



## Research article

The effect of brewery sludge biochar on immobilization of bio-available cadmium and growth of *Brassica carinata*Yordanos Kiros G. Tsadik<sup>a</sup>, Abrha Mulu Hailu<sup>a,b</sup>, Seyoum Leta Asfaw<sup>a,\*\*</sup>, Yedilfana Setarge Mekonnen<sup>a,\*</sup><sup>a</sup> Center for Environmental Science, College of Natural and Computational Sciences, Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia<sup>b</sup> Department of Chemistry, College of Natural and Computational Sciences, Aksum University, P.O. Box 1010, Axum, Ethiopia

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## ABSTRACT

Biochar has gained an attention in reducing the bio-availability of toxic heavy metals and minimize threat of entering into food chain from contaminated soil. This study was aimed at evaluating the potential use of brewery sludge biochar (BSB) as a soil amendment for reducing cadmium bio-availability and uptake by *Brassica carinata* in a pot experiment. In this pot experiment, artificially cadmium spiked, moderately fertile, and slightly basic silty-loam soil was used. The biochar was produced by pyrolyzing of the brewery sludge at 500 °C. The obtained biochar was sieved with 0.5 mm mesh size and applied at the rate of 4 % (w/w) on the *Brassica carinata* grown cadmium spiked soil. The additions of BSB to the soil contributed a significant reduction of the bio-availability of cadmium in the soil and its accumulation in the shoot of *Brassica carinata* by 86% and 93%, respectively. Besides, it remarkably increased the dry weight of the edible part of *Brassica carinata* by 228%. The results revealed that BSB is very effective additive in cadmium immobilization, in turn, significantly (p-value = 0.00) promoting vegetable (*Brassica carinata*) growth. Therefore, BSB can be used as agricultural soil remedy for cadmium contamination and as safe disposal of brewery sludge.

## 1. Introduction

Brewery sludge is a form of biomass residue obtained from the wastewater treatment plant at a different stage of the treatment process. It is composed of organic matter and essential nutrients (Mukhtar et al., 2015). It also encompasses phosphorous, nitrogen, micro-nutrients and organic matter rich that can positively influence soil-plant behavior (Pathak et al., 2009). It is one of the most challenging waste materials to manage due to its huge amount and pathogenic load (Hossain et al., 2010). The pyrolysis conversion of beer brewery wastewater sludge to biochar can be an alternative management and utilization of the sludge for the agricultural soil amendment. Since, the process of pyrolysis is taking place at high temperature that decomposes the organic pollutants and kills microorganism. Besides, the incineration process during the pyrolysis is taking place in the limited oxygen environment, it causes an

unfavorable condition for the discharged pollutants in the treatment (Caballero et al., 1997; Strezov and Evans, 2009).

Unlike other charcoal materials, biochar is highly porous charcoal substance which is mainly intended for agricultural use as a soil amendment (Hunt et al., 2010). Novak et al. reported that the effects of biochar on intensifying soil fertility rely on its physicochemical and biological properties, such as having high porosity and contain various functional groups (Novak et al., 2009). Such properties also effective in the adsorption of heavy metals (Liu and Zhang, 2009). The application of biochar as soil amendment enhances plant growth and toxic metal immobilization through binding or precipitation of contaminants that lessen metal uptake by vegetable crop (Beesley et al., 2011; Bolan et al., 2014).

Biochar heavy metal adsorption capacity is mainly reliant on the type of feedstock as well as on the pyrolysis conditions (Zhao et al., 2019). Different types of biomass-derived biochars were widely studied for

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remediation of Cadmium and other heavy metals toxicity from soil in order to prevent plant toxicity and human health risk through food chain. For instance, sewage sludge biochar (Zhao et al., 2019; Zhou et al., 2017); agriculture biomass waste based biochar (Medyńska-juraszek and Ćwieląg-piasecka, 2020; Zhao et al., 2019); plant and wood biomass derived biochar (Boni et al., 2018; Tian et al., 2017; Xu et al., 2014). However, brewery sludge biochar not yet studied for such purpose. Furthermore, now a day in Ethiopia brewery sludge production increased significantly due to the wide expansion and increase of beer production. So, it is crucial to focus on the safe disposal of brewery waste sludge with an economically and environmentally acceptable manner. Pyrolytic conversion of such sludge into biochar, for agricultural use as soil amendment, could be one of the plausible cost effective and environmentally friendly waste management mechanisms. Therefore, this paper focus on the effect of brewery wastewater sludge biochar on plant growth, improvement of soil physicochemical properties and the immobilization of bio-available cadmium in *Brassica carinata* grown on artificially cadmium (Cd) contaminated soil.

