

Effect of Rice Husk Biochar on Cadmium Immobilization in Soil and Uptake by Wheat Plant Grown on Lacustrine Soil

Amal H. Mahmoud¹, Maher E. Saleh² and Abdel-Salam A. Abdel-Salam²

¹Soil Salinity and Alkalinity Research Laboratory, Institute of Soil, Water and Environment Research, Agricultural Research Center, Bakous, Alexandria.

²Department of Soil & Water Science, Faculty of Agriculture, Alexandria University, postal code 21545 El-Shatbi, Alexandria, Egypt

Received on: 5/7/2011

Accepted: 31/7/2011

ABSTRACT

Production of biochar from crop residues using pyrolysis technology is considered one of the recent technologies to use the pyrolyzed residues as recalcitrant adsorbent materials to remove heavy metals from wastewater and immobilize metallic contaminants in soils. Rice husk biochar (RHB) was produced by pyrolysis of rice husk (RH) at 450 °C for 15 min. in the laboratory. Surface area, pore volume and FTIR techniques were used to characterize both RH and RHB. Adsorption isotherm experiments were carried out to measure the adsorption of Cd²⁺ (875 mg Cd²⁺ kg⁻¹) on RH and RHB for 96h. Greenhouse experiment was conducted to investigate the effect of biochar application (by rate of 30t ha⁻¹) to soil in presence of Cd²⁺ (0, 5 and 35 mg kg⁻¹ soil) on the yield and Cd²⁺ uptake by wheat plants. Produced biochar had higher surface area and total pore volume by about 10 and 2.73 times, respectively, than the feedstock (RH). Adsorption Isotherm showed that about 97.3 and 63.2% of Cd²⁺ were removed within the first 2 h of reaction by RHB and RH, respectively. There was increase in pH values only associated to RH adsorption of Cd²⁺ which reflects an increase in electronegativity or changing in the status of surface functional groups of RH. The high values of adsorption and stable pH values during Cd²⁺ adsorption on RHB reveals the stability of active surfaces and surface groups of biochar with time. There was a significant increase in concentrations of DOC with reaction time only in RH treatment and it was not observed in RHB treatment. DOC results pointed out the potentiality of degrading and decaying the RH adsorption system with time, and reflects the recalcitrant feature of RHB system. The Results of greenhouse showed a significant reduction in grain and straw yield and high rates of Cd²⁺ uptake with increasing concentrations of added Cd²⁺. Application of RHB greatly reduced the hazardous effect of Cd²⁺ on the growth and yield and significantly diminished the accumulation of Cd²⁺ in both wheat grain and straw.

Key words: rice husk, rice husk biochar, cadmium, wheat, FTIR, surface area, lacustrine soils

INTRODUCTION

Biochar is a product of thermal decomposition of biomass produced by the process called pyrolysis. Biochar has been found to be biochemically recalcitrant as compared to un-charred organic matter and possesses considerable potential to enhance long-term soil carbon pool (Lehmann *et al.*, 2006). Biochar has been shown to improve soil structure and water retention, enhance nutrient availability and retention, ameliorate acidity (Glaser *et al.*, 2002), and reduce heavy metals toxicity to plants and soil microorganisms (Park *et al.*, 2011 and Beesley *et al.*, 2010). Biochar possesses organic functional groups on its surfaces and the negatively charged organic functional groups increase over time during its oxidation in soil (Cheng *et al.* 2008). The formation of surface functional groups and adsorption sites on biochar could influence its retention capacity (Liang *et al.*, 2006) and consequently the capacity of biochar amended soils to form complexes with metal ions.

Presence of heavy metals in several wastes, added to the cultivated soils today, has imposed a need for a better understanding of the processes of

soil-heavy metal interactions, in particular, their mobility and retention. The waste disposal, whether in sanitary landfill or, when processed for agricultural use demands understanding of the adsorption phenomena and pollutant mobility in soil profiles, since these are essential factors that control groundwater contamination (Krishnani and Ayyappan, 2006 and Bittell and Miller, 1974).

Cadmium (Cd) is one of the most toxic trace metals found in sewage sludge-treated soils and extensively phosphate fertilized soils (Logan *et al.*, 1997 and Merrington *et al.*, 1997). When sewage sludge is used on farmland, it generally dominates the fluxes of several trace metals, including Cd²⁺ (Andersson, 1992). Cadmium has been linked to negative health effects, so it is desirable to reduce its concentrations in crops entering the human diet. Due to high Cd²⁺ mobility in the soil-plant system, it can easily enter into food chain and can create risk for human and environmental health (Grant *et al.*, 1998). Therefore, significant research attention addresses the mechanisms of Cd²⁺ uptake, translocation and grain accumulation, especially in crops having ability to accumulate high Cd²⁺, such as wheat, sunflower and some others (Hariss and

Taylor, 2001). Cadmium concentration in crops is influenced by a wide range of factors, including crop genotypes, soil characteristics such as texture, pH and salinity, weather, crop sequence, crop management practices and soil Cd^{2+} concentration (Grant *et al.*, 1998).

