REMOVAL OF HEAVY METALS AND BIOFERTILIZATION ACTIVITY OF BIOCHAR

Su Su Aung[1], Myat Hla Wai[2], Myo Myo Myat[3]

Abstract

This research work deals with the removal of heavy metals and biofertilization activity of contaminated soils by using biochar (biomass): two organic residues rice husks from husker and bamboo leaves. These contaminated soil samples were collected from the Pagaye mining site S_c(I), Pagaye village S_c(II) and Battery service area from Weigyun S_c(III), Dawei Township. The three contaminated soil samples and biochar (rice husks and bamboo leaves) were treated under a close atmosphere using plastic housing. Soils were incubated at 27 °C for three months. Physiochemical properties (moisture, pH, texture, organic carbon, humus) of contaminated soils and treated soils were determined and major nutrients contents (total N, available P and available K), exchangeable cations (K^+, Ca^{2+} and Mg^{2+}) were studied by using instrumental and analytical methods. Generally, it was found that moisture, pH, organic carbon and humus were improved in treated soils and nutrients and exchangeable cations: K^+ and Ca^{2+} were also improved. Elemental compositions and heavy metals (Pb and Cd) in these soils were also determined with different interval of times by EDXRF and AAS methods. Both biochars removed the toxic metals Pb and Cd in all the contaminated soil samples. In addition, the comparison of the soil fertility on the contaminated and treated soils was carried out within one month. The soil fertility was also improved in the treated soil samples.

Keywords: Contaminated soils, biochar, treated soils, heavy metals, soil nutrients

Introduction

Myanmar is the agricultural country. Globally 30.4 million ha of agricultural land are currently managed organically. Organic farming is basically a simple idea, beginning with soil, compost, natural cycles that need to return garbage, sludge and wastes back to land, the hazards that pesticides, artificial fertilizers and toxic heavy metal from industrial waste cause to the environment and personal health benefits that result from eating quality nutrition food (Bhawalker, 1989). From the stand point of crop yields and quality, nutrient supply both from organic and inorganic sources are important. As such it is essential to substitute the inorganic fertilizers with nutrients from organic sources (Roy *et al* ., 2006). A number of diverse organic sources are available for use in agriculture. These source can be reduced the mining of soil nutrients and improve overall soil productivity. Recycling of wastes and their conservation into easily transportable and usable forms. Improper solid waste disposal (farm wastes) poses a major threat to the environment and high risks to human health. Most of these wastes are biodegradable and can be converted into valuable resources the reduces their otherwise negative impacts. To convert solid wastes into a valuable resources bio-fertilizer and its subsequent utilization as a source of plant nutrients, soil health and productivity (Birkeland, 1999) .

Soil is made up of minerals (rock, sand, clay and silt), air, water and organic material (dead plants and animals). Soil provides a substrate for plants (roots anchor in

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soil), a source of food for plants. Soil is a natural body consisting of layers (soil horizons) of mineral constituents of variable thicknesses. A layer of natural materials on the earth's surface contains both organic and inorganic materials and capable of supporting plant life. The material covers the earth's surface in a thin layer. It may be covered by water, or it may be exposed to the atmosphere. Soil contains four main components; inorganic material, organic matter, water and air(Biswas and Kherjee ,1994).

The post green revolution era witnessed a multiple nutrient deficiency because of higher crop harvest in the intensively cultivated areas where use of organic manure had declined while chemically pure fertilizers like Urea, Di-ammonium phosphate, and other allied items became the major source of plant nutrients (Blakemore *et al*, 1987). As a result of continued use of chemical fertilizer soil became poorer due to the deficiency of microbial contents of the soil. Agriculture devoid of organic manures crop residues has resulted in reduction of physicochemical and biological properties of the soil (Zin May Paing , 2014) .

Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults (Johns,1998). Ingestion is the most common route of exposure in children. Children may develop toxic levels from the normal hand-to-mouth activity of small children who come in contact with contaminated soil or by actually eating objects that are not food dirt or paint chips (FAO, 2008). Generally the research aimed to (a) develop and disseminate technology on solid waste composting for the production of composted soil (b) remove the toxic heavy metals from contaminated soil and (c) determine the efficacy with which composted soil under anaerobic conditions generates major nutrients for vegetable production and it effect on some physical properties.