## 2. Materials and methods

### 2.1. Brewery wastewater sludge and soil sample

The soil sample was collected from river side vegetable farming site called Jaja, Nefas Silk Lafto sub-city, Addis Ababa, Ethiopia. It was taken from the upper horizon at a depth of up to 20 cm. The brewery sludge was obtained from the BGI Beer brewery anaerobic treatment facility, after dewatered in the factory dewatering facility, Addis Ababa, Ethiopia.

### 2.2. Biochar preparation

The brewery sludge was air dried and crushed for pyrolysis to produce biochar. It was pyrolyzed at 500 °C using a muffle furnace (SX-2.5-10, China) for 2 h. As 400–500 °C temperature has been recommended for biochar formation (Hossain et al., 2009). The biochar sample was allowed to cool to room temperature after heating for 2 h of residence time. The obtained biochar was collected, ground to pass through a 0.5 mm sieve to obtain a uniform particle size for use and characterization.

### 2.3. Biochar characterization

The physicochemical properties of the biochar such as moisture, ash content, pH, Electric Conductivity (EC), extractable base cations, Cation Exchange Capacity (CEC), Available Phosphorous (AP) and morphology were characterized by using different electroanalytical and spectroscopy advanced techniques consisting of Elemental Analyser (CHNS-O), Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR) spectroscopy.

The determination of moisture and ash content was conducted according to the American Society for Testing and Materials standards (ASTM D1762-84, 2011). The pH and EC were determined in the 1:2.5 (w/v) biochar to distilled water after shaking for an hour in a mechanical shaker using digital pH Meter (SX 711 pH/mv Meter, China) and electrical conductivity meter (EUTECH INSTRUMENT, CON 2700, China), respectively (Cheng et al., 2006). Available phosphorus (AP) concentration was done by Olsen method (Olsen et al., 1954). The exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{K}^{1+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{1+}$ ) of biochar were determined after leaching the biochar with the ammonium acetate method. The concentrations of Ca and Mg in the leachate were determined by atomic absorption spectrometer (Analytikjena novAA400P, Germany). The K and Na concentration were estimated by a flame photometer (CL 378, India). The CEC of the biochar was estimated at pH = 7.0 using ammonium acetate method titrimetrically (Gaskin et al., 2008).

C, H, N and S contents of the biochar were estimated using CNHS-analyzer (Flash EA 1112 Elemental Analyzer, USA). The percentage of O content of the sample was determined by subtraction of the measured

elemental components from 100% (Ramola et al., 2014). These results were used to calculate atomic H/C and C/N ratios. Besides, the surface morphology and elemental composition of the biochar were investigated by using Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDX) (JEOL, JSM-IT300 LV, Japan). The FTIR analysis was performed using FT-IR Spectrometer (PerkinElmer, USA) and spectra were collected in the range of 4000–400  $\text{cm}^{-1}$ .

### 2.4. Soil characterization

The pH, EC, AP, CHNS content, CEC and exchangeable cations of the soil were measured with same procedures and techniques used for the analysis of the biochar. The particle size distribution (texture) of the soil was determined by means of the hydrometer method after removing organic matter (OM) using hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and dispersing of the soil with sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub>.

### 2.5. Pot experiment inside greenhouse

Pot experiments were performed in a greenhouse at the national soil testing center (Addis Ababa, Ethiopia). The experiment includes two treatments: soil without biochar (CON) and soil amendment with brewery sludge derived biochar (BSB). Cadmium was applied to soil as solution of cadmium (II) nitrate tetrahydrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) at the rate of 25 mg Cd/kg. Then the brewery sludge-based biochar was homogenized with air-dried Cd spiked soils at the rate of 4% w/w inside the plastic pot.

The soil amended with brewery sludge biochar was placed in a plastic pot (16.2 m in diameter and 20 m in height) in a greenhouse temperature for 12 days. The soil was moistened with tap water in the incubation period and mixed twice a week in order to ensure the full equilibration between the naturally-occurring soil component and the treatment fractions. The design of the pot experiment was employed three replicates for each treatment in a complete randomized design (CRD). Three weeks after sowing 10 seeds of Ethiopian kale (*Brassica carinata*), the excess germinated seedling was removed and four healthy plants per pots were allowed to grow for the next six weeks. Pots were placed on plastic saucers to prevent leachate drainage.

