB), and water treatment residuals (nWTR) used in the experiment.

Properties	Units	Soil	nB	nWTR
		Particle size distribution		
Clay		41	-	68.6
Silt	%	33	-	-
Sand		26	-	-
Texture		clay loam	-	-
pH		7.95	8.24	7.49
EC	dSm^{-1}	4.58	2.45	1.12
Ca^{++}		9.60	55.11	5.56
Mg^{++}		5.50	24.30	5.50
K^+		0.89	-	-
Na^+	cmol kg^{-1}	31.10	-	-
Cl^-		21.80	-	-
HCO_3^-		5.00	-	-
SO_4^{--}		3.60	-	-
SAR		11.33	-	-
OM	g kg^{-1}	13.6	498.0	48.20
CEC	cmol kg^{-1}	-	31.30	38.85
Total Al	%	-	-	0.25
Available P	%	-	856.02	14.46

(-) data was not determined.

2.2. Nanobiochar (nB)

Rice straw from neighboring fields was used as feedstock to produced rice straw biochar, using a batch pyrolysis facility under conditions of limited oxygen, and the temperature reached more than 400 °C for a retention period of 2 h. In this study, a mill (DING CANG DC-500A) at the Nano Institute for Science and Technology, Kafr El-Sheikh

University, Egypt was used to produce nanobiochar (nB) by crushing rice straw fractions with a diameter of less than 0.5 mm as raw materials.

2.3. Nanowater Treatment Residue (nWTR)

The bulk WTR was taken from the sedimentation basins of the drinking water treatment plant in Al-Murasha Tanta, Gharbia Governorate, Egypt. The nWTR was obtained by grinding raw WTR fractions with a diameter of less than 0.5 mm into powders, and then by using a mill to produce nWTR (DING CANG DC-500A).

2.4. Pot Experiment

The pot experiment was conducted in Sakha Agricultural Research Station, Kafr El-Sheikh Governorate, Agricultural Research Center, Egypt (31° 07° N Latitude, 30° 05° E Longitude). This was carried out during the winter season (8 December to 10 May, 2020). Canola seeds (*Brassica napus*) of the Serw6 variety were sown in plastic pots containing 10 kg of soil each. Nine treatments were performed in a completely randomized experimental design with five replicates as follows: control (C): soil without amendments, biochar treatment at a rate of 4200 mg kg^{-1}, as a recommended treatment according to a study conducted by Mahmoud et al. [26]; (B) nanobiochar rate of 50 mg kg^{-1} (nB_{50}); nanobiochar rate of 100 mg kg^{-1} (nB_{100}); nanobiochar rate of 250 mg kg^{-1} (nB_{250}); and WTR at a rate of 4200 mg kg^{-1} as a recommended treatment according to a study conducted by Mahmoud et al. [27]; (WTR) nWTR rate of 50 mg kg^{-1} (nWTR $_{50}$); nano-WTR rate of 100 mg kg^{-1} ($nWTR_{100}$); and nano-WTR rate of 250 mg kg^{-1} (n WTR $_{250}$). The composite soil sample was air-dried and passed through an 8 mm sieve. Then it was packed into a plastic pot (10 kg) with a diameter of 30 cm and a height of 25 cm which was irrigated before planting. The nanomaterials were mixed by taking about 500 g of the same soil. They were smoothed and mixed well, and then placed in a sieve and added to surface soil to ensure a homogeneous distribution after placing the seeds (about 8 seeds) in each pot. They were added two hours after irrigation with an amount of water to stabilize the soil. Water was then added in the form of a spray until the soil reached 75% of the field capacity, to ensure that the nanomaterials were not washed out. Canola plants were thinned to three plants per pot three weeks after planting. During the experiment, an equal amount of irrigation was added as needed, and no chemical fertilizer was applied. The temperature during the experiment was between 17 and 20° C. Harvest was carried out 22 weeks after sowing. Plant height, weight of the crop, number of pods per plant, and weight of 1000 seeds were recorded.

2.5. Analysis of Soil Samples and Nanobiochar

pH and electrical conductivity (EC) of soil, nB, and nWTR were measured in ratio of 1:10 (w/v) using the pH meter and conductivity meter (Model: HANNA, HI98130), respectively. Organic carbon of nWTR and soil were determined by the Walkley and Black method after the wet digestion process by 1 N potassium dichromate ($K_2Cr_2O_7$) solution and concentrated sulphur (H_2SO_4) according to Nelson and Sommers [28], from where organic matter was calculated. Organic matter (OM) = organic carbon (%) × 1.724.

Organic matter of nB was determined by combustion method as reported by Page et al. [29]. Cation exchange capacity (CEC) was determined according to Graber et al. [30] using ammonium acetate solution 1.0 mol L^{-1} with pH 7.0. The determination of the total Al was measured by atomic absorption spectrophotometer (Perkin–Elmer AA model 2380, ARTISAN TECHNOLOGY GROUP, Champaign, IL, USA) after wet-digesting the air dried by wet WTR by H_2SO_4 + H_2O_2 [29].

2.6. Spectroscopic Analysis

The result of the crushing or grinding process on the size of WTR and B particles were examined using transmission electron microscopy (TEM) analysis, which was performed using a microscope (type FEI TECNAI G20, 200 KV-LaB6 emitter, FEI, Hillsboro, OR, USA) at the Electron Microscope Unit, Mansoura University, Egypt. The surface morphology of the nB and nWTR samples was conducted using scanning electron microscopy (SEM) system JEOL (JSM-7610F FEG-SEM, JEOL Ltd., Akishima, Tokyo). Samples were first coated with a sputter coater with a conductive layer to minimize the charging. The functional groups of nB and nWTR samples were characterized using Fourier transform infrared (FTIR-pectroscopy) [MATTSON 5000, Fremont, CA, USA] using KBr as a sample medium to confirm FTIR spectra of these samples with wavelength between 400 cm^{-1} and 4000 cm^{-1}. The mineralogical and chemical composition of nB and nWTR were identified by GNR X-ray Diffractometer (APD 2000 PRO, Detroit, MI, USA) using X-ray radiation with wavelength $\lambda = 1.54$ Å, step size 0.05° and the diffraction peaks were reported between $2\theta = 15°$ and $2\theta = 75°$. The formed minerals were identified by matching with 2003–2004 CRYSTAL IMPACT, Bonn, Germany.