Materials and Methods

Materials

All chemicals and reagents used in this research were analytical grade and purchased from the British Drug House (BDH) Chemical Ltd, England. All other chemicals used were of analytical reagent grade. In all investigations, the recommended standard methods and techniques involving both conventional and modern methods were provided.

General

Two kinds of organic residues (rice husk and bamboo leaves) were used as biochar to remove toxic heavy metals from contaminated soils and to determine biofertilization activities.

Sample Collection

The contaminated soil samples were collected from Pagaye mining site S_c(I), Pagaye village S_c(II) and Battery service area from (Weigyun) S_c(III), Dawei Township. Tanintharyi Region in the month of July, 2016 (Figure 1). Soils which contained the greatest amount of organic matter from the upper position near to the surface about (15 cm) was dug in zigzag manner according to the according to the soil sampling method. The two plant residues such as rice husks (**R**) from husker, Launglone Township and bamboo leaves **(B)** were collected from Launglone township area, Dawei District. The kind of collected bamboo leaves was Wabo.

Sample Treatment

The contaminated soil samples and two plant residues (biochar) such as rice husks (R) and bamboo Wabo leaves (B) were placed in six polyethylene pots. In the pot, the first layer was contaminated soil with thickness 2 cm and biochar from rice husks (R) was placed in the second layer 2 cm thickness and then covered with contaminated soil 2 cm thickness. Another plant residue: bamboo leaves and another contaminated soil sample were placed in each pot as the above procedures and labeled the pots were labeled as S_c(I), S_c(II) and S_c(III) for contaminated soil samples, S_c(I)+R, S_c(II)+R, S_c(III)+R, S_c(I)+B, S_c(II)+B and S_c(III)+B for treated soil samples, respectively (Figure 2). The pots were covered with plastic sheet and placed in plastic housing to maintain ambient temperature and pressure. The soil samples were moisturized with water and temperature was measured every day. The experiments were conducted in August 2016 to November 2016. The incubation experiment; two types of biochar such as rice husks and bamboo leaves were applied to contaminated soil (three replicates per treatment) at 20 kg^{-1}, was conducted in August 2016 to November 2016 under a close atmosphere using plastic housing; 6 plastic pots were using as a soil treated pile and covered with plastic sheets. Soils were incubated at 27 °C for three months and rewetted to 70 % of water holding capacity.

