Preparation and Characterization of Biochar from Rice Straw and Its Application in Soil Remediation

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ABSTRACT

In many developing countries, there is a large quantity of agricultural wastes that cause severe pollution problems. Also, the agricultural soils are polluted with heavy metals and there is a need to find an environmentally friendly approach for both getting rid of agro-wastes and helping in having more available soil for agriculture. In the present study, rice straw was used for the production of biochar for application in soil remediation. The biochar prepared by rice straw pyrolysis at 450 °C was characterized by different tools such as X-ray diffraction, Fourier-transformation infrared and scanning electron microscopy. The characterization results indicated that rice straw biochar (RSB) has amorphous porous structure with several functional groups and mainly composed of silicates. RSB was then investigated as soil remediating material for a silty clay soil. In this context, a synthetic polluted soil was prepared to contain 10 and 500 mg/kg of cadmium and lead, respectively. Rice straw biochar (RSB) was applied to the soil at the following (w/w) rates: 0% (control), 1.25% (T1), 2.50% (T2), 5.00% (T3) and 10.00% (T4). After 30 days of incubation, the soil samples were analyzed. The results showed that biochar addition resulted in a significant increase in soil pH, EC, CEC, total organic matter, total carbon and moisture. Application of biochar slightly increased the available N, P and K. The concentrations of plant available Pb and Cd in all biochar treatments were significantly lower than those of the control treatment. It can be concluded that biochar prepared from agricultural wastes is of both economic and environmental interest, especially in developing countries. Rice straw biochar could be further explored for remediating other types of soil pollutants with continuous monitoring of soil properties.

1. INTRODUCTION

Agricultural wastes represent a major environmental problem and re-using these wastes by turning them into valuable materials is an increasing challenge. About 25% of crop straws are burned during harvest season to remove crop residues, which is detrimental to air quality and human health (Xu et al., 2016). Rice straw is a major agricultural residue, accounting for 731 million Tons annually in the world (Park et al., 2014). In Egypt, processing of rice in the river Nile Delta yields large amounts of rice straw as residue; this residue is usually burned causing air pollution and formation of "black cloud" (El-Adly et al., 2015). It is thus imperative to find safe and beneficial ways of getting rid of rice straw instead of burning it and thus, transforming agricultural wastes to biochar may be a good solution. Biochar is a carbon-rich product prepared by combusting biomass (such as agricultural wastes), at temperatures between 350 °C and 700 °C in a closed chamber with insufficient air or no air (Liu et al., 2015). Biochar has several proven applications including its application for soil remediation. The properties and characteristics of biochar depend mainly on the starting material used for its preparation and also on its preparation conditions.

Biochar as soil amendment is of appealing global interest owing to its many benefits, including

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sequestration of carbon, decrease of greenhouse gases, enhancement of soil fertility and crop growth (Zhang et al., 2017). The application of biochar to agriculture soils has many positive effects such as decreasing the phytotoxicity of heavy metals, and increasing cation exchange capacity, water-use efficiency and holding plant nutrients, along with enhancing the nutrient uptake and growth of plants (Sahin et al., 2017). Also, soil amendments have been commonly utilized for in situ remediation of metal polluted soil. Several types of organic and inorganic materials were employed to immobilize heavy metals in soil by converting them into less available forms (Lu et al., 2017). It is thus a challenging issue to find environmental friendly ways to overcome soil pollution. So, the aim of the present study is to use an agricultural waste (rice straw) to prepare biochar and to investigate the effect of applying this biochar for soil remediation and heavy metals immobilization.

2. METHODOLOGY

2.1 Biochar preparation

Rice straw was collected during the harvesting season of rice in Egypt. The collected straw was washed with tap water to remove any adherent dust. The biochar was prepared according to the method described by Cao et al. (2011). Rice straw was oven dried oven-dried for 12 h at 80 ºC and grinded. The dried rice straw material was then placed in tightly covered containers to create an oxygen-limited condition during biochar production and moved to a pyrolysis furnace which was heated by 5 ºC/min to 450 ºC under anaerobic conditions and then maintained for 4 h until no further smoke exhaust. The resulting biochar was then ground and sieved through a 0.25-mm mesh before further application. The resulting biochar was abbreviated RSB.

2.2 Biochar characterization

The produced biochar was characterized by different tools including Fourier transformation infrared spectroscopy (FTIR) using Perkin-Elmer FT-IR 1650 spectrophotometer with a working wave number range (200-4,000 cm^{-1}), X-ray diffraction (XRD) using PanlyticalX'pert Pro X-ray diffractometer and Scanning electron microscopy (SEM) using a JSM-6390LV (JEOL Ltd, Japan).