2.7. Zeta Potential

The zeta potential of the nB and nWTR samples was determined with a 0.02 g sample weight in a 250 mL conical flask that contained 100 mL of 0.1 M NaCl solution. The pH of the suspension was adjusted to 7.0 with 0.01 mol L^{-1} HCl or NaOH. Then, the suspension was ultrasonically dispersed using a bath-type sonicator with a 300 W power supply line, and tuned at 40 kHz for 120 min at 30 °C [31]. Zeta potential of the dispersed suspension was measured by a Zetasizer Nano Brookhaven, Nova Instruments Company.

2.8. Catalase Activity

Catalase activity was measured by back-titrating residual hydrogen peroxide (H_2O_2) with $KMnO_2$ [32]. A measurement of 2 g of soil samples were added to 40 mL distilled water with 5 mL of 0.3% H_2O_2 solution. The mixture was shaken for 20 min with the addition of 5 mL of 1.5 mol L^{-1} H_2SO_4. Afterwards, the solution was titrated by 0.02 mol L^{-1} $KMnO_4$. The activity of catalase was calculated from the reacted amount of 0.02 mol L^{-1} $KMnO_4$ per gram of dry soil [33].

2.9. Dehydrogenase Activity (DHA)

DHA activity was determined according to the method described by Thalmann [34] after 24 h of incubation of a mixture of 2 g soil, air-dried in the dark at 37 °C, with 2 mL of tetrazolium chloride, which resulted in the formation of 2,3,5-triphenylformazan (TPF) extracted with 10 mL acetone. The color of the formazan concentration was measured at 485 nm using a spectrophotometer (Varian Cary 50 UV-Vis spectrophotometer, Agilent Technologies, Santa Clara, CA, USA). The enzyme activity was determined using a standard curve for TPF according to the following equation:

$$\text{Dehydrogenase activity } \mu\text{g TPF/g dry} = (\text{OD}/\text{K})/\text{DW}$$

where OD: Optical density; DW is soil dry weight; K = the factor obtained from the standard curve.

2.10. Microbial Biomass Carbon

Microbial biomass carbon (MBC) was determined with 25 g of soil samples and fumigated with ethanol-free chloroform for 24 h at 25 °C [35]. Then, the soil was extracted with K_2SO_4 and the extractable organic C was estimated using $K_2Cr_2O_7$ and H_2SO_4 for 30 min at 170 °C, and titrated against ferrous ammonium sulphate with ferroin as the indicator. Microbial biomass carbon (MBC) was calculated from:

$$\text{MBC} = (\text{EC fumigated soil} - \text{EC un-fumigated soil})/\text{Kc}$$

where EC = extractable carbon; Kc = 0.379 (Kc is the K_2SO_4 extract efficiency factor [36].

2.11. Statistical Analysis

All obtained data were analyzed statistically using SAS software. Duncan's multiple domain test (DMRT) was used to compare treatments with a statistical significance level of $p < 0.05$.

3. Results

3.1. Properties of Recycled Nanomaterials

Figure 1 illustrates the FT-IR spectrum of nWTR and nB. It shows the presence of several peaks. The two materials indicate different peaks at 3540.26 cm^{-1}, 1440.83 cm^{-1}, and 471.61 cm^{-1}, and the most noticeable peaks appeared in nB, being sharper than in nWTR. The peaks at 2928.00 cm^{-1}, 1101.34 cm^{-1}, and 1638.54 cm^{-1} appeared in nB, but did not appear in nWTR. Likewise, the peak at 537.67 cm^{-1} appeared in nWTR, but it did not appear in nB.