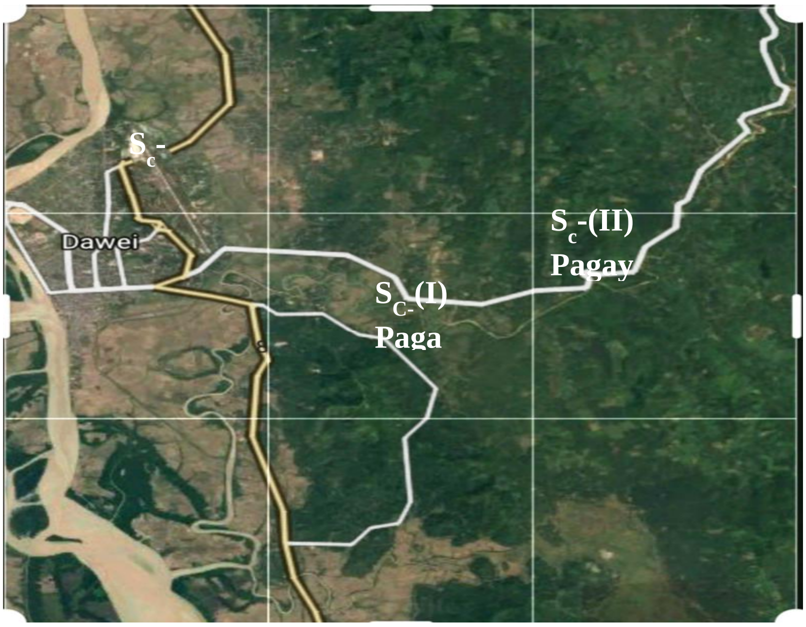

Figure 1 Soil sampling sites of contaminated soil samples

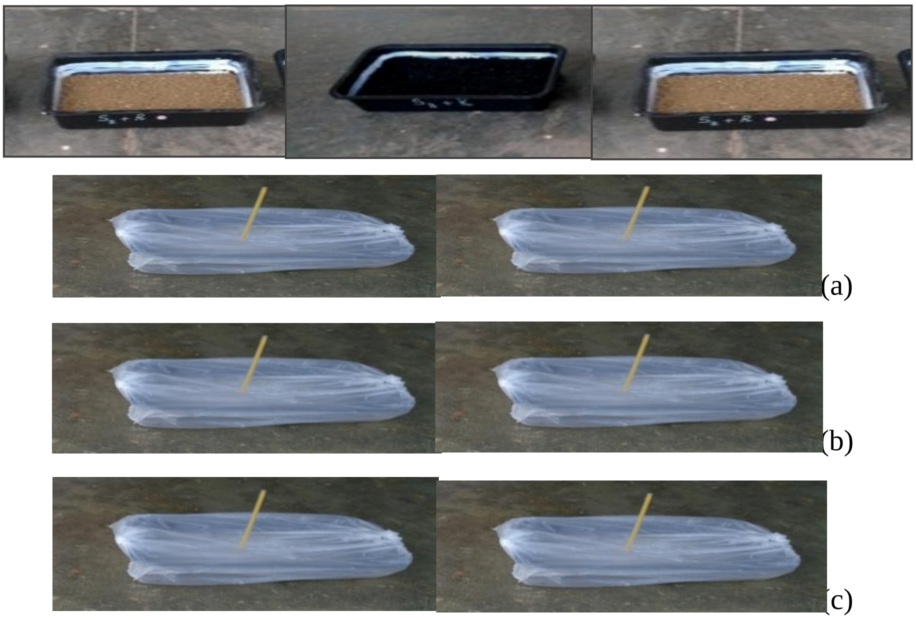

Figure 2 (a) Treated soil sample S_c(I) with rice husks (R) and bamboo leaves (B)
(b) Treated soil sample S_c(II) with rice husks (R) and bamboo leaves (B)
(c) Treated soil sample S_c(III) with rice husks (R) and bamboo leaves (B)

Soil Fertility by Cultivation of Plant (Lettuce)

The contaminated soil sample S_c(III) and treated soil samples with (S_c(III)+B and S_c(III)+R) were placed in provided containers and then inserted the lettuce seeds in each container 0.25 to 1 inch (0.6 to 2.5 cm) depth. The seed were covered with 0.5 inch (1.3 cm) of soil. The seeds were kept moist and then the soil fertility were also determined by growing plants within one month.

Results and Discussion

Physicochemical Properties of Contaminated Soil Samples

The type of contaminated soil samples for S_c(I) and S_c(II) were loam type but S_c(III) was sandy loam (Table 1). Moisture is constantly being taken by plants together with nutrients and lost by transpiration. The moisture percents of soil samples indicated that contaminated soil from near battery service area of S_c(III) was highest than the other (Table 2). The pH range for soils were 3.68 to 6.22. The pH showed that all the contaminated soil S_c(I), (II) and (III) were in acidic condition and S_c(III) was most acidic than the others. The organic carbon and humus percent of contaminated soil samples from battery service area S_c(III) was found to have the highest percent than the others. The major nutrients such as total nitrogen, phosphorus and potassium in three contaminated soil samples, total nitrogen were determined found to be in the range of 0.11 to 0.17 %, available phosphorus for 6.05 to 178.49 ppm and potassium were found to be in the range of 4.96 to 9.91 mg/100g (Table 3). And exchangeable cations : K^+ was highest amounts found in S_c(I), $Mg^{2+}$and Ca^{2+} were highest amounts found in S_c(II) (Table 4).