Rice husk, as one of the major crop residues, showed a great ability to remove various heavy metal pollutants from aqueous solution and wastewater (Kumar and Bandyopadhyay, 2006 and Ajmal *et al.*, 2003). It is considered one of the potentially bio-sorbents of heavy metal ions. Lui and Zhang (2009) demonstrated the feasibility of biochars as adsorbents for lead removal from aqueous solution based on the irregular surfaces and much more oxygen-containing functional groups. Rice husk and rice husk biochar showed a great ability to remove and retain Cd^{2+} from both municipal and industrial waste waters (Krishnani *et al.*, 2008; Srivastava *et al.*, 2006; Ajmal *et al.*, 2003).

This investigation was conducted to determine the ability of rice husk and rice husk biochar to remove Cd^{2+} from water, immobilize it in soils enriched by Cd^{2+} and reduce Cd^{2+} accumulation in wheat grains and straw.

MATERIALS AND METHODS

Soil and rice husk:

Lacustrine soil samples were collected from the top 20 cm of soil layer from Abis area located southeast Alexandria Governorate. Some soil properties are listed in Table (1). The soil samples were air dried, crushed and sieved using 4-mm polypropylene sieve and 25 kg soil were transferred to the Mischerlich pots (40-cm height and 25 cm diameter) for experimental purposes.

Rice husk (RH) was obtained from a private sector rice mill located in Housh Isa City, Behairah Governorate. The RH samples were washed several times by distilled water and oven-dried at 70 °C for 48 hr then stored in plastic jars. Part of RH was crushed and passed through 0.5-mm stainless steel sieve then stored in plastic jars for subsequent experiments.

Preparation and characterization of rice husk biochar

To prepare the rice husk biochar (RHB), the oven-dried RH was put into aluminum sheet envelopes and was completely closed with making few small holes. Envelops were transferred to muffle furnace and heated to a temperature of 450 °C for 15 min. After cooling to ambient temperature, the product of RHB was crushed and sieved using 0.5-mm stainless steel sieve then stored in plastic jars. Elemental analysis (Si, P, K, Fe, Mn, Zn, Cd and Cu) of RH and RHB were carried out using dry ashing method according to Jones and Case (1990). Measurement of metals was conducted by ICP-OES Spectrometer Thermo Model ICAP 6000 Series,

Thermo Scientific, UK. Total organic carbon was determined using the dichromate oxidation method (Walkley-Black procedure, Schumacher, 2002). Total nitrogen in RH and RHB was determined using Kjeldahl methods in both digestion and distillation of samples according to Nelson and Sommers (1973).

Surface characterization and reactivity of Biochar

Surface area and FTIR measurement techniques were used to explore the surface properties of both RH and RHB. The surface area and pore volume of the RH and RHB was determined using N_2 sorption isotherms run on Beckman Coulter SA(TM) 3100 Surface Area and Pore Size Analyzer and the Brunauer-Emmett-Teller (BET) method was used to determine mesopore-enclosed surfaces. Fourier transform infrared (FTIR) spectra of the adsorbent were recorded in the range 400–4000 cm^{-1} using SHERMATZU infra red spectrophotometer; model FT/IR-5300, JASCO Corporation, Japan.

Adsorption Isotherm of Cd

In The present investigation, batch mode of operation was selected in order to measure the progress of Cd adsorption isotherm for intervals extended to 96 h. Four gm of RH or RHB ($\leq 500 \mu\text{m}$ particles) as adsorbents with 800 ml aqueous solution of adsorbate (cadmium chloride with concentration of 875.0 $\text{mg Cd}^{2+} \text{kg}^{-1}$ adsorbent in the presence of 0.01M KCl solution as background electrolyte) were continuously stirred at 400 rpm at temperature of 30 °C. At the completion of predetermined time intervals, the adsorbate and adsorbent were separated by filtration using 0.45 μm membrane filter (Gelman Science, MI, USA) and Cd^{2+} was measured in part of the supernatant by ICP-OES Spectrometer. The adsorbed Cd^{2+} was calculated by subtraction of remained Cd^{2+} in solution from the total added Cd^{2+} . In another part of supernatant, the concentration of dissolved organic carbon (DOC) was determined by wet digestion method according to EPA (2009).

Effect of RH and RHB Application on Cd Uptake by Wheat

Using complete randomized design (CRD), a greenhouse experiment was conducted. Two levels of RH or RHB (0 and 30 ton ha^{-1}) were thoroughly mixed with the top 15-cm soil in the pots. Each pot (25-cm diameter x 40-cm height and containing 25 kg soil) was fertilized with a basal dose of N, P and K at 40, 40 and 50 mg kg^{-1} , as ammonium nitrate, single super phosphate and potassium sulfate, respectively. Three rates of Cd^{2+} (0, 5.0 and 35.0 mg kg^{-1} soil) were added to soils, with the first irrigation water, in the form of CdCl_2 . Wheat cultivar (Sakha 104) seeds were sown in each pot, and the germinated seedlings were thinned to five plants per pot. After 5 and 10 weeks of growth, additional doses of N were added by a rate of 30 mg kg^{-1} soil each in the form of ammonium nitrate. At harvest,

the dry matter yield and yield parameters were recorded. Dried samples of wheat grains and straw were crushed and sieved on 0.5-mm sieves then were dry-ashed at 550 °C according to Jones and Case (1990). The digests were analyzed for Cd²⁺ using ICP-OES spectrometer. Cadmium uptake by wheat grains and straw were calculated. All data were statistically analyzed using Costat software (Costat, 1985).

RESULTS AND DISCUSSION

Properties of Rice Husk Biochar

Table (1) showed that charring the RH increased the nutrients content in biochar. Sharp increase in silicon and carbon was observed in RHB (about 2.8 and 1.31 folds, respectively, over than occurred in RH). Cadmium contents in RH and RHB were generally similar.