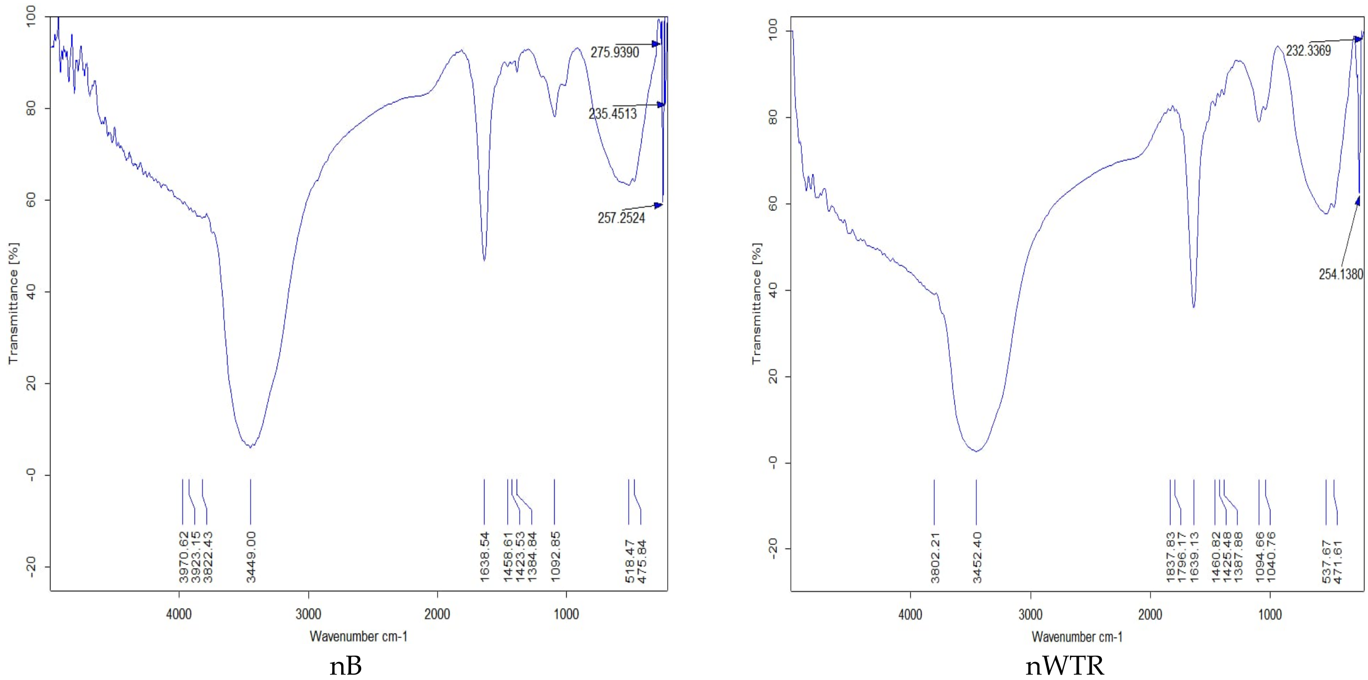
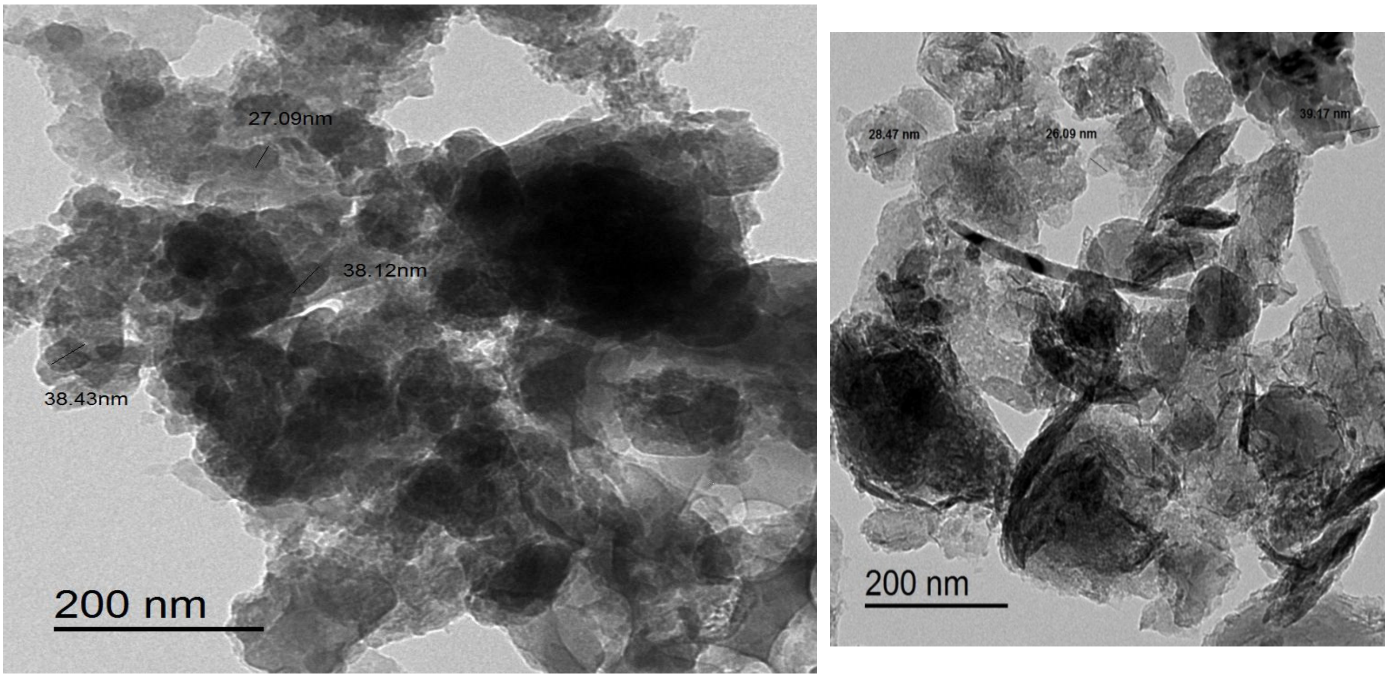


Figure 1. Fourier-transform infrared (FTIR) for nanobiochar (nB) and nanowater treatment residuals (nWTR).