### 2.6. Plant tissue analysis

After the plants became matured, four plants per pot were harvested from each treatment. The harvested Ethiopian kale was washed once with tap water and twice with distilled water to remove any adhering soil and dried in an oven at 75 °C for 48 h. The plant shoots total Cd concentration was determined after nitric-hydrochloric acid digestion (1:3) according to Ang and Lee (2005). The digestives were analyzed for Cd by using atomic absorption spectrophotometer (AAS) (Analytikjena novAA400P, Germany) equipped with a graphite furnace.

### 2.7. Soil and soil-biochar mixture analysis

The soil and soil-biochar mixture samples were collected separately from each pot after harvesting the *Brassica carinata*. The pH and EC of the soil and soil-biochar mixture were measured in water suspension at 1:2.5 (w/v) ratio after shaking for 1 h. The wet digestion method was used to determine Organic Carbon (OC) content (Walkley and Black, 1934). Total Nitrogen (TN) was analyzed using the Kjeldahl method. To evaluate the mobility and potential bio-availability of Cd in soil was extracted using calcium chloride ( $\text{CaCl}_2$  (0.01M)) according to the procedure used by Houba et al. (2000) and then the concentration of  $\text{CaCl}_2$  extractable Cd were determined by using Atomic Absorption Spectrophotometer (Analytikjena novAA400P, Germany) equipped with a graphite furnace. The immobilization of Cd was calculated using the equation below (Park and Choppala, 2011).

$$\text{Immobilization(\%)} = \frac{(\text{CaCl}_2\text{Cd for control} - \text{CaCl}_2\text{Cd for amended sample}) \times 100}{\text{CaCl}_2\text{Cd for control}}$$

## 2.8. Statistical analysis

The mean, standard deviation, and the mean variances before and after the biochar treatment were performed with a paired-sample t-test at a 95% confidence interval by using Origin8.0 software. Besides, all the graphs were also presented using the same software.

## 3. Results and discussion

### 3.1. Characteristics of soil and biochar

#### 3.1.1. Physicochemical characteristics

The physicochemical properties and elemental composition of the brewery sludge biochar and the soil were as presented in Table 1 and Table 2. The textural class of the soil was confirmed as silt loam, with 45% silt, 37% sand and 18% clay. Its pH was slightly basic (pH = 7.66) and an electrical conductivity (EC) is 0.15 ms. The low value of EC indicated that the soil is non-saline that exhibits the major dissolved mineral solutes such as K, Na, Ca and Cl concentrations in the soil solution is low (Brady and Weil, 2002; Scudiero et al., 2016). The carbon, nitrogen and available phosphorus status of the soil were found to be 1.95%, 1.23% and 5.25 mg kg<sup>-1</sup>, respectively as presented in Table 1 and Table 2. The results revealed that the soil was nutrient poor and additional nutrient amendments are required for optimal plant growth.

The brewery sludge biochar (BSB) had high pH (pH = 9.18) implying that potential for an increase the low pH (pH = 7.66) of the soil upon application (Table 1). The available phosphorus (AP) of BSB was also found to be higher than the soil as biochars are nutrient rich biomass pyrolysis product. Its CEC value (46.62 meq/100g<sup>-1</sup>) was two times higher than the soil that might be attributed due to its high negative charge with imminent functional groups surface. The exchangeable cations of the BSB were exhibited relatively lower except sodium. The CaCl<sub>2</sub> extractable Cd concentration in the BSB was higher (3.98 mg/kg) compared to the soil (0.054 mg/kg), but still does not exceed the IBI guidelines limit (1.4–39 mg/kg) (IBI-STD-2.0, 2014).

#### 3.1.2. Elemental composition

The BSB exhibited the lowest carbon (14.76%) content but shows the highest in ash content (79.89%) Table 2. This may be due to its richness

in Si (21.16%) which highly associated with ash content. Similarly, Mukome et al. also reported biochar derived from rice has a high ash content (40–60%) due to the highest Silica content (Mukome et al., 2013). The elemental analysis result reported in Table 2 was used to calculate the atomic carbon to nitrogen ratio (C/N) and hydrogen to carbon ratio (H/C) ratios to evaluate the aromaticity of brewery sludge biochar (BSB). The higher C/N ratio has been attributed to the aromaticity of biochar and will cause slow decomposition and higher stability in soil (Lehmann, 2007). Whereas, the higher H/C ratio of biochar specified lower carbonization and aromaticity (Mohan et al., 2014). The BSB was showed a lower H/C ratio, the lower aromatic structure, as a result, may have more sorption sites for inorganic contaminants (Ahmad et al., 2014; Paul Chen and Lin, 2001). This high H/C corresponds to low aromaticity that still provides more sorption sites due to the cation (Cd) interaction with existing  $\pi$ -electronic systems from C=C bounds of the aromatic structure of the BSB (Domingues et al., 2017).

