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EFFECT OF RICE STRAW BIOCHAR AND COMPOST APPLICATION AT DIFFERENT RATIOS ON HEAVY METALS IMMOBILIZATION IN THE CANOLA PLANTS GROWN IN CONTAMINATED SOIL

E. K. Mahmoud(1)*, M. M. Ibrahim(1), Nehal Ali (2)
and Hanan M. Ali(1)

(1) Department of soil and water science, Faculty of agriculture, Tanta University, Egypt
(2) Department of Engineering Physics and Mathematics, Faculty of Engineering, Tanta University, Egypt
* Corresponding author email: esawy.rezk@agr.tanta.edu.eg
Tel No: +20403455584 Fax No: +20403455570
Postal address: Soil and water department, faculty of agriculture, University of Tanta, Egypt. P.O. Box: 31527 Tanta, Egypt.

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ABSTRACT: *Industrial activities can contribute to the heavy metal accumulation in soils, which could potentially threaten human health, agricultural crop productivity and the environment. This research was conducted to use metal uptake and spectroscopic analysis (X-Ray Diffraction (XRD), Energy Dispersive spectroscopy by X-rays (EDX) and Fourier Transmission Infrared Spectroscopy (FTIR) to evaluate the effect of application of both rice straw biochar and compost with different ratios on heavy metal immobilization in the canola plants grown in the contaminated soil. The results showed that the Cd, Pb, Ni and Zn uptake in the root and shoot of canola plants significantly decreased with the addition of rice straw compost (RC) and biochar (RB) to contaminated soil. The addition of 1% mixture of RC and RB gives the most effective immobilizing metals as 100% and 74.2%, reduction in Cd and Pb accumulation by canola shoots, respectively. The biochar and compost obtained from rice straw showed high carbon content, silica and a high absorption character. The use of spectroscopic analysis observed the precipitation, inner-sphere complex reaction and electrostatic attraction are the dominating mechanism for heavy metal immobilization with organic amendments. Our results indicate that the metal uptake is considered to be the effective tool to assess the efficiency of immobilizing agents on metal phyto-availability.*

Key words: *Rice straw biochar; Rice straw compost; Heavy metals; Spectroscopic analysis; Canola plants.*

INTRODUCTION

Heavy metal contamination due to geological and anthropogenic activities is a widespread environmental problem with serious consequences for human health and agricultural crop productivity. These activities include atmospheric deposition of emissions from industrial processes, mining, sewage sludge application, and use wastewater in irrigation (Alloway 1990 and Neilson and Rajakaruna 2014). Heavy metals cannot be destroyed biologically, are non degradable, and are toxic to living organisms (Nriagu 1991). Furthermore, some heavy metals are accumulated in plant tissue or grains and when transferred to the food chain may adversely affect their health (Kelly *et al.* 1996). Uptake of Cd by carrot roots was about five times more than the regulatory limits for men, eight times more for women, and 12 times more for children when it's grown in soils from Spelter,

WV, USA, contaminated with a variety of metals including lead (Pb), zinc (Zn), cadmium (Cd), and copper (Cu). From this result, carrot and lettuce grown in these soils have the potential to cause toxicological problems for men, women, and young children due to Cd and Zn accumulation (Roy and McDonald 2015). In a study carried out by EL- Shall (2010) on Kafer El- Zaiyat soils in Egypt. These soils received atmospheric emissions from the adjacent factories and irrigated from some polluted drains, the amounts of heavy metals in these soils were very high and reached more than the permissible limits. Abd El- Salam (1994) showed that in both soils surrounding Alexandria Factory for soap and El- Suif Electric Power Station; the soil pollution by heavy metals is dependent on the distance from the pollution source, type of pollutant, soil properties and the agronomic practices.