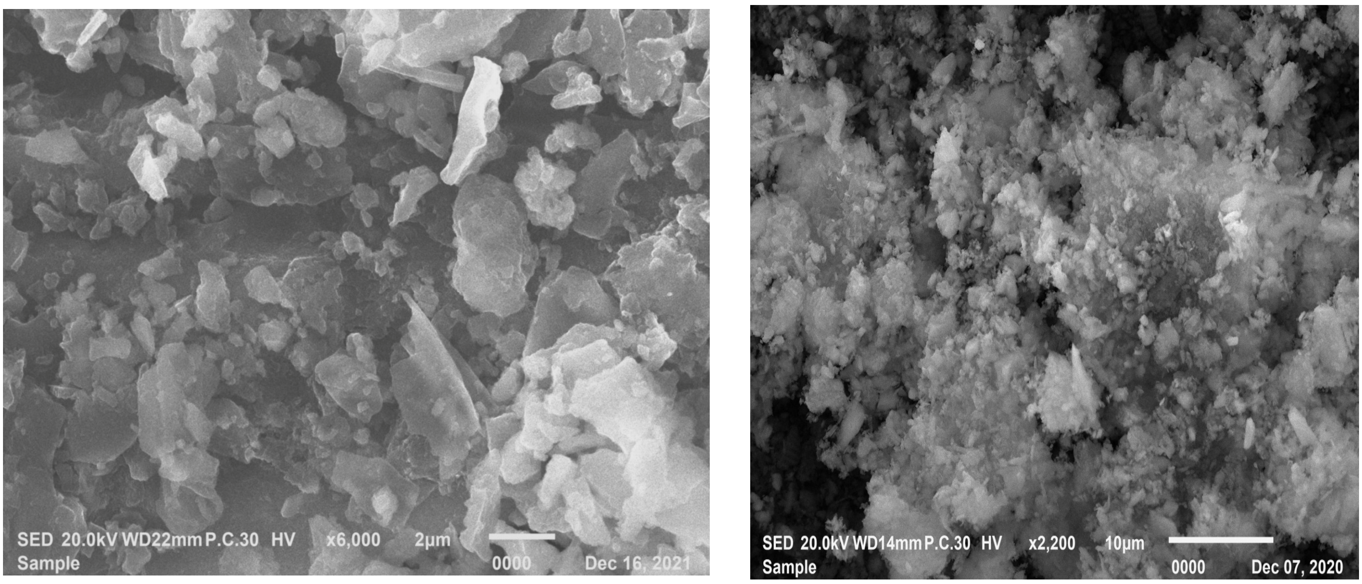
The morphology of nWTR and nB was shown by TEM and SEM (Figures 2 and 3). It was observed that the nB surfaces had some porous texture and contained spherical particles, with an average diameter of 34.546 nm for nB. These particles help increase the surface area and porosity of nB. However, nWTR showed a rough surface shape with a random particle size with an average of 34.98 nm. This was confirmed by the measured surface area obtained for nB = (289.57 $m^2\ g^{-1}$) compared to (nWTR) = (114.33 $m^2\ g^{-1}$).

The XRD spectra of nWTR and nB were shown in Figure 4. Sharp peaks in nB indicate the presence of cellulose, quartz, calcite, sodium carbonate, sylvite, hydrozincite, and whitlockite. The peaks in nWTR indicate the presence of quartz, calcite, goethite, illite, calcium silicate hydrate, calcium aluminate hydrate, magnesium aluminate hydrate, and kaolinite.



nB nWTR

Figure 2. Transmission electron microscope (TEM) image for nanobiochar (nB) and nanowater treatment residuals (nWTR).



nB nWTR

Figure 3. Scanning electron microscopy (SEM) images for nanobiochar (nB) and nanowater treatment re-siduals (nWTR).

The zeta potential of nanoparticles provides important information on surface charging, and it is essential for many applications, including the adsorption of pollutants from water and soil, improving soil quality, and reducing emissions of carbon dioxide and nitrogen oxides. As shown in Figure 5, the zeta potentials of nB and nWTR were −31.08 mV and −65.25 mV, respectively. In this study, the zeta potential nB value was greater than that of the nWTR. Cation exchange capacity (CEC) of the nB and nWTR was 31.3 cmol $_c$ kg^{-1} and 38.85 cmol $_c$ kg^{-1}, respectively (Table 1).

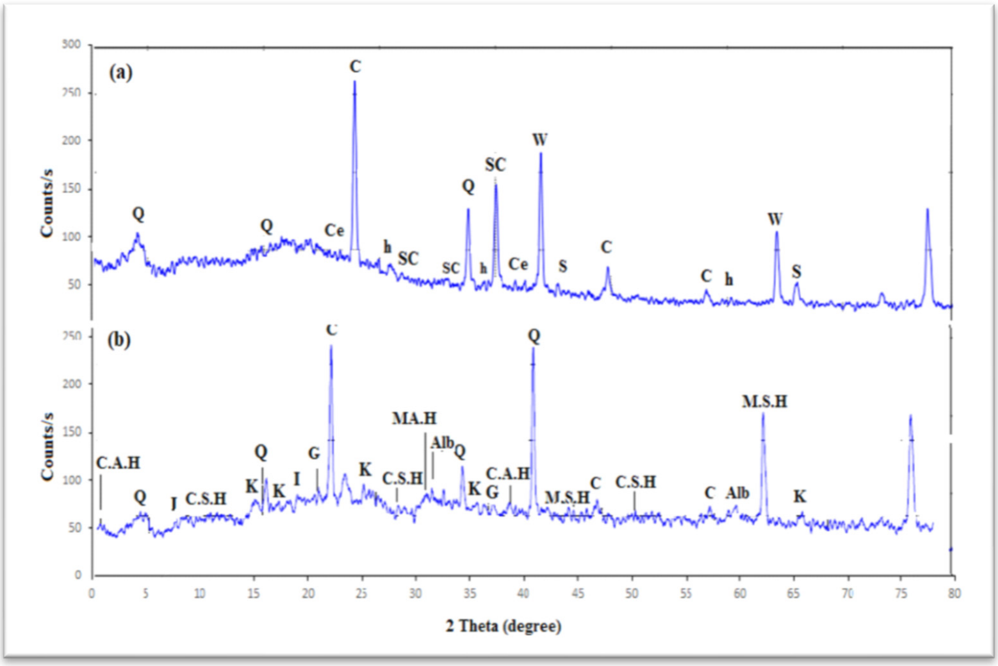


Figure 4. (**a**) X-ray diffraction (XRD) spectrum of nB (Q is quartz; S is sylvite; C is calcite; Ce is cellulose; SC is sodium carbonate; W is whitlockite; and h is hydrozincite). (**b**) X-ray diffraction (XRD) spectrum of nWTR; (Q is quartz; C is calcite; K is Kaolinite; I is illite; G is goethite; C.A.H is calcium aluminate hydrate; C.S.H is calcium silicate hydrate; M.A.H is magnesium aluminate hydrate; and C.S.H is calcium silicate hydrate).