2.3 Application of biochar for soil remediation

Agricultural soil was obtained from Agricultural Research Center (ARC), Giza, EGYPT. Physical, chemical and mechanical properties of soil were determined in the "Soil, Water and Environmental Research Institute" at the Agricultural Research Center, Giza, Egypt. These properties included: soil texture, EC and pH, CEC, moisture, macro and micronutrients and some heavy metals. All tests were done according to the standard methods given by Estefan et al. (2013). In order to assess the effect of RSB application on soil properties and heavy metals immobilization; a synthetic polluted soil was prepared by adding 500 mg/kg lead in the form of lead nitrate and 10 mg/kg cadmium in the form of cadmium nitrate. The effectiveness of biochar in remediating synthetic polluted soil was tested using the procedure of Abdelhafez et al. (2014). Four levels of biochar were used: 1.25% w/w (T1), 2.5% w/w (T2), 5.0% w/w (T3), 10% w/w (T4) and a control without biochar was also used. At the beginning of the experiment 200 g of soil were thoroughly mixed (on weight basis) with rice straw biochar (RSB) at the suggested rates in plastic pots and the samples were moisturized with deionized water. Soil samples were then incubated at room temperature for 30 days without direct exposure to sunlight with continuous moistening (3 pots /treatment). At the end of incubation, soil samples were collected, dried, sieved and kept for analysis.

Soil samples before and after biochar treatments were analyzed for available macro-nutrients as well as available lead and cadmium concentrations by extracting 20 g of air dried soil in 0.5 M solution of ammonium acetate and 0.02 M EDTA (Lakanen and Erviö, 1971). The element concentrations were then determined using inductively coupled plasma (ICP Ms/Ms QQQ8800 Agilent) (Hartley et al., 2013).

2.4 Statistical analysis

Complete Randomized design was employed to analyze the data (Snedecor and Cochran, 1980) and the significant differences between means were obtained by Duncan's multiple range test (Duncan, 1955) at 5% probability.

3. RESULTS AND DISCUSSION

3.1 Soil properties before biochar application

The results of soil analysis before the addition of biochar are summarized in Table 1.

Table 1. Soil characteristics

Measured property	Result
Fine sand (%)	11.20
Coarse sand (%)	2.50
Silt (%)	44.70
Clay (%)	41.60
Soil texture	Silty Clay
$CaCO_3$ (%)	7.70
Total organic matter (TOM) (%)	7.92
Total organic carbon (TOC) (%)	4.60
Moisture (%)	2.24
pH	8.20
Electrical conductivity (EC; dS/m)	0.818
Cationic exchange capacity CEC (meq/100g)	15.30
Macro-elements (%)	
N	0.1100
P	0.0068
K	0.0586
Ca	0.8295
Na	0.0877
Mg	0.0958
Micro-elements (mg/kg)	
Al	49.48
Cr	0.358
Mn	360.33
Fe	42.33
Cu	15.86
Zn	30.44
Heavy metals (mg/kg)	
*Cd	N.D.
*Pb	N.D.

Remark: 1) N.D. not detected and 2) *detection limit for Cd = 0.012 ppb and for Pb = 0.009 ppb (Sakai, 2015)

3.2 Fourier Transformation Infrared Spectroscopy (FTIR) characterization of rice straw biochar

The surface properties of biochar have a strong effect on its capability of removing metal ions from soil and the FTIR spectroscopy gives a great tool to observe this surface composition. Figure 1 shows the FTIR spectrum of rice straw biochar (RSB) and Table 2 summarizes the main bands and their assignments. The results indicate the presence of many surface functional groups that could be involved in heavy metals adsorption from soil.