#### 3.1.3. SEM-EDX analysis

The Scanning Electron Microscope (SEM) image for BSB was as showed in Figure 1. It was noted that the BSB has an irregular surface with pores surface structure. The SEM is not only used for high magnification and imaging but also make a quantitative chemical analysis of unknown materials with a combination of Energy Dispersive X-ray Spectroscopy (EDX). Therefore, the EDX result (Table 3) revealed that the BSB has more minerals such as Na, Mg, Al, K, Ca, Si, P, Ti, Fe and S.

#### 3.1.4. Fourier Transform Infrared (FTIR) analysis

The FTIR analysis revealed the presence of several functional groups on the surface of the BSB. Changes in surface functional groups are also reflected by the FTIR spectra as shown in Figure 2. The BSB has broad-band peak at 3419 cm<sup>-1</sup> which revealed the presence O–H stretch of hydroxyl groups due to the presence of hydroxyl or phenol groups. The peak at 2923 cm<sup>-1</sup> was due to the presence of aliphatic group in the BSB. The peak at 1616 cm<sup>-1</sup> represented C=C alkene, aromatic ring, were existed in BSB. The peak at 795 cm<sup>-1</sup> indicates the existence of aromatic C–H bending in the BSB. This indicates that aromatic structure was found in this biochar. The peak at 618 cm<sup>-1</sup> was due to S–O bending found in the BSB. The presence of oxygen containing functional groups such as –COOH, –OH, –NO and –SO in the biochar could likely form strong

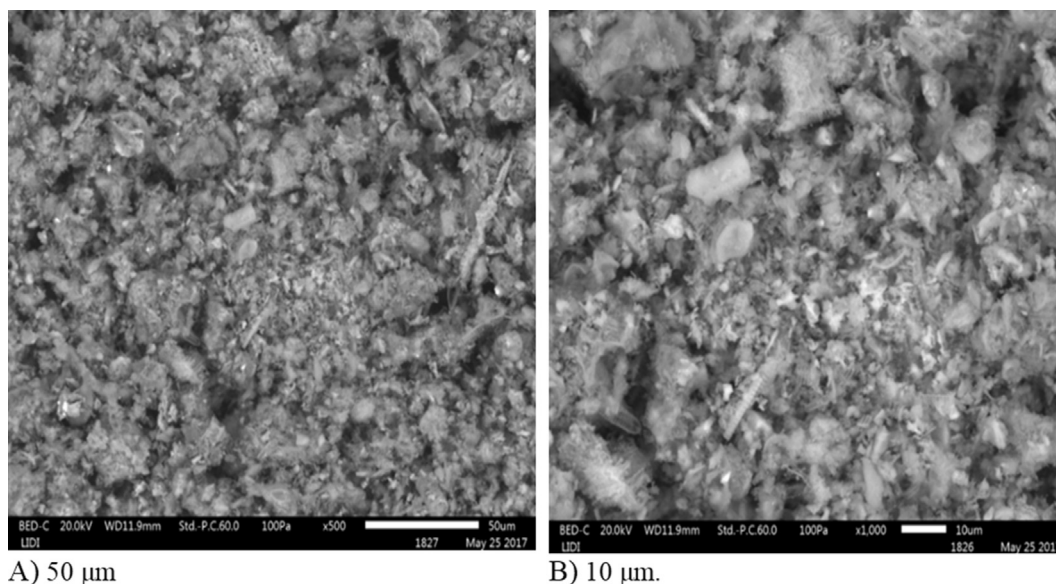
**Table 1.** Physiochemical properties of the soil and the brewery sludge biochar (BSB).