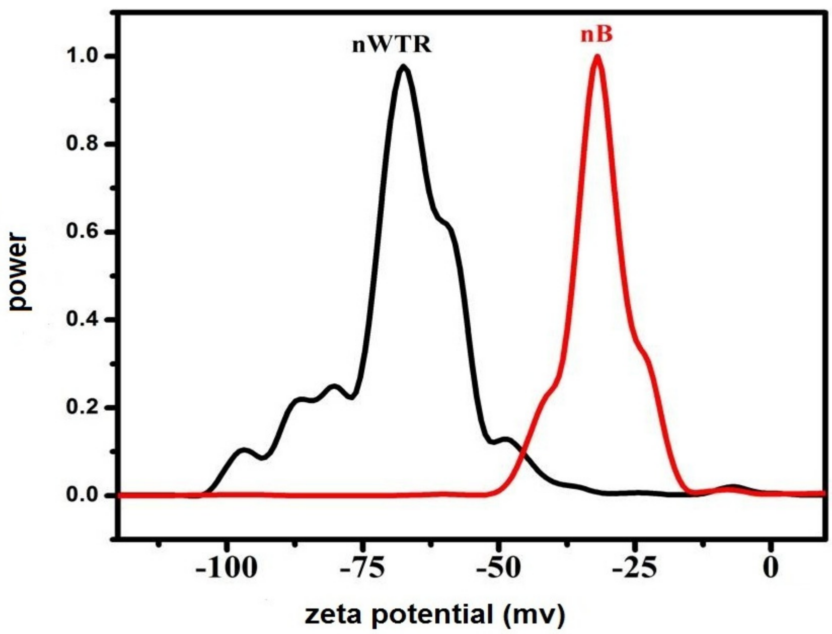


Figure 5. Zeta Potential for nanobiochar (nB) and nanowater treatment residuals (nWTR).

3.2. Effect of Recycled Nanomaterials on Soil Biological Activity

As shown in Table 2, the activity of dehydrogenase (DHA) and catalase (CLA) increased significantly in the treated pots with the addition of the studied nanomaterials at different rates. The activity of DHA and CLA decreased in the studied soil when the application rate of nB and nWTR increased. The highest DHA and CLA activity were found in nWTR-treated soils at 50 mg kg^{-1}, with increases of 32.8% and 566.7% relative to the control, respectively. Dehydrogenase activity increased in the soil treated with nB_{50} from 0.64 for the control to 0.82 mg TPF/g dry soil, with an increase of 26.5%, whereas in soil treated with WTR_{250} it increased by 7.8% compared to the control treatment. Catalase activity increased in the soil treated with nB 250 from 0.03 for the control to 0.11 mL $KMnO_{4/}$g dry soil with an increase of 266.6%. In soil treated with WTR $_{250}$, it increased by 166.6% compared to the control treatment. The significant difference in DHA and CLA activity was not observed between B and $nWTR_{250}$.

Table 2. Effect of nanoparticles of biochar (nB) and water treatment residuals (nWTR) on soil microbial biomass carbon and enzymes activity.

Treatments	Soil Microbial Biomass Carbon mg kg^{-1}	Dehydrogenase Activity mg TPF/g Dry Soil	Catalase Activity (mL of 0.02 mol/L $KMnO_4$ g^{-1})
C	162.3 ^{h} ± 0.12	0.64 ^{g} ± 0.01	0.03 ^{c} ± 0.01
B	277.8 ^{b} ± 0.09	0.68 ^{f} ± 0.01	0.07 ^{b,c} ± 0.01
nB_{50}	164.5 ^{g} ± 0.12	0.82 ^{b} ± 0.01	0.1 ^{b} ± 0.00
nB_{100}	271.3 ^{c} ± 0.12	0.77 ^{c} ± 0.02	0.08 ^{b,c} ± 0.01
nB_{250}	277.8 ^{b} ± 0.06	0.76 ^{c} ± 0.01	0.11 ^{b} ± 0.01
WTR	219.2 ^{e} ± 0.06	0.74 ^{d} ± 0.09	0.08 ^{b,c} ± 0.01
$nWTR_{50}$	388.9 ^{a} ± 0.11	0.85 ^{a} ± 0.01	0.2 ^{a} ± (0.06
$nWTR_{100}$	222.2 ^{d} ± 0.13	0.71 ^{e} ± 0.02	0.07 ^{b,c} ± 0.01
$nWTR_{250}$	169.7 ^{f} ± 0.06	0.69 ^{f} ± 0.01	0.08 ^{b,c} ± 0.01
F-test	**	**	**
$LSD_{(0.05)}$	0.251	0.017	0.059
$LSD_{(0.01)}$	0.344	0.023	0.081

Control (C): soil without amendments. Biochar rate of 4200 mg kg^{-1} (B), nanobiochar rate of 50 mg kg^{-1} (nB_{50}), nanobiochar rate of 100 mg kg^{-1} (nB_{100}), nanobiochar rate of 250 mg kg^{-1} (nB_{250}), WTR rate of 4200 mg kg^{-1} (WTR), nWTR rate of 50 mg kg^{-1} ($nWTR_{50}$), nWTR rate of 100 mg kg^{-1} ($nWTR_{100}$), and nWTR rate of 250 mg kg^{-1} ($nWTR_{250}$). Note: values of each row followed by the same letter indicate no significant differences ($p \leq 0.05$) according to Duncan test. ** means high significant.