The results of specific surface area analysis demonstrated that the pyrolysis of RH at 450 °C for 15 minutes increased surface area from 5.54 m² g⁻¹ for RH to 56.07 m² g⁻¹ for biochar (Table 2). On the other hand, transforming the RH to RHB increased the total pore volume by about 2.73 times (from 0.0147cc g⁻¹ for RH to 0.0402 cc g⁻¹ for RHB). Similar results were obtained by Lataye *et al.* (2009) where heating of RH at 700 °C increased the SA to 52.29 m² g⁻¹. In another study, after burning out of RH at 700 °C for 6 h, SA was increased to 54.0 m² g⁻¹ (Della *et al.*, 2002). Specific surface area and pore volume are considered central values for the characterization of biochar. Both values depend on the type of pyrolysed biomass (feedstock) and the pyrolysis process used especially maximum temperature, residence time and particle size (Guerrero *et al.*, 2008 and Lehmann and Rondon, 2006). Therefore, the values of SA and pore volume of RHB should be specified by 450 °C, 15 minutes and 500 micron particle size.

Infrared spectroscopy provides information on the chemical structure and surface functional groups of the RH and RHB samples. The different groups in which silicon exists, e.g. siloxane Si-O-Si and silanol Si-OH, are best observed in IR spectra.

Figure (1) presents FTIR absorption spectra of raw feedstock (RH) and after pyrolysis (RHB). The IR spectra of rice husk gave typical bonds of Si-O-Si stretching (strong at 1035.7 for RH and 1091.63 cm⁻¹ and very strong at 794.62 cm⁻¹ for RHB) and bending vibrations (very strong at 457.1 cm⁻¹). The bands at 3392.55 and 2925.81 cm⁻¹ in RH spectrum and 3415.7 cm⁻¹ in RHB spectrum correspond to the O-H vibrations (Liou, 2004; Chaudhary and Jollands, 2004, Ibrahim *et al.*, 1980). It can be observed from Fig. 1 (spectrum of RHB) that pyrolyzed rice husks are characterized by very broad band extended from 3965.37 to about 2000 cm⁻¹. The O-H stretching mode of hexagonal groups and adsorbed water can be assigned to this band. The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds. The adsorption band observed at 2925 cm⁻¹ in RH spectrum was related to aliphatic C-H groups and the very small peak near 1710.74 cm⁻¹ in RHB spectrum was attributed to the C=O stretching vibrations of ketons, aldehydes, lactones or carboxyl groups. Further description of surface functional groups characterized both RH and RHB are illustrated in Table (3). The predominant absorbance peak at 1320 cm⁻¹ was due to stretching vibrations and the one at 457 cm⁻¹ was due to bending vibration of siloxane bonds (Si-O-Si). The peaks at 1035.7 cm⁻¹ in RH spectrum and 1091 and 794 cm⁻¹ in RHB spectrum are attributed to vibration modes of the Si-O network. After the pyrolysis of rice husk, the IR spectrum of the biochar obtained did not differ significantly from that of raw rice husks, except for the quite higher intensities of the bands at 1091 and 457 cm⁻¹. This can be explained with the decrease of organic matter content and its transformation into active carbon. In other words, FTIR emerged the importance of both organic and inorganic groups located on RH and RHB surfaces and the pyrolysis process imposes to more occurrences of inorganic (resistant) surface groups on biochar.

Table 1: Selected characteristics of rice husk (RH), rice husk biochar (RHB) and soil used in the study.

	Total carbon	Total SiO ₂	Total N	Total P	Total K	Total Fe	Total Mn	Total Zn	Total Cu	Total Cd
	%					mg kg ⁻¹				
RH	27.90	25.81	1.19	0.40	0.62	233.40	78.60	41.60	16.00	0.04
RHB	36.60	72.10	0.52	0.54	0.88	248.20	90.60	50.00	17.60	0.05
	EC, dSm ⁻¹	pH	OC, %	mineral N, mgkg ⁻¹	DTPA-extractable micronutrients, mgkg ⁻¹					
Soil	6.23	7.81	2.90	104.60	Fe	Mn	Zn	Cu	Cd	
					3.17	2.93	2.58	0.14	0.11	

Table 2: Specific surface area (SA) and total pore volume of rice husk and rice husk biochar.

Sample	BET surface area, m^2g^{-1}	Total pore volume, ccg^{-1}
RH	5.540	0.0147
RHB	56.069	0.0402