Parameters	Soil sample	BSB
pH	7.66	9.18
EC (ms)	0.15	0.60
Exchangeable cations (Cmol (+) kg <sup>-1</sup> )		
Ca <sup>2+</sup>	17.12	1.09
Mg <sup>2+</sup>	8.70	3.29
Na <sup>+</sup>	0.85	38.41
K <sup>+</sup>	0.69	5.25
CEC (meq/100g)	32.77	46.62
AP (mg kg <sup>-1</sup> )	5.21	34.55
Cd (mg kg <sup>-1</sup> )	0.05	3.98
Particle size (%)		
Sand	37	-
Silt	45	-
Clay	18	-

**Table 2.** Elemental composition and the atomic ratio of the soil and brewery sludge biochar.

Component (%)							Atomic ratio	
	C	H	N	S	O <sup>a</sup>	Ash	H/C	C/N
Soil	1.95	1.26	1.23	-	95.56	-	-	-
BSB	14.76	0.61	2.14	0.28	82.21	79.89	0.49	8.04

<sup>a</sup> By difference.

**Figure 1.** SEM images of brewery sludge biochar (BSB) taken at 50 µm and 10 µm.**Table 3.** Compositional analysis of BSB obtained from EDX result.

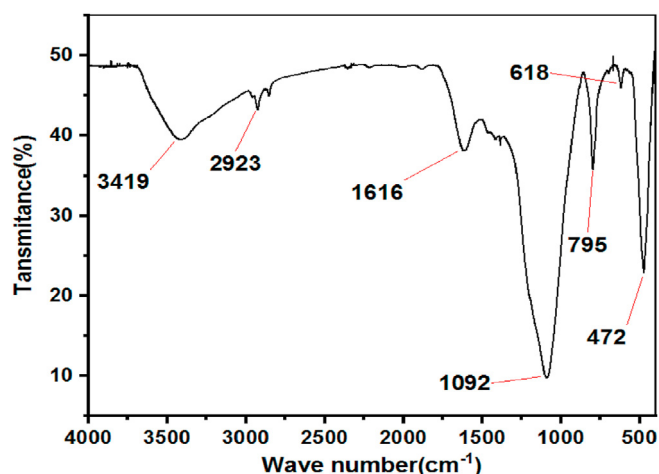
Element	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe	H/C
BSB (%)	0.95	0.49	1.78	21.16	0.85	0.36	0.59	1.16	0.32	1.34	0.49

surface complexes with cadmium. Similarly, Uchimiya et al. reported that cotton seed hull-derived biochar produced at 350 °C contains high oxygen content of functional group which were resulting in high uptake of Cu, Cd and Pb (Uchimiya et al., 2011).

### 3.2. Effect of BSB on soil properties

The results revealed that most of the physical and chemical properties of the soil significantly influenced by the addition of brewery sludge biochar (BSB) (Table 4). The addition of BSB to the soil resulted in a remarkable increase in AP, TN, EC, CEC, and exchangeable bases, as well as a slightly increased pH and OC as shown in Table 4. Other studies also reported that make use of various biochars as a soil amendment increase soil pH (Albuquerque et al., 2014; Lucchini et al., 2014; van Zwieten et al., 2010). As described by Mohan et al. (2014) the high pH value of the biochar could be linked with the separation of alkali salts during pyrolysis. Moreover, the release of basic cations such as Ca, Mg, Na and K into the soil could be accountable for increasing soil pH (Nguyen and Lehmann, 2009). In the present study, the BSB amended soil pH value increased by 1.01 times compared to soil without biochar. Khan et al. reported a similar effect, increased the soil pH compared to the soil without biochar, using the same concentration of maize stalk, bamboo, and cow manure biochar application (Khan et al., 2016). Likewise, the application of BSB exhibited higher EC value compared with the soil untreated with biochar. The amount of available phosphorus (AP) also increased in the soil amended with BSB (15.06–17.44) compared to the soil without biochar (4.13–5.14). The observed increase in the AP was

due to the use of biochar, and was responsible for the improvement in the soil pH that could minimize the activity of iron and aluminum. Lehmann et al. and Chan et al. also reported an increase in available phosphorus in the soil after the addition of biochar (Chan et al., 2008; Lehmann et al., 2003). Poulton et al. reported that the presence of high available phosphorus in the soil improves tomato plant growth and yield (Poulton et al., 2002). Hence, additional phosphorus input to the soil from added