Table 1 Texture of Three Different Contaminated Soil Samples

Sr.No	Sample	Texture (%)			Total (%)	Soil type
		Sand	Silt	Clay		
1	S_c(I)	42.00	41.40	15.15	95.55	Loam
2	S_c(II)	40.70	40.70	17.50	98.90	Loam
3	S_c(III)	60.85	21.70	15.70	98.25	Sandy Loam

S_c(I) = Original sampling contaminated soil sample from Pagaye mining site
S_c(II) = Original sampling contaminated soil sample from Pagaye village
S_c(III) = Original sampling contaminated soil sample from Battery service area

Table 2 Moisture, pH, Organic Carbon and Humus Values of Three Different Contaminated Soil Samples

Sr. No.	Sample	Moisture (%)	pH	Organic Carbon (%)	Humus (%)
1	S_c(I)	3.07	6.27	0.40	0.69
2	S_c(II)	5.33	5.10	1.32	2.29
3	S_c(III)	3.26	3.68	1.68	2.89

Table 3 N, P and K Contents of Soil Samples

Sr. No.	Sample	Nitrogen (%)	Phosphorous (ppm)	Potassium(mg/100g)
1	S_c(I)	0.11	6.05	9.91
2	S_c(II)	0.17	23.95	7.60
3	S_c(III)	0.15	179.49	4.96

Table 4 Exchangeable K^+, Ca^2, Mg^{2+} Contents of Three Different Contaminated Soil Samples

Sr.No.	Sample	Potassium (meq/100g)	Calcium(meq/100g)	Magnesium (meq/100g)
1	S_c(I)	0.21	4.13	0.69
2	S_c(II)	0.16	4.93	2.11
3	S_c(III)	0.11	3.45	0.69

Physicochemical Properties of the Treated Soil Samples

Generally, it was found that moisture, pH, organic carbon and humus were improved in treated soils and nutrients (Table 5) and exchangeable cations: K^+ and Ca^{2+} were also improved (Table 6). Moisture values were found to be in the range from (3.26 to 8.50)%. The pH range for treated soils ranged from (3.72 to 9.12). According to pH values, it was found that the treated soil samples with biochar (rice husks) were acidic soils and with biochar (bamboo leaves) were acidic soil for S_c(I) and alkaline soils for S_c(II) and S_c(III). The major nutrients values of treated soil samples were higher than the contaminated soil samples (Table 6). Both biochars can remove the toxic metal (Pb and Cd) in all contaminated soil samples. The cadmium content in treated soil samples were decreased with time due to the absorption properties of biochar (rice husks and bamboo leaves). Lead contents in treated soil samples were found to be in the range of 83.040 ppm to 0,189 ppm within three months (Table 9).

Table 5 Moisture, pH, Organic Carbon and Humus Contents of the Treated Soil Samples (at Average Temperature 27°C)

Sample	Moisture (%)	pH	Organic Carbon (%)	Humus (%)	Time
S_c(I)+R	5.61	6.26	0.52	0.89	after one month
S_c(II)+R	5.74	5.40	1.44	2.48	
S_c(III)+R	5.86	3.72	1.69	2.92	
S_c(I)+B	3.38	8.54	0.56	0.96	
S_c(II)+B	4.55	6.11	1.42	2.45	
S_c(III)+B	3.45	4.47	1.81	3.13	
S_c(I)+R	5.12	6.39	0.60	1.03	after two months
S_c(II)+R	7.02	5.55	1.36	2.34	
S_c(III)+R	7.57	3.76	1.70	2.94	
S_c(I)+B	5.04	9.06	0.40	0.69	
S_c(II)+B	5.03	6.64	1.32	2.27	
S_c(III)+B	4.59	4.23	1.59	2.74	
S_c(I)+R	6.60	6.27	0.44	0.76	after three months
S_c(II)+R	5.04	5.34	1.32	2.29	
S_c(III)+R	8.50	3.81	1.71	2.96	
S_c(I)+B	3.91	9.12	0.40	0.69	
S_c(II)+B	3.27	6.45	1.32	2.29	
S_c(III)+B	5.73	3.99	1.37	2.35	