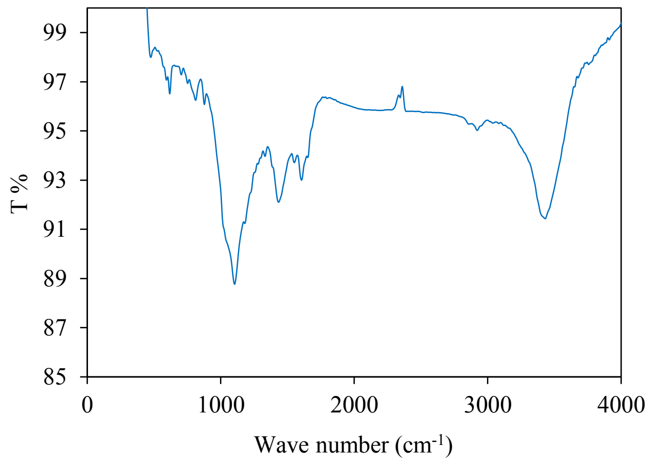

Figure 1. FTIR of rice straw biochar

Table 2. FTIR band assignments

Band	Assignment	Reference
3430.74 cm^{-1}	OH group	(Akhtar et al., 2010)
1605 cm^{-1}	oleifinic C-C and carbonyl C=O stretching	(Akhtar et al., 2010)
1430 and 1020 cm^{-1}	cyclic structures, such as cellulose or lignin	(Velazquez-jimenez et al., 2013)
811.88 and 1104.05 cm^{-1}	SiO_2	(Jindo et al., 2014)
618 cm^{-1}	aliphatic CH_2 deformation	(Han et al., 2013)

3.3 X-ray diffraction (XRD) analysis of rice straw biochar

Another characterization tool that was employed in this work was the XRD. In Figure 2, the XRD pattern of rice straw biochar is given. The results were comparable to previously reported XRD patterns for rice straw based biochars. The figure showed a characteristic peak of Silica (SiO_2) at 2 Theta position ~28°.

The XRD pattern also reveals the presence of potassium as potassium chloride, known to be found as an impurity. Compared with other materials, rice straw is low in lignin and high in Si and K, which gives rise to a high content of SiO_2 and KCl in rice straw biochars (Wu et al., 2012). Rice straw loses its crystalinity at 400 °C, it is thus agreed that in the present work the XRD pattern of RSB is indicative of an amorphous, poorly crystalline and carbon-rich material.

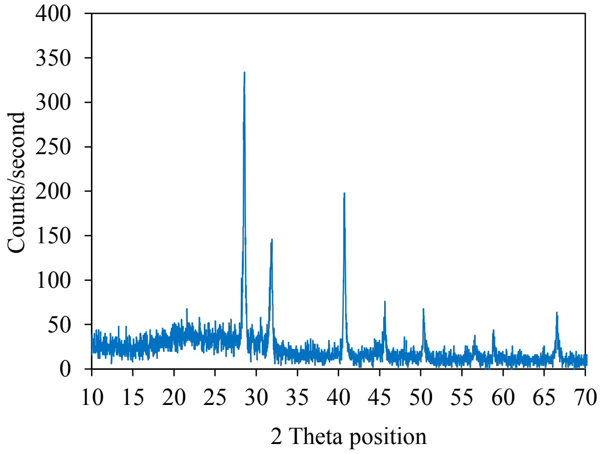

Figure 2. X-ray diffraction pattern of RSB

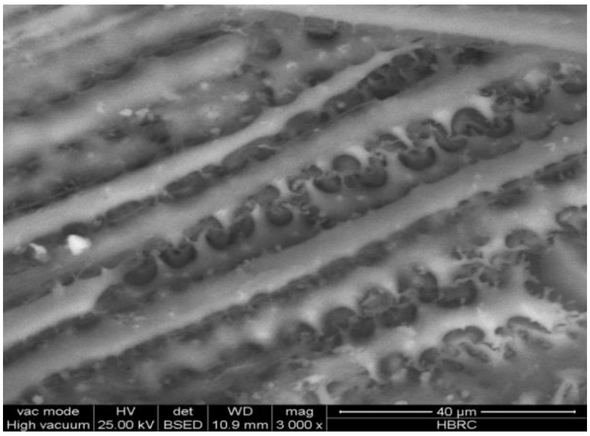

Figure 3. SEM of rice straw biochar (x3000)

3.4 Scanning electron microscopic analysis of RSB

In order to get more characterization about the surface structure of rice straw biochar, the biochar surface was scanned by scanning electron microscope (SEM) and the results are shown in Figure 3.

Figure 3 shows the surface features of rice straw biochar as obtained by SEM at magnification of 3,000. The micrograph shows that RSB consists of non-regular plates with porous structure and a large, accessible surface area which offers effective adsorption sites (Jiang et al., 2012).

3.5 Effect of RSB application on soil properties

The effect of biochar modifications on soil pH, electrical conductivity (EC), ash, humidity, total organic matter (TOM), total carbon (TC), N, P and K is shown in Table 3.