Microbial biomass carbon (MBC) in soil ranged from 162.30 mg kg^{-1} in the control to 388.90 mg kg^{-1} in the $nWTR_{50}$, and a significant difference appeared between the different treatments (Table 2). Microbial biomass C increased with the increase of the application rates of nB, whereas it decreased with the increase of nWTR. MBC increased with the addition of nB_{50}, nB_{100}, and nB_{250} by 1.01, 1.67, and 1.71 times, respectively, when compared to the control treatment. The MBC in the nB-treated plots was higher than that in the nWTR-treated plots at the same rate, except for the 50 mg kg^{-1} rate. In this study, the MBC was not significant between B and nB $_{250}$.

3.3. Effect of Recycled Nanomaterials on Canola Yield

As shown in Table 3, the weight of canola plant seeds increased significantly in pots treated with the addition of B, nB, WTR, and nWTR. The seed weight of the canola plant increased from 14.3 (C) to 23.5 g $plant^{-1}$ for B, and to 36.9 g $plant^{-1}$ for WTR. Seed weight of the canola plant increased with the increase of nB, whereas it decreased with the increase of nWTR. In this study, the weight of canola seeds was not significant between WTR and nWTR $_{50}$ as well as between B, nB_{50}, nB_{100}, and $nWTR_{100}$.

It was observed that the effect of soil amendments addition on 1000-seed weight of canola was significant (Table 3). Biochar and WTR at rate of 4200 mg kg^{-1} soil addition increased 1000-seed weight by 5.0 and 2.5%, respectively. The 1000-seed weight of canola in the soil amended with nB_{50}, nB_{100}, and nB_{250} were 4.2, 4.0, and 4.2 g, respectively. The application of $nWTR_{50}$ gave the highest significant increase in canola seed yield compared to other treatments.

Table 3. Effect of nanoparticles of biochar (nB) and water treatment residuals (nWTR) on canola productivity.

Treatments	Plant Height, cm	1000 Seeds Weight, g	Pod Number per Plant	Seeds Weight, g per Plant
C	91.66 ^{f} ± 0.88	3.97 ^{f} ± 0.04	94 ^{g} ± 0.58	14.77 ^{d} ± 0.27
B	107 ^{b} ± 0.58	4.19 ^{b} ± 0.02	105 ^{e} ± 0.58	23.45 ^{c} ± 0.65
nB_{50}	121.66 ^{a} ± 0.88	4.17 ^{b,c} ± 0.01	108 ^{d} ± 0.33	23.18 ^{c} ± 0.33
nB_{100}	119 ^{a} ± 0.58	4.02 ^{e} ± 0.02	116 ^{b} ± 0.88	25.04 ^{c} ± 0.78
nB_{250}	96.33 ^{e} ± 0.88	4.15 ^{c} ± 0.02	115 ^{b} ± 0.58	34.35 ^{b} ± 0.48
WTR	101 ^{c,d} ± 1.15	4.08 ^{d} ± 0.01	112 ^{c} ± 0.33	36.87 ^{a} ± 0.36
$nWTR_{50}$	110 ^{b} ± 0.58	4.32 ^{a} ± 0.02	119 ^{a} ± 0.88	37.02 ^{a} ± 0.91
$nWTR_{100}$	98.33 ^{d,e} ± 0.67	4.19 ^{b} ± 0.02	96 ^{f,g} ± 0.33	23.79 ^{c} ± 0.7
$nWTR_{250}$	102.33 ^{c} ± 1.2	3.98 ^{f} ± 0.01	98 ^{f} ± 0.058	16.97 ^{d} ± 0.33
F-test	**	**	**	**
$LSD_{(0.05)}$	2.535	1.777	1.777	1.711
$LSD_{(0.01)}$	3.474	2.435	2.435	2.344

Note: values of each now followed by the same letter indicate no significant differences ($p \leq 0.05$) according to Duncan test. ** means high significant.

The number of pods per canola plant increased significantly with the addition of soil amendments at different rates (Table 3). The number of pods per canola plant increased by 14.9%, 23.4%, and 22.3% for nB_{50}, nB_{100}, and nB_{250}, respectively, compared to the control treatment. The addition of $nWTR_{50}$ gave the highest significant increase in the number of pods per canola plant compared to other treatments.

Canola plant height increased significantly with the addition of soil conditioners at different rates (Table 3). The addition of nB_{50} gave the highest significant increase in the canola plant height compared to other treatments. Canola plant height decreased with increasing rate of application of nB.

The increase in seed weight of canola plant is correlated with MBC (R^2 = 0.82, $p < 0.05$, (Figure 6) and soil organic matter (R^2 = 0.91, $p < 0.05$, (Figure 7).

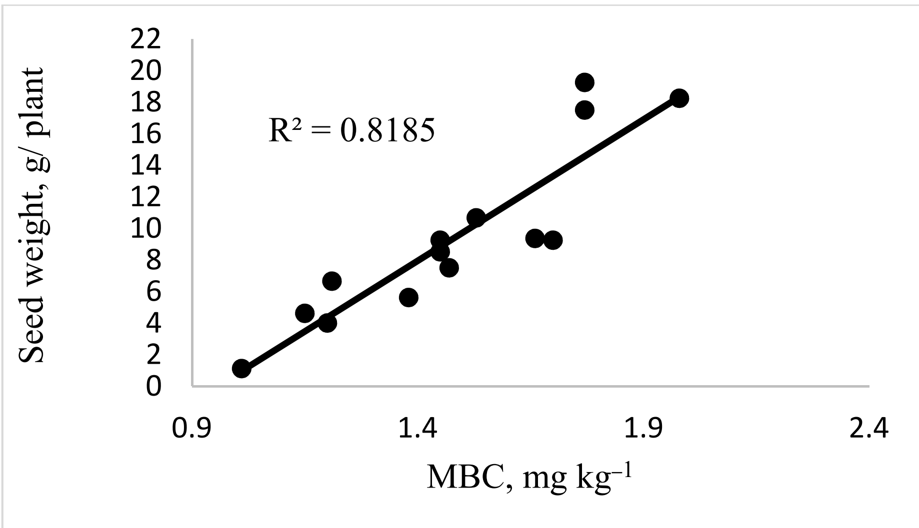


Figure 6. Relationship between MBC and seed weight of canola.