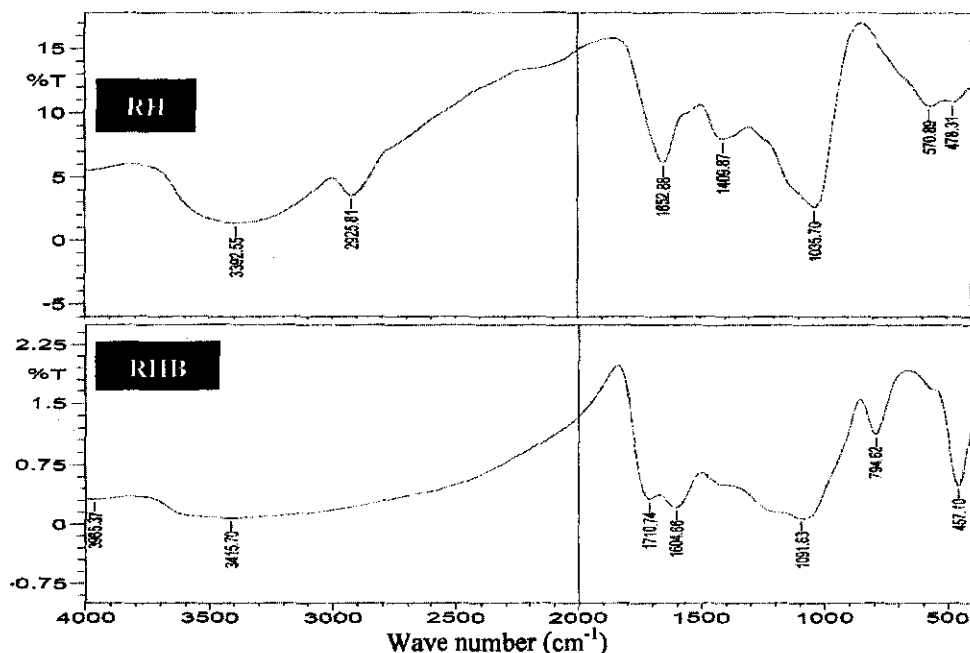
Adsorption isotherm of Cd

Rice husk biochar showed a great affinity to remove cadmium from aqueous solutions. Figure (2) characterizes the adsorption isotherm of Cd^{2+} by RH and RHB. The immobilization process was rapid, and completed in first 2 hours by RHB (97.28%) while only 63.2% of Cd^{2+} was removed in the same time by RH. After 96 h of retention reaction, 98.99 and 88.34% of Cd^{2+} in aqueous solutions were immobilized by RHB and RH, respectively. This behavior of Cd^{2+} sorption can be explained on the

basis of surface charge of the biosorbents. It has been reported that such biosorbents have net negative charge in the aqueous phase (Kapoor et al., 1999). With pH increase, from 5.65 after 2 h of reaction to 6.16 after 96 h, the net electronegativity of the biosorbent increased due to deprotonation of different functional groups on rice husk particles. The fast sorption of Cd^{2+} on surfaces of RHB depended totally on the functional groups resulted on surfaces as a result of charring process (pyrolysis), however, the change in pH was not observed during the retention reaction of Cd^{2+} on RHB (Fig. 3). Similar results were observed by Uchimiya *et al.* (2010) where Cd^{2+} in aqueous solutions was strongly immobilized on broiler manure biochar produced at different temperatures (350–700 °C). Also, there were similar results obtained from the study on lead adsorption by rice husk biochar by Liu and Zhang (2009).

Table 3: Expected functional groups corresponded the obtained frequencies of RH and RHB.

Rice Husk (RH)		Rice Husk Biochar (RHB)	
Frequency, (cm^{-1})	Functional group	Frequency, (cm^{-1})	Functional group
3392.55, m	OH (alcoholic)	3965.37, w	O-H
2925.81, s	OH (carboxylic), C-H aliphatic	3415.70, w	O-H (alcohols, phenols)
1652.88, s	C=C alkenes	1710.74, m	C=O stretch (ketones, saturated aliphatic)
1409.87, m	C-H alkenes in plane bend	1604.66, s	C=C alkene, aromatic ring
1035.70, s	Si-O-Si, C-O stretch (ethers)	1091.63, m	Si-O-Si, C-N stretch (aliphatic amines)
570.89, w	C-Cl (alkyl halides stretch)	794.62, s	Si-O network, C-H aromatic
478.31, w	Si-O-Si network	457.10, s	Si-O-Si

**Fig. 1: FTIR spectra of rice husk (RH) and rice husk biochar (RHB) obtained by slow pyrolysis at 450 °C.**

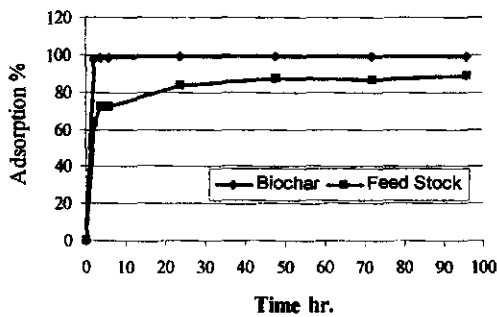


Fig. 2: Cadmium adsorption isotherm on rice husk and rice husk biochar.

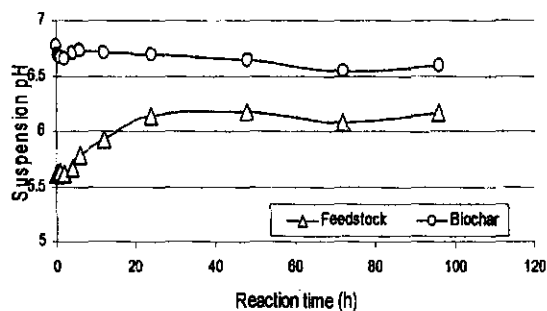


Fig. 3: Changes in suspension pH during the retention reactions of RH and RHB with cadmium.