Removal of Heavy Metals by Using Biochar

In this study, lead contents in three soil samples were found to be the range of 4.920 ppm to 91.02 ppm (Table 8). Both biochars removed the toxic metals (Pb and Cd) in all contaminated soil samples. The cadmium content in treated soil samples were decreased with time due to the absorption properties of biochar (rice husks and bamboo leaves). Lead contents in treated soil samples were found to be reduced range from 83.040 ppm to 0.189 ppm within three month (Table 9).

Table 6 Available Nutrients (N , P and K) Contents of the Treated Soil Sample

Sample	Total Nitrogen (%)	Available (P) ppm	Available (K_2O) mg/100 g	Time
S_c(I)+R	0.13	8.21	18.43	after one month
S_c(II)+R	0.17	31.19	12.72	
S_c(III)+R	0.11	187.92	10.20	
S_c(I)+B	0.11	46.17	416.77	
S_c(II)+B	0.17	48.05	115.00	
S_c(III)+B	0.18	158.36	115.65	
S_c(I)+R	0.13	9.10	23.39	after two months
S_c(II)+R	0.15	37.00	17.43	
S_c(III)+R	0.13	239.81	12.33	
S_c(I)+B	0.11	56.41	424.23	
S_c(II)+B	0.17	30.28	193.46	
S_c(III)+B	0.17	234.34	226.40	
S_c(I)+R	0.09	9.99	23.77	after three months
S_c(II)+R	0.13	55.11	19.60	
S_c(III)+R	0.15	291.7	14.45	
S_c(I)+B	0.11	53.05	38.09	
S_c(II)+B	0.18	54.54	161.94	
S_c(III)+B	0.15	310.30	337.15	

Table 7 Exchangeable Cations (Calcium, Magnesium and Potassium) Contents in the Treated Soil Samples (at Average Temperature 27°C)

Sample	Exchangeable Cations (meq/100 g)			Time
	K^+	Ca^{2+}	Mg^{2+}	
S_c(I)+R	0.39	5.65	2.82	after one month
S_c(II)+R	0.27	4.95	0.71	
S_c(III)+R	0.22	3.54	1.12	
S_c(I)+B	8.88	6.21	0.69	
S_c(II)+B	2.45	6.29	0.70	
S_c(III)+B	2.46	3.45	0.68	
S_c(I)+R	0.50	6.32	non	after two months
S_c(II)+R	0.37	5.74	2.15	
S_c(III)+R	0.26	2.89	2.16	
S_c(I)+B	9.04	5.62	0.70	
S_c(II)+B	4.12	5.62	non	
S_c(III)+B	4.82	4.89	0.69	
S_c(I)+R	0.51	8.56	non	after three months
S_c(II)+R	0.42	3.51	non	
S_c(III)+R	0.30	2.24	2.31	
S_c(I)+B	0.81	7.63	0.72	
S_c(II)+B	3.45	6.20	non	
S_c(III)+B	7.18	6.33	0.72	

Table 8 Removal of Heavy Metals (Lead and Cadmium) from the Contaminated Soil Samples by Atomic Absorption Spectrophotometer

Toxic Element	Contaminated soil		
	S_c(I)	S_c(II)	S_c(III)
Cd (ppm)	0.287	0.276	0.447
Pb (ppm)	4.920	5.935	91.02

Table 9 Removal of Heavy Metals (Lead and Cadmium) from the Treated Soil Samples by Atomic Absorption Spectrophotometer