Table 3. Effect of biochar on soil properties

	Control	T1	T2	T3	T4
pH	8.20^{b}	8.30^{b}	8.30^{b}	8.95^{a}	9.15^{a}
EC (dS/m)	0.818^{e}	1.859^{d}	2.016^{c}	3.170^{b}	4.900^{a}
CEC meq/100g	15.30^{d}	15.90^{c}	16.00^{c}	16.40^{b}	17.10^{a}
Ash %	87.47^{a}	87.25^{b}	87.43^{a}	87.02^{c}	86.28^{d}
Moisture %	4.61^{c}	4.49^{d}	4.31^{e}	4.67^{b}	4.72^{a}
TOM %	7.92^{d}	8.25^{c}	8.25^{c}	8.31^{b}	8.98^{a}
TC (g/kg)	46.0^{d}	48.0^{c}	48.0^{c}	48.3^{b}	52.2^{a}
N %	0.11^{c}	0.11^{c}	0.11^{c}	0.12^{b}	0.13^{a}
P %	0.0068^{e}	0.0078^{d}	0.0084^{c}	0.0095^{b}	0.0113^{a}
K%	0.0586^{e}	0.1226^{d}	0.1967^{c}	0.3151^{b}	0.6248^{a}

Remark: Different superscripts of a, b, c, d and e illustrated the significant difference ($p<0.05$) of values in the same row

The data in Table 3 revealed a significant ($p<0.05$) increase in pH, EC and CEC values due to addition of biochar. The highest mean values of pH, EC and CEC were observed in the soil treated with 10% biochar (T4), while the lowest values were recorded at the control. A rise in soil pH will support the adsorption and precipitation of heavy metals, and thus decrease their bioavailability. This could be important for the reduction of plant concentrations of Cd and Pb, metal adsorption to biochar may be one of the routes of metals immobilization (Lu et al., 2014). The CEC is an essential sign of soil fertility and the increase in soil CEC was demonstrated to be effective in the immobilization of metal cations mainly through metal precipitation and surface complexation (Yin et al., 2017).

Biochar addition to soil significantly resulted in greater soil total C content compared to the control soil. The biochar treatment at the level of 10% (52.20 g C/kg) increased soil C by 13.4% compared to 'control' (46.00 g C/kg). These results are consistent with numerous biochar studies where researchers recorded soil C storage (Gao et al., 2016). The organic matter of the soil significantly increased ($p<0.05$) following the application of biochar. The results showed that the total organic matter increased by increasing the biochar amendment level meaning that organic matter is conserved more competently and keeping the activity of the microorganisms accountable for soil organic matter biodegradation (Méndez et al., 2012). Biochar addition significantly increased moisture content of soil indicating increasing soil water holding which is ascribed to the porous structure of biochar (Al-Wabel et al., 2015).

It is generally agreed that biochar application usually increases the essential nutrients in soil, including nitrogen (N), phosphorus (P) and potassium (K), which facilitates plant growth (Agegnehu et al., 2017). In the present work, the application of RSB up to 10% slightly increased the N contents of the treated soils as compared to control. Also, available phosphorus increased after adding the biochar to the soil and increased by increasing the biochar level. The application of biochar at a level of 10% led to a significant ($p<0.05$) increase of available P compared to the control and other treated groups. The concentration of potassium in biochar amended soils significantly ($p<0.05$) increased by increasing the amount of biochar application rates. The increased nutrients' retention of biochar modified soil could be attributed to the biochar surface area, making it easier for nutrients to interact with surface function groups on the biochar (Randolph et al., 2017).

3.6. Effect of biochar on lead and cadmium levels in soil

Heavy metals in soil extracted with EDTA are considered to be plant available (Lu et al., 2017). Regarding the effect of biochar application on available heavy metals in soil, Figures 4 and 5 show the plant availability of lead and cadmium in soils after biochar application. The available concentrations of plant Pb and Cd were considerably ($p<0.05$) lower than those in the control treatment in all biochar treatments. The results showed that lead and cadmium available concentration significantly decreased ($p<0.05$) with increased rates of application of rice straw biochar.