**Figure 2.** FT-IR spectra of brewery sludge derived biochar.

**Table 4.** Physicochemical properties of the soil as a result of BSB.

Parameter	CONT	BSB + Soil	P-value
pH	7.63 ± 0.35	7.71 ± 0.08	0.66
EC (ms)	0.24 ± 0.01	0.47 ± 0.03	0.00*
OC (%)	7.84 ± 0.46	8.23 ± 0.64	0.07
TN (%)	0.23 ± 0.05	0.41 ± 0.04	0.00*
AP (mg kg <sup>-1</sup> )	4.90 ± 0.68	16.26 ± 1.19	0.00*
CEC (meq/100g)	32.02 ± 1.52	39.14 ± 1.81	0.00*
Ca <sup>2+</sup> (cmol (+) kg <sup>-1</sup> )	4.57 ± 0.28	4.28 ± 0.37	0.03*
Mg <sup>2+</sup> (cmol (+) kg <sup>-1</sup> )	4.57 ± 0.24	4.79 ± 0.27	0.01*
Na <sup>+</sup> (cmol (+) kg <sup>-1</sup> )	1.35 ± 0.04	3.56 ± 0.08	0.00*
K <sup>+</sup> (cmol (+) kg <sup>-1</sup> )	0.87 ± 0.04	1.21 ± 0.02	0.00*

\* means the difference is significant at the 0.05 level.

biochar has a vital role in incremental crop yield. Furthermore, the organic carbon also increased importantly upon addition of BSB, this is mainly caused by addition of extra carbon into the soil.

The application of BSB importantly enhanced soil CEC and available nutrients (exchangeable cations). The CEC of soil without biochar treated pot was 32.02 cmol/kg and increased to 39.14 cmol/kg BSB treated soil, which corresponds to increment by 22.23%. Since addition of biochar to soils increased nutrient availability (Tryon, 2014) and improved CEC (Rondon et al., 2007). Liang et al. reported that, soil fertility increased through biochar treatment by rising soil CEC (Liang et al., 2006). The increment of CEC after biochar addition, contributed to the metal immobilization, because the CaCl<sub>2</sub> extractability of metal is negatively related to CEC.

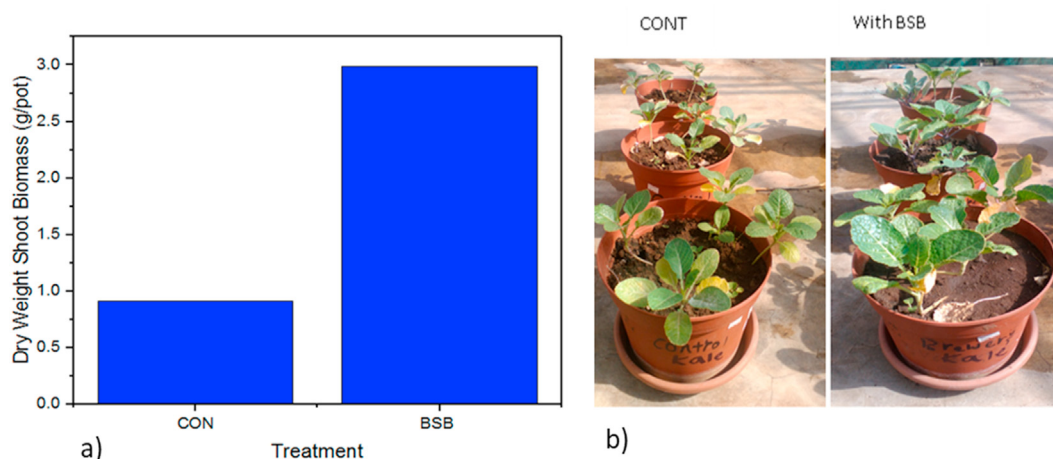
### 3.3. Effect of BSB on plant dry shoot yield

The result obtained from the pot experiment indicated that the *Brassica carinata* (Ethiopian kale) plant grew in the soil without biochar found lower biomass production (1.18 ± 0.91) compared to BSB amended soil (2.99 ± 0.93) as shown in Figure 3. The dry matter (DM) of *Brassica carinata* shoot in BSB treated soil exceedingly increased by 228.5%. Song et al. also reported considerably improved garlic yields (253%) even at lower sewage sludge derived biochar to soil (Song et al., 2014). The positive influence of BSB on the growth performance of *Brassica carinata* as compared to the control may be associated with combined effects of improved the pH, phosphorus content, and the reduced Cd toxicity. Since plant growth improved through the application of the biochar amendment due to improving soil properties and nutrients supply (Chen et al., 2006; Lehmann et al., 2006). Therefore,

brewery sludge biochar production has the potential to reduce the amount of fertilizer demand for the cultivation of agricultural crops and increase the vegetable biomass yield significantly (P = 0.00) as can be seen in Table 5. This was mainly due to the reduced Cd toxicity as well as the supplied additional nutrients from the improved soil physico-chemical properties after it had been treated with BSB. Generally, the application of biochar to soil commonly increases crop yield but depends on the nature of biochar (Jeffery et al., 2011).