Element	Treated soil samples with biochar (rice husks and bamboo leaves)					
	(**after one month**)					
	S_c(I)+B	S_c(I)+R	S_c(II)+B	S_c(II)+R	S_c(III)+B	S_c(III)+R
Cd(ppm)	0.227	0.231	0.234	0.219	0.289	0.257
Pb(ppm)	4.709	4.108	3.689	3.053	75.460	83.040
	(after two months)					
	S_c(I)+B	S_c(I)+R	S_c(II)+B	S_c(II)+R	S_c(III)+B	S_c(III)+R
Cd(ppm)	0.162	0.161	0.182	0.194	0.215	0.199
Pb(ppm)	2.761	2.582	1.588	0.896	46.342	43.023
	(after three months)					
	S_c(I)+B	S_c(I)+R	S_c(II)+B	S_c(II)+R	S_c(III)+B	S_c(III)+R
Cd(ppm)	0.108	0.123	0.104	0.067	0.014	0.068
Pb(ppm)	0.245	1.498	0.365	0.189	13.371	12.140

Both biochars can remove the toxic metals (Pb and Cd) in all contaminated soil samples. The cadmium content in treated soil samples were decreased with time due to the absorption properties of biochar (rice husks and bamboo leaves). Lead contents in treated soil samples were found to be the range from 83.040 ppm to 0.189 ppm within three month. Among the treated soil samples, the maximum value of lead content were 83.040 ppm with biochar (rice husks) and 75.460 ppm with biochar (bamboo leaves) and minimum value of lead content were 0.189ppm with biochar (rice husks) and 0.245ppm with biochar (bamboo leaves) respectively.

ED XRF Analysis of Relative Composition of Elements in the Contaminated Soil Samples

Relative compositions of elements were measured by ED XRF. The results are shown in Table 10.

The content of silicon in three contaminated soil samples were the highest relative to that of other elements and iron content is the second highest. The other elements such as Pb, K, Ca, Ti, Mn, Ba, Cu, Zn, V, Rb, W, Y, Sn and Se were also investigated. The contents of toxic metal: Pb were 0.155 %, 0.148 % and 7.230 % in the contaminated soil samples (I, II, III) respectively. Among the three contaminated soil samples, lead content of S_c(III) was the highest percent because the soil samples S_c(III) was collected from Battery service area.

Study on Soil Fertility by Using the Treated Soil Sample S_c(III) with Biochars

Removal of heavy metals and soil fertilization activities of biochars were also determined by growing plants (lettuce plants) within one month (Figure 4). It was found that the treated soil samples S_c(III)+B and S_c(III)+R were improved the soil fertility than the contaminated soils by studying the growth of lettuce plants within one month. Therefore, the soil fertility was improved when the soil samples were treated with biochar (rice husks and bamboo leaves) (Table 11).

Table 10 Relative Composition of Elements in the Treated Soil Samples Using Biochar