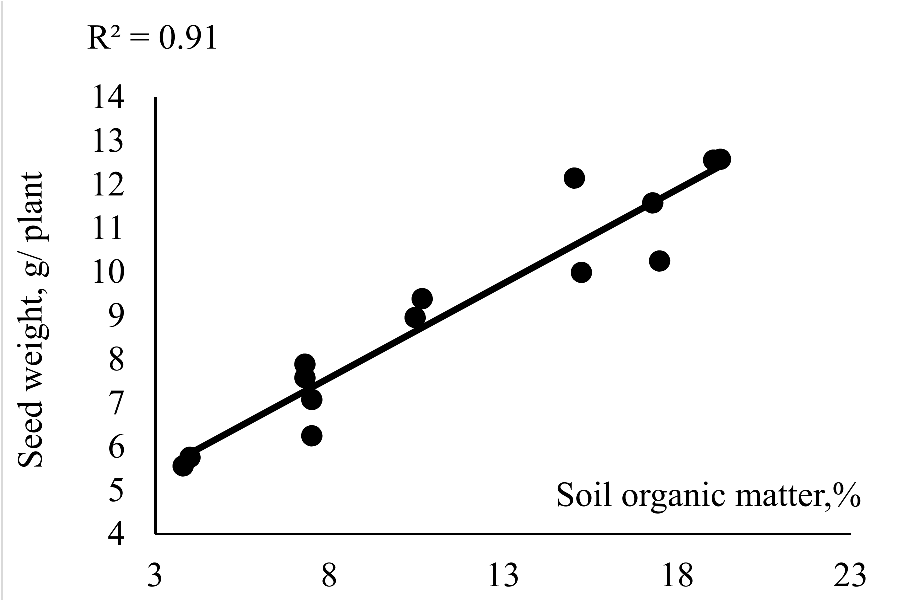


Figure 7. Relationship between soil organic matter and seed weight of canola.

A meta-analysis of recycled nanomaterials amendments on increasing canola yield and its relationship to improving biochemical and physical traits in degraded soils can only be pursued after several relevant reports emerge in the future.

4. Discussion

The study of the FTIR spectrum showed that nWTR and nB contain many functional groups. The bands at 3452.40 cm^{-1} in nWTR and 3540.26 cm^{-1} in nB were assigned to the O–H stretching [37]. The bands at 2928.00 cm^{-1} in nB were assigned to the C–H stretching [38]. The noticed bands at 1425.48 cm^{-1} in nWTR and 1440.83 cm^{-1} in nB were ascribed to the aromatic C=C bending [37]. The peak at 1638.54 cm^{-1} observed in nB is responsible for the presence of the covalent bond (C=C) [39]. In addition, the peaks at 537.67 cm^{-1} and 471.61 cm^{-1} in nWTR are, respectively, corresponding to the Si–O–Al and Si–O–Si bending vibration [40]. The presence of these bands was the result of the addition of alum during the water treatment processes and the sedimentation of suspended solids and clay from the raw water. The bands are around 1101.34 cm^{-1} and 474.00 cm^{-1}, which were assigned to SiO_2, and the bands as observed in nB are due to SiO_2 as a major component in the chemical composition of the rice material [3]. The functional groups on nB and nWTR are negatively charged. They interact with cations, thus contributing to an increase in the cation exchange capacity, which leads to an increase in plant growth [41]. The nB components can act as adsorption sites for some pollutants through electrostatic interaction and ion exchange [42,43] and surface complexity [44,45]

The XRD data of nB in this study are consistent with Tsai et al. [46] and Cao and Harris [47], who found that different types of biochar contain calcite, quartz, sylvite, periclase, and whitlockite. Furthermore, the XRD data for biochar is consistent with that found by other authors [21,48,49]. The XRD data of nWTR in this study is consistent with that of Ippolito et al. [50] and Ahmad et al. [51]. The presence of calcite in the nWTR is due to the geology of the site of the water source entering the water treatment plant. The presence of quartz in nWTR is due to the composition of the material precipitated during the water treatment process, particularly the presence of clay minerals [52]. The presence of calcium aluminate hydrate and magnesium aluminate hydrate could be related to alum being used as a coagulant in water treatment plant [52]. The SEM image showed that the nB surfaces have a beneficial porous texture. Pores increase nutrient absorption capabilities, which act as slow-release fertilizers [53].

The zeta potential represents the net charge between the surface plane and the slip plane of the colloidal particle [54]. The magnitude of its electronegativity reflects the value of the surface negative charges [54]. The results showed that nB and nWTR have high zeta potential with negative charges. Hotta et al. [55] indicate the zeta potential of kaolinite as –65 and –85 mV, which confirms the high kaolinite content of nWTR. The zeta potential of compost and vermicompost, reported by Méndez et al. [56], was −28.40 mV and −26.04 mV, respectively. This is lower than nB in this study, and confirms that the pyrolysis and size particles of nB are very important in increasing the zeta potential. Song et al. [57] reported zeta potentials that range from −22 to −35 mV for manure or sludge biochar, from −31 to −40 mV for plant biochar, and from −20 to −50 mV for biochar colloids [58]. Zeta potential is associated with the presence of negative charges on nB and nWTR surfaces. It works on adsorption and the preservation of cations, which are important in improving soil fertility and adsorbing heavy elements [59].