### 3.4. CaCl<sub>2</sub> extractable cadmium in the agricultural soil

In this study, the CaCl<sub>2</sub> extractable cadmium concentrations in the Cd contaminated soil before (control) and after the BSB amendment found averagely between (1.89 ± 0.02 mg kg<sup>-1</sup>) and (0.27 ± 0.16 mg kg<sup>-1</sup>), respectively (Figure 4). The result from the pot experiment revealed that the application of BSB to the Cd contaminated soil caused a significant (P = 0.002, Table 5) immobilization of the bioavailable Cd by 86%. Similarly, Zheng et al. and Houben et al. reported the substantial immobilization of metals using biochar derived from miscanthus straw in contaminated soil (Houben et al., 2013; Zheng et al., 2012). Houben et al. achieved a reduction of Pb, Zn, and Cd in CaCl<sub>2</sub> extract by 92%, 87%, and 71%, respectively (Houben et al., 2013). Similarly, Hmid et al. also reported 5% and 15% biochar addition reduces Ca (NO<sub>3</sub>)<sub>2</sub> extractable cadmium (14 and 37%) with increasing rates of olive mill waste-derived biochar at 30 days equilibration (Hmid et al., 2014). Furthermore, Woldetsadik et al. recognized a significant reduction of NH<sub>4</sub>NO<sub>3</sub> extractable cadmium in contaminated soil by using fecal matter and cow manure derived biochars by 84–87% and 65–68%, respectively (Woldetsadik et al., 2016). The high available phosphorus (34.55 mg kg<sup>-1</sup>)

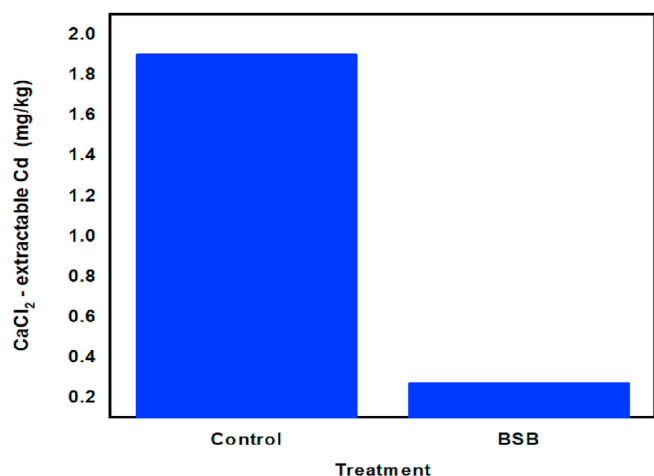


**Figure 3.** a) Dry weight shoots biomass b) the pot experiment of Ethiopian kale.

**Table 5.** Statistical analysis of CaCl<sub>2</sub> extractable Cd, Cd uptake by plants and dry matter (DM) measurements.

parameters	CaCl <sub>2</sub> extractable Cd	Cd uptake by plant	DM yield
Control	1.89 ± 0.02	2.67 ± 0.37	1.18 ± 0.91
BSB	0.27 ± 0.16	0.74 ± 0.30	2.99 ± 0.93
P-Value	0.00*	0.00*	0.00*

\* means the difference is significant at the 0.05 level.



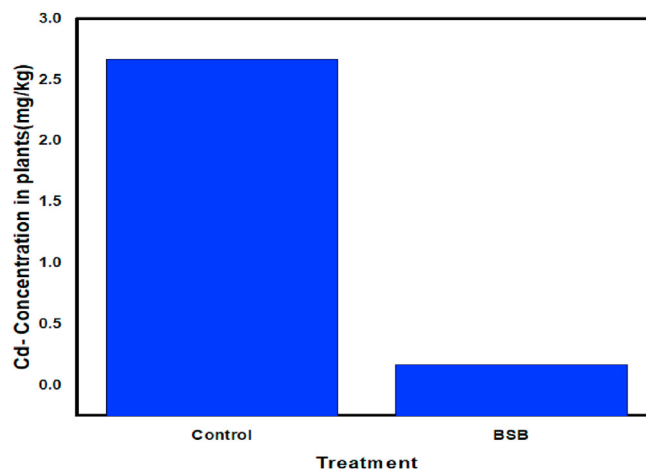
**Figure 4.** The bio-available Cd after the addition of BSB in Cd-contaminated soil.