Effect of biochar and Cd application on the yield of wheat and Cd uptake

The grain and straw yield of wheat was significantly affected by RH and RHB application in the presence of various concentrations of cadmium (Figure 4). In soils treated with 5 mg Cd kg⁻¹ soil, grain yield decreased 24.3, 13.2, and 7.75% in control, RH and RHB treatments, respectively, compared with the Cd²⁺-nontreated pots. Whereas in pots treated with 35 mg Cd kg⁻¹ soil, the corresponded relative reductions were 42.5, 31.87 and 12.45%. Straw yield also showed similar reductions, therefore, the results illustrated in Fig. 4 reflect the vulnerable effects of Cd on plant growth in the absence of RH or RHB. Nangay et al. (2010) found that application of Cd to soil by the rates 10 and 50 mg Cd²⁺ kg⁻¹ soil significantly reduced the dry matter yield of 10-weeks harvested maize shoot by 27%.

In the current study, addition of RH or RHB to soil eliminated the inhibition effect of Cd²⁺ on plant growth and improved the yield by different degrees depending on the characteristics of each amendment. Consequently, biochar showed a great

barrier against the harmful effect of added Cd²⁺ (Fig. 4). In the presence of Cd²⁺ by 35 mg kg⁻¹ soil, application of RHB maintained high grain and straw yield by about 1.65 and 1.58 fold than those obtained from biochar-nontreated pots. Cadmium content in wheat grains and straw demonstrated a high uptake rates corresponded to its high application rates (Fig. 5). In pots not treated with RH or RHB, addition of CdCl₂ by 5 and 35 mg Cd²⁺ kg⁻¹ soil increased Cd²⁺ uptake by plant up to 11.1 and 67.0 times in grain and 9.6 and 62.3 times in straw, respectively, more than those taken up from Cd-nontreated pots. Application of RHB to soil by the rate of 30 tone ha⁻¹ (12.6 ton per Feddan) sharply reduced Cd²⁺ uptake in all treatments. In the Cd²⁺-nontreated soils, RHB reduced Cd²⁺ content in grains and straw by 72.6 and 31.03%, respectively, comparing with 13.7 and 14.8% reductions were observed in RH-treated soils (Fig. 5). From the illustration of Fig. 5, it can be found that in the pots treated with 5 mg Cd²⁺, mixing of RHB with soil decreased Cd²⁺ uptake by plants by 83.6 and 77.5% in grains and straw, respectively; and in 35 mg Cd²⁺-treated one, the mixture reduced Cd²⁺ in plant

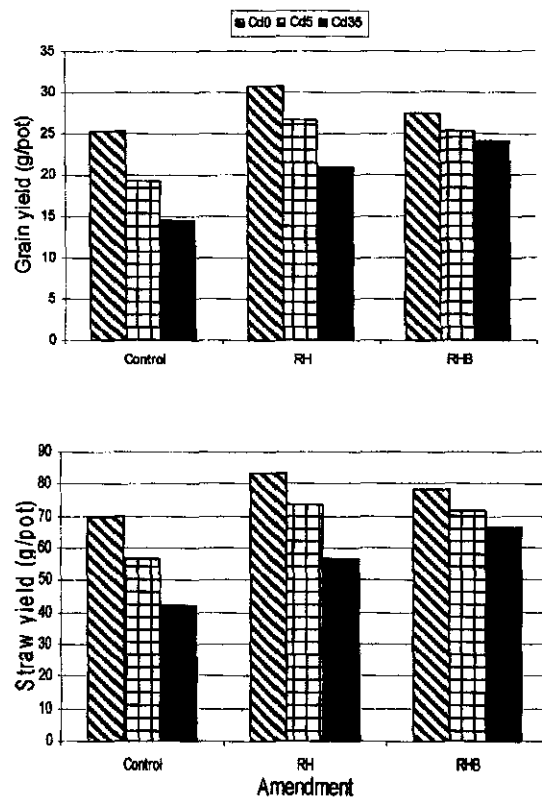


Fig. 4: Effect of RH and RHB application on the grain and straw yield of wheat plants grown on cadmium-treated soil (Cd0 = 0.0 mg Cd/kg⁻¹ soil, Cd5 = 5.0 mg Cd/kg⁻¹ soil and Cd35 = 35.0 mg Cd/kg⁻¹ soil).

by 91.8 and 88.9% in grains and straw, respectively. Rice husk application had a lesser effect in reduction of Cd²⁺ accumulation in plant (Fig. 5). These results are consistent with those reported by Namgay et al., (2010) where the biochar application significantly reduced Cd²⁺ accumulation in maize shoots. Also, in the field study conducted by Cui et al. (2011), the wheat straw biochar applied by rates 10, 20 and 40t ha⁻¹ significantly reduced Cd²⁺ concentration in rice grain by 16.8, 37.1 and 45.0%, relative to the control, respectively.