Sample	Elemental Composition (%) of Samples																			
	Si	Fe	K	Ti	W	Rb	Mn	Zr	Zn	Al	V	Y	Se	Au	Cu	Ca	Cr	Pb	Sn	
S_c(I)+R	40.504	41.07	12.747	2.802	0.485	0.500	0.752	0.334	0.175		0.104	0.082	-	0.186	-	-	-	-	0.256	
S_c(II)+R	55.230	31.46	9.049	2.717	-	0.140	0.348	0.407	0.132	0.174	-	0.055	0.194	0.092	-	-	-	-	-	one month
S_c(III)+R	52.828	34.77	4.078	3.581	-	-	0.436	0.922	-	-	0.109	-	-	0.272	-	-	-	3.004	-	
S_c(I)+B	47.003	32.33	14.841	-	1.085	0.624	0.672	0.255	0.107	0.160	0.104	0.071	0.086	0.104	-	-	-	-	-	
S_c(II)+B	49.437	35.97	9.440	2.650	-	0.067	0.387	0.383	0.128	0.182	0.099	0.048	-	-	-	-	-	-	1.030	
S_c(III)+B	54.072	31.90	5.015	3.818	-	-	0.340	0.578	0.120	-	-	-	-	-	-	-	-	3.091	-	
S_c(I)+R	34.729	45.14	12.606	3.074	0.660	1.150	0.918	0.602	0.242	0.229	0.154	0.123	-	0.101	0.260	-	-	-		
S_c(II)+R	53.043	33.50	9.312	2.595	-	0.148	0.376	0.534	0.114	0.217	0.111	0.051	-	-	-	-	-	-		two months
S_c(III)+R	67.914	4.527	0.820	0.880	-	0.158	0.064	0.034	0.010	25.41	0.028	-	-	-	0.010	0.09	0.017	0.220		
S_c(I)+B	34.402	39.30	17.076	3.022	1.771	1.350	0.962	0.488	0.164	0.162	0.140	0.112	0.049	0.019	-	-	-	-	0.061	
S_c(II)+B	52.646	32.05	10.774	2.761	-	0.152	0.387	0.527	0.109	0.324	-	0.069	-	0.194	-	-	-	-	-	
S_c(III)+B	65.197	4.739	1.459	0.935	-	0.239	0.069	0.054	0.010	27.05	0.027	-	-	-	0.010	0.065	0.011	0.239	-	
S_c(I)+R	34.729	45.14	3.736	3.074	0.660	1.150	0.918	0.602	0.242	0.229	0.154	0.123	-	0.101	0.260	-	-	-	-	
S_c(II)+R	53.043	33.50	2.801	2.595	-	0.148	0.376	0.534	0.114	0.217	0.111	0.051	-	-	-	-	-	-	-	three months
S_c(III)+R	67.914	4.527	0.724	0.880	-	0.158	0.064	0.034	0.010	25.41	0.028	-	-	-	0.010	0.090	0.017	0.220	-	
S_c(I)+B	34.402	39.30	4.554	3.022	1.771	1.350	0.962	0.488	0.164	0.162	0.140	0.112	0.049	0.019	-	-	-	-	-	
S_c(II)+B	52.646	32.05	2.467	2.761	-	0.152	0.387	0.527	0.109	0.324	-	0.069	-	0.194	-	-	-	-	-	
S_c(III)+B	65.197	4.739	1.320	0.935	-	0.239	0.069	0.054	0.010	27.05	0.027	-	-	-	0.010	0.065	0.011	0.239	0.061	

Table 11 Plant Height of Lettuce after Fertilizer Application Rate for Vegetables Production

No	Sample	Plant Height (cm) after Sowing			
		7 days	14 days	21days	28days
1	S(III)	1.1	1.9	3.5	5.6
2	S(III)+B	1.1	1.9	3.8	6.1
3	S(III) +R	1.1	1.9	3.9	6.7

Figure 4 The growth of lettuce plants within one month

Conclusion

In this research work, physicochemical properties of treated soil samples were determined by different time intervals. Generally, it was found that moisture, pH, organic carbon and humus were improved in treated soils and nutrients and exchangeable cations: K^+ and Ca^{2+} were also improved. The major nutrients values of treated soil samples were more than the contaminated soil samples. The minor nutrients such as exchangeable potassium and calcium, magnesium ions in treated soil samples were found to be in the range of 0.22 to 9.04 meq/100 g for K^+, 2.24 to 8.56 meq/100 g for Ca^{2+} and (0 to 2.82) meq/100 g for Mg^{2+}. Both biochars can remove the toxic metals (Pb and Cd) in all contaminated soil samples. The cadmium content in treated soil samples were decreased with time due to the absorption properties of biochar (rice husks and bamboo leaves). Lead contents in the treated soil samples were found to be decreased from 83.040 ppm to 0.189 ppm within three month. Among the treated soil samples, the maximum value of lead content was 83.040 ppm removed by biochar (rice husks) and 75.460 ppm with biochar (bamboo leaves) and minimum value of lead content were 0.189 ppm removed by biochar (rice husks) and 0.245 ppm with biochar (bamboo leaves) . In addition, it was the comparison of the soil fertility on the contaminated and treated soils were carried out within one month. It was found that the soil fertility in the treated soil samples: Sc (III) +B and Sc (III) +R were improved than the contaminated soil. Therefore, the soil fertility was improved when the soil sample was treated with biochar. It was concluded that treating the contaminated soil with biochar (rice husks and bamboo leaves) improved the soil fertility and using these biochars can remove the toxic metals in soils.

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