The surface area of the alum sludge was 61.00 m^2 g^{-1}, as reported by Lee et al. [22]. This is lower than the nWTR in this study. This difference can be attributed to the WTR, which is in nanoscale, as well as to the quality of the drinking water source and the system of the treatment plant. Caporale et al. [60] noted that reducing the particle size of WTR in the nanoscale resulted in an increase in surface area. The surface area of nB was 289.57 m^2 g^{-1}, which is larger than that of nWTR. This is due to the heat treatment of biochar at 400 °C, which enables many pores to increase its surface area. The high surface area of nWTR and nB are important for the adsorption of large quantities of organic and inorganic pollutants [61,62].

Cation exchange capacity (CEC) is the ability to bind and exchange positively charged cations. CEC value of nB was 31.30 $cmol_c$ kg^{-1}. This value was lower than those identified by Song and Guo [57] in the biochar of pepper residues and canola with values of 79.5 and 179.0 cmol $_c$ kg^{-1}, respectively. Silber et al. [63] and Günal et al. [64] reported that CEC values for different types of biochar ranged from 5 to 50 cmol $_c$ kg^{-1}. Munera-Echeverri et al. [65] stated that the CEC of biochar depends on the raw materials and functional carboxyl and phenol groups on the biochar surface. High CEC of nWTR and nB can be used to improve soil properties, increase soil fertility, and contribute to soil carbon sequestration. The CEC for the nWTR was significantly lower than those reported for the 2: 1 clay minerals (70–250 cmol $_c$ kg^{-1}) [66].

Enzyme activity is a good indicator of soil fertility, soil biological activity, agricultural productivity, soil quality, and correlated organic matter and nutrients [67]. In this study, the high DHA and CLA activity and MBC in soils treated with nB is likely due to their higher content of nutrients, organic carbon, and CEC (Table 1). These results are similar to those reported by Mierzwa-Hersztek et al. [68] who observed an increase in dehydrogenase activity in treatments with the addition of biochar, which was 1.6 to 4 times higher compared to the control. The addition of materials rich in organic matter and nutrients increases the numbers of microbes in the soil and thus increases the soil microbial biomass and its enzymatic activity. This means that soil fertility is related to enzymatic activity and sustainable productivity [69]. Some studies have reported that applying biochar to soil enhances the activity of soil enzymes [70,71]. Biological activity and microbial biomass were increased in WTR-amended soils [27,72]. The WTR used in the study contained organic carbon, clay, and nutrients which may have contributed to the higher DHA and MBC activity (Table 1). Mahmoud et al. [1] found similar results, as they revealed that MBC and DHA significantly increased with the addition of WTR.

The weight of canola plant seeds increased by more than 62.5% when amended with nB. Similarly, in another study by Wang et al. [73], it was found that fertilizing with nanobiochar increased crop yields by more than 20% and reduced the amount of fertilizer required by 30% to 50%. Nanobiochar-loaded nutrient ions are transported to the rhizosphere through the epidermis, cortex, and xylem to reach the xylem [74]. Moreover, nanobiochar has high surface area, surface functional groups, adsorption capacity, and acts as a reservoir for nutrient ions while controlling their release rate. Nanobiochar plays an important role in reducing nutrient loss and improving fertilizer use efficiency [75]. The results showed a significant increase in the weight of canola seeds with an increase in the rate of adding nB. Likewise, Yang et al. [76] found that the weight of a 1000-grain and maize yield increased with the addition of nanobiochar. These results are in accordance with Mahmoud et al. [77] who found that flag leaf area, number of grains per spike, and grain yield of wheat plants increased in soil amended with biochar. In this study, the increase in seed weight of canola plant is correlated with MBC (R^2 = 0.82, $p < 0.05$, (Figure 6) and soil organic matter (R^2 = 0.91, $p< 0.05$, (Figure 7). Ali [78] found a strong positive correlation between the dry weight of canola plants with MBC (R^2 = 0.80), CEC (R^2 = 0.72), and OM (R^2 = 0.83). Xiao et al. [79] suggested that the application of biochar may be a promising option for increasing productivity in semi-arid farmlands. The addition of nB or nWTR improves the growth of canola plants in soil, which is evidenced by the increased seed weight, 1000-grain weight, and pod number per plant. However, when nWTR was added at high rates (>50 mg kg^{-1} soil), this reduced canola plant growth, likely caused by Al toxicity and the potential harm of nWTR to plants. Similar results were reported by Zhao et al. [80]. The difference in the response between the nB and nWTR is due to their different properties, such as pH, organic matter, clay content, elemental content, and as soil properties. The results obtained indicate that high concentrations of nWTR reduce the yield of canola plant and soil enzyme activity in the studied soils and these results may serve as an important clue in regulating the application of nanomaterials in agriculture.

5. Conclusions

In this study, we demonstrated the properties of recycled nanomaterials, which were characterized by their high surface area, high CEC, and high negative zeta potential, in addition to containing functional groups (such as C=O, OH, C=C, C-H, Si-O-Al, and Si-O-Si) and minerals. The addition of the investigated soil amendments improved soil MBC, DHA, and CLA, which had a significant effect on increasing canola yield. The canola yield was higher when nB and nWTR were added at 50 mg/kg soil than at the levels 100 and 250 mg kg^{-1} soil. However, the high rate of nWTR reduced canola yield and soil enzyme activity in the studied soils, and these results may be an important guide in regulating the application of nanomaterials in agriculture. Therefore, it is necessary to determine appropriate application rates of nWTR to avoid negative effects on the soil environment. The results recommended that the application of 50 mg kg^{-1} of nWTR and 250 mg kg^{-1} of nB was optimized to achieve high productivity and improve soil biology in the degraded soils.

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