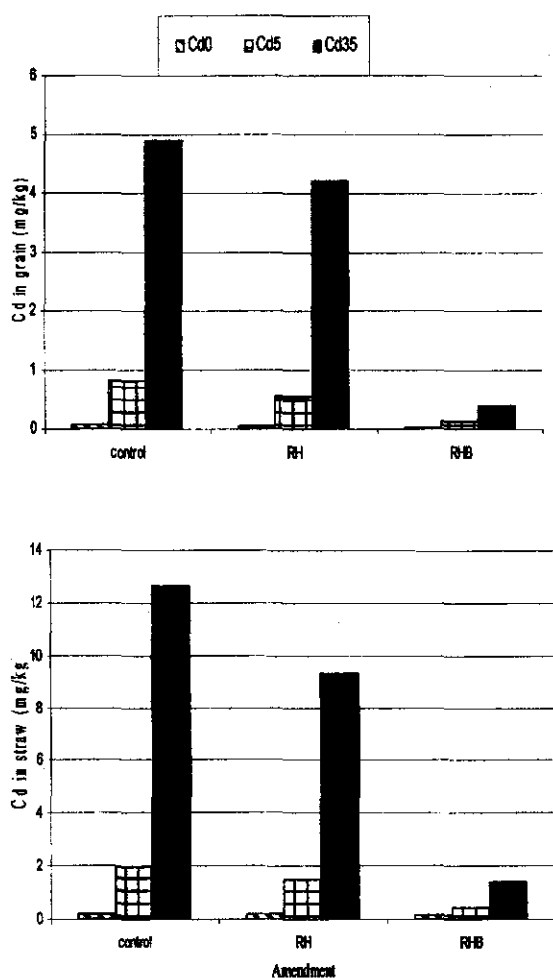


Fig. 5: Effect of RH and RHB application on cadmium content in grain and straw yield of wheat plants grown on cadmium treated soil (Cd0 = 0.0 mg/kg⁻¹, Cd5 = 5 mg Cd/kg⁻¹ and Cd35 = 35.0 mg Cd/kg⁻¹ soil).

The statistical analysis in Table (4) presents the independent and interaction effects of RH and RHB amendments application and Cd²⁺ addition on the averages of wheat grain and straw yield and their Cd²⁺ contents. Both amendments and Cd²⁺ application and their interaction were highly significant in their effects on the obtained results.

The relationship between adsorption isotherm of Cd²⁺ on RH and RHB and the efficiency of these amendments to eliminate Cd²⁺ accumulation in grains and straw of wheat plant interpreted that pyrolysis of rice husk gained it a recalcitrant nature and expanded its surface area and porosity and, subsequently, produce a more surface reactivity. Therefore, these properties well qualified the RHB to be introduced as a strong adsorbent material since it retained most amounts of added Cd²⁺ to soil. In contrast, application of RH as soil amendment and adsorbent material is a fragile situation and, with the progress of time, the biological degradation will govern the occurrence of RH in soil. In the current work, the concentration of released dissolved organic carbon (DOC), during the adsorption reaction, was used as an indicator for biodegradation of RH and RHB. Figure (6) revealed that DOC concentration from RH significantly increased with adsorption reaction time (until 96 h) as compared with those in RHB medium. Therefore, it is expected that, in contaminated soils with heavy metals such as Cd²⁺, application the recalcitrant crop residues (biochar) will be effective in immobilizing soil contaminants and reducing the hazardous effects of heavy metals.

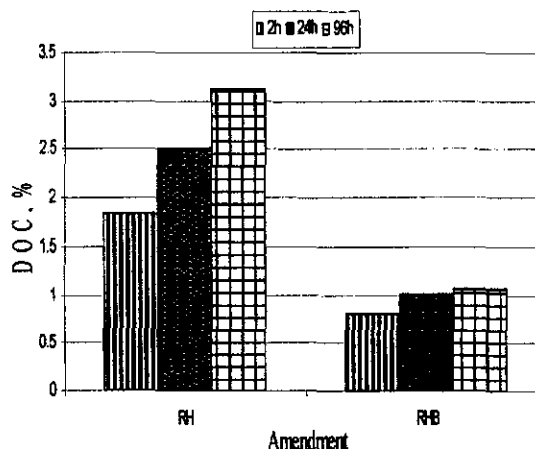


Fig. 6: The concentration of released dissolved organic carbon (DOC) during the adsorption reaction of Cd²⁺ on RH and RHB surfaces as influenced by time.

Table 4: Analysis of variance of the effects of RH and RHB soil amendments and cadmium addition on wheat yield and cadmium uptake.

Factors	Grain yield	Straw yield	Cd ²⁺ in grain	Cd ²⁺ in straw
Amendment				
control	19.706 b	56.284 b	1.926 a	5.039 a
RH	26.074 a	71.152 a	1.603 b	3.677 b
RHB	25.622 a	71.124 a	.186 c	0.606 c
LSD 0.05	0.988	2.412	0.127	0.421
Cd²⁺				
0	27.840 a	77.110 a	0.052 c	.181 c
5	23.723 b	67.380 b	0.499 b	1.286 b
35	19.838 c	54.071 c	3.163 a	7.909 a
LSD 0.05	0.988	2.412	0.127	0.421
Significance				
Amendment	***	***	***	***
Cd²⁺	***	***	***	***
interaction	***	**	***	***

CONCLUSION

This study has shown that transformation of rice husk to biochar by pyrolysis increased the surface area by 10 times, the total pore volume by 2.73 times and the active carbon percent. The development of carboxylic-C and aromatic-OH functional groups as well as inorganic silanole and siloxane groups on RHB surfaces during their carbonization possibly increased Cd²⁺ immobilization capacity of soil.

Rice husk biochar was more effective than RH in removing of Cd²⁺ from aqueous solutions. In addition, the concentrations of released DOC during the adsorption reaction of RH and RHB can be used to judge on the biodegradation and/or recalcitrant properties and subsequent on its persistence in reaction media.