and ash content (with low carbon 14.76%) of the BSB could be accountable for the immobilization of cadmium. Since the formation of slightly soluble solid cadmium phosphate could be evident due to the occurrence of high phosphorus in BSB treated soil (Park and Choppala, 2011; Woldetsadik et al., 2016). Besides, the electrostatic attraction of Cd with negatively charged BSB surfaces might be the other possible mechanism to immobilize the bioavailable Cd in the soil. Therefore, the reuse of brewery wastewater sludge for soil amendment in form of biochar can solve the problem of waste disposal such industrial waste and also provide a financial income as a useful product.

### 3.5. Effect of biochar on plant uptake of cadmium

The application of brewery wastewater sludge (BSB) as soil amendment significantly ( $P = 0.00$ ) reduced cadmium concentration in the edible part of the *Brassica carinata* compared to the control which did not amend with BSB. This was averagely reduced from  $2.67 \pm 0.37 \text{ mg kg}^{-1}$  in control to  $0.74 \pm 0.30 \text{ mg kg}^{-1}$  in the BSB treated soil as shown in Figure 5. According to Zheng et al. the use of rice residue-derived biochar significantly increased metal immobilization during rice cultivation and proved by a decrement in Cd, Zn, and Pb concentration in rice by 98%, 83% and 72%, respectively (Zheng et al., 2012). Likewise, in this study, the cadmium concentration in the shoot of *Brassica carinata* was decreased by 93% in BSB treated soil compared with *Brassica carinata* shoot in control soil. The main reason for significant decrease the concentration of cadmium in the shoot of *Brassica carinata* was due to the application BSB on the soil that affect the Cd mobility in the soil directly and indirectly. The direct immobilizations mechanisms could be the electrostatic attraction between Cd-cation with negatively charges on the biochar, and with existing  $\pi$ -electronic systems. Besides, the removal of heavy metals (Cd) may be caused by diffusional movement of metal ions into biochar (sorbent) pores without the formation of chemical bonds (Rodríguez-vila et al., 2018).

The other possible mechanism for the reduction of cadmium uptake in *Brassica carinata* is commonly determined by cadmium mobility in soil, in turn, extremely relied on soil pH, AP, and CEC. Since, some indirect



**Figure 5.** Effect of BSB on Cd concentration in the shoots of *Brassica carinata*.

immobilization mechanisms, such as the enhancement of soil pH and cation exchange capacity due to the application the biochar, could also promote immobilization of toxic metals in soil (Bandara et al., 2019). Moreover, the reduction in cadmium amount in shoot may also be associated with the accumulation of the cadmium in the root of *Brassica carinata*. Similarly, Yang et al. reported that cadmium translocation to shoot of rye-grass was insignificant however exceedingly high concentration remained in its root (Yang et al., 1996). In general, this study reported insignificant accumulation of cadmium present in the cultivated *Brassica carinata* shoot upon using brewery sludge biochar (BSB) soil amendment due to the above stated possible immobilization mechanisms.

## 4. Conclusion

Brewery wastewater sludge biochar (BSB) is a promising material for immobilizing cadmium metal in the contaminated agricultural soil. It remarkably reduced the bio-available cadmium uptake by *Brassica carinata* (Ethiopian kale) compared to biochar untreated soil. Furthermore, the application of BSB significantly improved the physico-biochemical properties of the soil that caused an enhanced *Brassica carinata* vegetable growth. Therefore, the application of BSB as a soil amendment could lower human health risks associated with the consumption of cadmium contamination soil-grown leafy vegetables. Meanwhile, the utilization of BSB material is a plausible means to manage the brewery industry sludge and promote urban agriculture.

## Declarations

### Author contribution statement

Yedilfana S Mekonnen, Seyoum L Asfaw: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Yordanos K Tsadik: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Abraha M Hailu: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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#### Data availability statement

Anyone can access the data presented on this paper.

#### Declaration of interests statement

The authors declare no conflict of interest.

#### Additional information

No additional information is available for this paper.

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