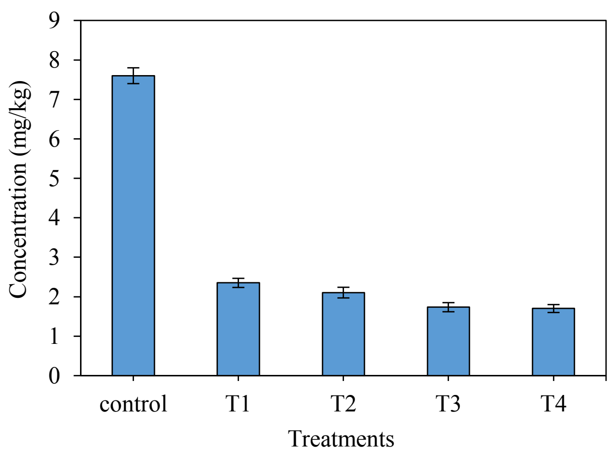

Figure 4. Effect of Rice straw biochar on Cd availability

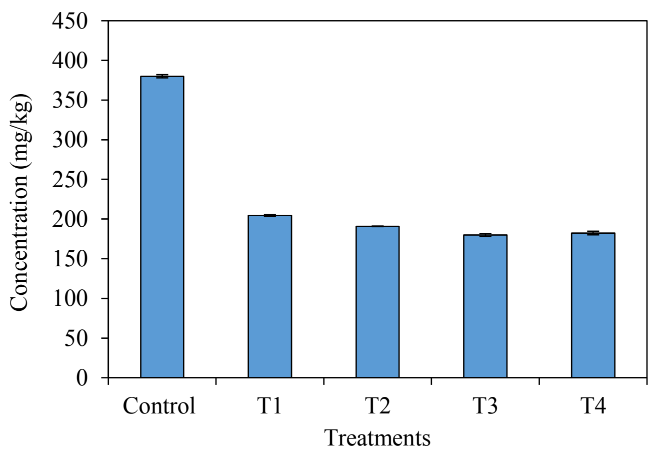

Figure 5. Effect of Rice straw biochar on Pb availability

The results also revealed that the soil amended with rice straw biochar at levels of either 5% (T3) or 10% (T4) possessed significantly lower Cd and Pb concentrations compared to all other treatments. Further results showed that the soil adjusted with rice straw biochar had significantly lower concentrations of Cd and Pb compared to all other treatments at levels of either 5% (T3) or 10% (T4). It was also conspicuous that there were no significant differences ($p>0.05$) in Cd and Pb concentrations of the soil treated with rice straw biochar at levels of either 5% or 10%.

Previous studies supported this finding, suggesting that the relatively high efficiencies of rice straw biochar in immobilizing Cd and Pb may result from the precipitation of Cd and Pb as hydroxides and phosphates (Ahmad et al., 2014; Ok et al., 2010). It is interesting to note that RSB was found to contain a high amount of SiO_2; in this respect, Li et al. (2012) found the addition of silicon to soil contaminated by lead reduced the exchangable fraction of Pb in soil. This reduction in metals availability corresponds to a reduction in metal uptake by plants.

Also in the present study, rice straw biochar had a high pH, Si and P concentrations; this can explain the increased solubility reduction of Cd and Pb with its application because of a metal restriction effect of biochar. This finding was previously verified by several authors (Beesley et al., 2010; Fellet et al., 2011; Lu et al., 2014; Méndez et al., 2012).

The high pH of rice straw biochar could be the reason for the reduction in Pb solubility with its use (Li et al., 2017). The use of biochar increases the pH of soil, therewith increasing complexation and adsorption of metal cations on biochar and lowering their mobility (Ahmad et al., 2014; Beesley and Marmiroli, 2011). The effect of Biochar on soil metal immobilization is influenced by the starting material used, pyrolysis considerations and levels of application. The fact that, most biochars have large microporous structure surfaces, high pHs and some soluble salts make them reduce the solubility of heavy metals in soil through adsorption and precipitation (Chan and Xu, 2009; Yuan et al., 2011; Zhang et al., 2013). The applications of rice straw biochar have also been reported by Jiang and Xu (2013) to increase the proportion of organic materials and immobilizing heavy metals in soil.

4. CONCLUSIONS

Biochar was effectively produced from rice straw and was applied as a soil amendment. The results of this study showed that rice straw biochar can effectively immobilize and reduce the availability of lead and cadmium in soil. Biochar application improved soil properties and increased the availability of macro nutrient elements. Thus, instead of burning agricultural wastes, they can be turned into valuable materials such as biochar that can be used to reduce metal availability of contaminated soils as well as to improve some soil properties. Moreover, caution must be considered due to the possible occurrence of a trace amounts of some heavy metals accumulation for long term application of biochar. This issue should be continuously followed up.

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