The dramatic reduction in the concentration of Cd²⁺ in wheat grain and straw in biochar-amended soil can be attributed to the formation of stable metal-organic complexes or metal-inorganic complexes. Thus, the results of adsorption isotherm and greenhouse experiment can introduce the RHB as potentially strong adsorbent of heavy metal and can be successfully used in the remediation of heavy metals contaminated soils.

REFERENCES

- Ajmal, M., R.A.K. Rao, S. Anwar, J. Ahmad and R. Ahmad. 2003. Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater. *Bioresource Technol.* 86: 147-149.
- Andersson, A., 1992. Trace elements in agricultural soils-fluxes, balances and background values. Report 4077. Swedish Environmental Protection Agency.
- Beesley, L., E. Moreno-Jiménez and J.L. Gomez-Eyles. 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environ. Pollution.* 158 (6): 2282-2287.
- Bittell, J.E. and R.J. Miller. 1974. Lead, cadmium, and calcium selectivity coefficients on montmorillonite, illite, and kaolinite. *J. Environ. Quality.* 3: 250-253.
- Chaudhary, D.S. and M.C. Jollands. 2004. Characterization of rice hull ash, *J Appl Polym Sci* 93: 1-8.
- Chang, C.H., J. Lehmann and M.H. Engelhard. 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochim. Cosmochim. Acta* 72: 1598-1610.
- Costat. 1985. User's Manual Version 3, Cohort, Tusson, Arizona, USA.
- Cui, L., L. Li, A. Zhang, G. Pan, D. Bao and A. Chang. 2011. Biochar amendment greatly reduced Cd uptake in a contaminated paddy soil: A two-year field experiment. *Bioresources.* 6 (3): 2605-2618.
- Della, V.P., I. Kühn, and D. Hotza. 2002. Rice husk ash as an alternate source for active silica production. *Materials Letters,* 57 (4): 818-821.
- EPA. 2009. Determination of total organic carbon and specific UV absorbance at 254 nm in source water and drinking water. USEPA Document #: EPA/600/R-09/122

- Glaser B, J. Lehmann, W. Zech. 2002. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review. *Biology and Fertility of Soils* 35, 219-230.
- Grant C., W. Buckley, L. Bailey and F. Selles. 1998. Cadmium accumulation in crops, *Can. J. Plant Science*. 78: 1-17.
- Guerrero, M., M. Pilar Ruiz, Ángela Millera, María U. Alzueta and Rafael Bilbao. 2008. Characterization of Biomass Chars Formed under Different Devolatilization Conditions: Differences between Rice Husk and Eucalyptus. *Energy Fuels*. 22 (2): 1275-1284.
- Harris N.S. and G.J. Taylor G.J., 2001. Remobilization of cadmium in maturing shoots of near isogenic lines of durum wheat that differ in grain cadmium accumulation, *J. Exp. Bot.* 52 (360): 1473-1481.
- Ibrahim, D.M., S.A. El-Hemaly and F.M. Abdel-Kerim. 1980. Study of rice husk ash silica by infrared spectroscopy, *Thermochim Acta* 37: 307-314.
- Jones jr, J.B. and V.W. Case. 1990. Sampling, Handling and Analyzing Plant Tissue Samples. In: R.L. Westerman (ed) "Soil Testing and Plant Analysis" Third ed. SSSA Book Series no 3, Soil Science Society of America, USA.
- Kapoor, A., T. Viraraghavan and D.R. Cullimore. 1999. Removal of heavy metals using the fungus *Aspergillus niger*. *Biores. Technol.* 70: 95-104.
- Krishnani K., X. Meng, C. Christodoulatos and V.M. Boddu. 2008. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, *J. Hazard. Mater.*, 153, 1222-1234.
- Krishnani, K.K. and S. Ayyappan. 2006. Heavy metal remediation of water using plants and lignocellulosic agrowastes. *Rev. Environ. Contam. Toxicol.* 188: 59-84.
- Kumar, U. and M. Bandyopadhyay. 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresouce Technol.* 97: 104-109.
- Lataye, D.H., I.M. Mishra, I.D. Mall. 2009. Adsorption of α -picoline onto rice husk ash and granular activated carbon from aqueous solution: Equilibrium and thermodynamic study. *Chem. Engin. J.* 147: 139-149.
- Lehmann, J. and M. Rondon. 2006. Bio-Char Soil Management on Highly Weathered Soils in the Humid Tropics. In: N. T. Uphoff (ed.) "Biological Approaches to Sustainable Soil Systems". CRC Press.
- Lehmann J, Gaunt J, Rondon M 2006. Bio-char sequestration in terrestrial ecosystems - a review. *Mitigation and Adaptation Strategies for Global Change* 11, 403-427.
- Liang, B., J. Lehmann, D. Solomon, J. Kinyangi, J. Grossman, B. O'Neill, J.O. Skjemstad, J. Thies, F.J. Luizão, J. Petersen and E.G. Neves. 2006. Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Am. J.*, 70: 1719-1730.
- Liou, T.H. 2004. Evolution of chemistry and morphology during the carbonization and combustion of rice husk, *Carbon* 42: 785-794.
- Logan TJ, B.J. Lindsay, L.E. Goins and J.A. Ryan. 1997. Field assessment of sludge metal bioavailability to crops: sludge rate response. *J Environ Qual.* 26: 534-550.
- Lui, Z. and F.S. Zhang. 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *J. Hazardous Materials*. 167: 933-939.
- Merrington, G., L. Winder and I. Green. 1997. The bioavailability of Cd and Zn from soils amended with sewage sludge to winter wheat and subsequently to the grain aphid *Sitobion avenae*. *The Sci. Total Environ.* 205: 245-254
- Namgay, T., B. Singh and B.P. Singh. 2010. Plant availability of arsenic and cadmium as influenced by biochar application to soil. 19th World Congress of Soil Sci., Soil Solutions for a Changing World. 1-6 Aug. 2010. Brisbane, Australia.
- Nelson, D.W., and L.E. Sommers. 1973. Determination of total nitrogen in plant material. *Agron. J.* 65:109-112.
- Park, J.H., D. Lamb, P. Paneerselvama, G. Choppala, N. Bolan and J. W. Chung. 2011. Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *Journal of Hazardous Materials* 185: 549-574.
- Schumacher, B.A. 2002. Methods for the determination of total organic carbon (TOC). In soils and sediments. USEPA NV 89193-3478.
- Srivastava, V.C., I.D. Mall, I.M. Mishra. 2006. Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *J. Hazardous Materials B134*: 257-267.
- Uchimiya, M., I.M. Lima, K.T. Klasson, S.C. Chang, L. H. Wartelle and J. E. Rodgers. 2010. Immobilization of Heavy Metal Ions (Cu^{II} , Cd^{II} , Ni^{II} and Pb^{II}) by Broiler Litter-Derived Biochars in Water and Soil. *J. Agric. Food Chem.*, 58: 5538-5544.

المخلص العربي

تأثير بيوتشار غلاف حبة الأرز (السرسة) على تقييد الكادميوم بالأرض وامتصاصه بواسطة نبات القمح النامي فى أرض بحيرية

أمل حسن محمود^١، ماهر السيد صالح^٢، عبد السلام عباس عبد السلام^٣

^١معمل بحوث الأراضي للملحية والقنوية - معهد بحوث الأراضي والمياه والبيئة - مركز البحوث الزراعية- الإسكندرية

^٢قسم علوم الأراضي والمياه - كلية الزراعة - جامعة الإسكندرية

إنتاج البيوتشار من المخلفات النباتية باستخدام تقنية البيروليس يعتبر من الاتجاهات الحديثة لاستخدام تلك المخلفات كمادة ادمصاص مقاومة للتحلل الميكروبي فى امتصاص العناصر الثقيلة من مياه المخلفات وفي تقييد تلك العناصر فى الأراضي الملوثة بها. تم إنتاج بيوتشار غلاف حبة الأرز (السرسة) بتعرضها للتسخين على ٤٥٠ درجة مئوية فى المعمل. واستخدمت قياسات مثل المساحة السطحية والحجم الكلى للمسام ومنحنيات الأشعة تحت الحمراء لتوصيف خواص البيوتشار المنتج. أجريت تجارب الامصاص ثابت الحرارة لدراسة ادمصاص الكادميوم (بتركيز ٨٧٥ ملليجرام/كجم من مادة الإدمصاص) على سطح كل من السرسة والبيوتشار لفترات زمنية امتدت حتى ٩٦ ساعة لاختبار كفاءة البيوتشار فى إزالة الكادميوم من المياه الملوثة به. كما أجريت تجربة لزراعة القمح (صنف سخا ١٠٤) داخل الصوب وذلك لدراسة تأثير إضافة البيوتشار والسرسة (بمعدل ٣٠ طن/هكتار) على كل من محصول الحبوب والتبن وعلى تركيز الكادميوم الممتص بواسطة القمح النامي فى أرض ملوثة بالكادميوم (تركيزات صفر، ٥، ٣٥ ملليجرام/كجم أرض). أوضحت النتائج أن تحويل السرسة إلى بيوتشار أدى الى زيادة كل من المساحة السطحية والحجم الكلى للمسام ١٠ مرات و٢،٧٣ مرة، على التوالي. وأوضحت نتائج الإدمصاص أن البيوتشار أزال ٩٧،٣% من الكادميوم من المحلول خلال الساعتين الأولى من التفاعل بينما أزال السرسة ٦٣،٢% فقط. صاحب تفاعل إدمصاص الكادميوم ارتفاع فى قيم pH الوسط مع الزمن فقط فى حالة السرسة ولم يشاهد ذلك فى حالة البيوتشار مما يعكس حدوث تغيرات فى المجاميع السطحية على سطح السرسة وثبات تلك المجاميع على سطح البيوتشار. كذلك صاحب ادمصاص الكادميوم زيادة معنوية فى تركيزات الكربون العضوي الذائب بزيادة زمن التفاعل وذلك فى حالة السرسة فقط ولم تلاحظ فى حالة البيوتشار مما يشير إلى تعرض السرسة إلى التحلل الميكروبي ومن ثم انهيار هذا النظام من الإدمصاص مع الوقت كما يعكس ثبات هذا النظام فى حالة البيوتشار. أشارت نتائج تجارب الصوب إلى حدوث انخفاض شديد فى محصول الحبوب والتبن وارتفاع تركيزات الكادميوم الممتص فى الحبوب والتبن نتيجة زيادة تركيز الكادميوم المضاف للأرض. أدى خلط البيوتشار مع الأرض بالمعدل المذكور إلى تقليل الأثر الضار للكادميوم على المحصول من ناحية وإلى حدوث انخفاض شديد فى تركيزات الكادميوم الممتص فى كل من الحبوب والتبن.