Soil remediation technologies of heavy metals such as soil solidification, excavation, land filling, and washing strategies can be an expensive and arduous task (Mulligan *et al.*, 2001 and Sruthy and Jayalekshmi 2014). As an alternative, in situ techniques such as immobilization of heavy metals can potentially be lower in cost and reduce the impact on the ecosystem than land filling, excavation and other soil remediation (Vangronsveld and Cunningham 1998). Heavy metals immobilization in contaminated soils can be remediated by biological, physical and chemical techniques (Bolan *et al.,* 2003). Heavy metal immobilization involves the addition of amendments to contaminated soils can reduce mobility and toxicity of metals through metal sorption and precipitation (Adriano *et al.,* 2004). Also, carbon-rich amendments such as compost (RC) and biochar (RB) have been used as a novel carbonaceous material and economically feasible technologies to adsorb metals in soil and water (Houben *et al.,* 2013a, b and Almaroai *et al.,* 2014). RB is produced by parolysis of organic wastes under low oxygen conditions. It is capable of improving chemical, biological, and physical properties in soils due to its high organic carbon content (Almaroai *et al.,* 2014). Incorporation of biochar into soil leads to increases in soil organic matter, soil fertility, and enhances plant growth (Houben *et al.,* 2013b and Mahmoud *et al.,* 2016). Green waste biochar application to spiked soils significantly reduced the phytoavailability of Pb, Cu, and Cd in Indian mustard (*Brassica juncea (L.) Czern*) and other plants (Park *et al.,* 2011). Orchard prune residue biochar application to contaminated soil significantly increased arsenic (As) concentrations in soil pore water, while shoot and root concentrations were significantly reduced compared to the control without biochar in a pot experiment. Moreover, concentrations in fruit were very low, indicating minimal toxicity and transfer risk (Hartley *et al.,* 2009). The application of biochar has been recommended as a sustainable means to promote the revegetation and the restoration of degraded lands (Beesley *et al.,* 2011 and Fellet *et al.,* 2011). The addition of rice straw compost to contaminated soil decreased Cd, Zn and Pb concentrations in the shoot and root of canola plants (Mahmoud 2011 and Mahmoud and Abd El-Kader 2014). Parka *et al.* (2011) found that, the ability of spending mushroom composts to decrease Pb, Cd and Zn accumulation in perennial rye-grass were related to the presence of phenolic and hydroxyl groups. Composts are rich in functional groups such as amino, carbonyl and hydroxyl groups were effective in heavy metal immobilization because of its ability to bind or complex metal (Basta *et al.,* 2005).

The adsorption mechanisms for heavy metals by biochar involved electrostatic attraction, precipitation on biochar and formation of complexes between metals and functional groups on biochar (Dong *et al.,* 2013 and Lu *et al.,* 2012). Heavy metals sorption by biochar or compost was mostly through the formation of surface complexes between these metals and –OH or –COOH groups (Tong *et al.,* 2011and Jiang *et al.,* 2012). Heavy metals sorption on the functional groups such as –COOH, phenolic –OH or alcoholic –OH groups may involve inner-sphere surface complexation and electrostatic attraction (Cao and Harris, 2010). Cao *et al.* (2011) observed by XRD analysis that dairy manure biochar contains high levels of available P, which may able to immobilize Pb in soils by forming insoluble hydroxypyromorphite ($Pb_5 (PO4)_3(OH)$). Cao and Harris (2010) found that the increasing of available P, Mg, and Ca of biochars is associated with high Pb stabilization in the form of carbonates, phosphates or oxides.

Canola (*Brassica napus*) is one of the most promising, hyper-accumulating plant species for heavy metals from contaminated soils (Gisbert *et al.,* 2006). Schmidt (2003) showed that corn (*Zea mays L.*), Indian mustard (*Brassica juncea*) or sunflower (*Helianthus annuus L.*) plants were high tolerance to heavy metals and therefore, can be recommended for planting in contaminated soils. Biochar and phytoremediation techniques have been used recently to soil remediation (Houben *et al.,* 2013b) using Brassica napus L. with Miscanthus biochar addition to multicontaminated soils (Fellet *et al.,* 2014). The application of biochar to metal-contaminated soils could thus serve two purposes: to improve the soil conditions thereby allowing energy biomass and biofuel production, and to sequester C by burying part of the produced biomass (Houben *et al.,* 2013)

The present study was conducted to use metal uptake by canola plants and spectroscopic analysis to evaluate the effect of application of both rice straw biochar and compost with different ratios on heavy metal immobilization from the contaminated soil.

MATERIALS AND METHODS

Basic of the soil studied

Fifteen composite soil samples after mixed were collected at a depth of 0 to 20 cm from agricultural farms of the Middle Nile Delta, at Kafer El- Zaiyat area (lat.30^0 40` N, 30$^0$ 43` E) El-Gharbia Governorate, Egypt. The soils of the studied area were classified as a *Vertic Torrifluvents*. The soil moisture regime of the studied area could be defined as *Torric* and soil temperature regime as *Thermic* according to EL- Shall (2010). The source of soil pollution in the studied area is mainly atmospheric emissions of the adjacent factories and irrigation from some polluted drains. These soils were contaminated with Cd, Pb, Ni, and Zn where the total concentrations exceed 10, 260, 350, and 300 mg kg^{-1} soil, respectively (EPA, 1993). Soil samples were dried in air and then crushed to pass through a 2-mm sieve. Chemical and physical analyses of the five composite soil samples were determined using the standard methods undertaken by Black *et al.* (1983) and Page (1982) and data are presented in (Table 1).

Biochar and compost production

The biochar (RB) used in this experiment was prepared from rice straw from a local producer using a batch pyrolysis facility at a final temperature (400 °C) with to 2 hours retention time. Biochar samples were ground and sieved < 0.5 mm, prior to be used and characterized. It is found that biochar product had high organic carbon of 62.5%. This value was characterized by electrical conductivity (EC) of 2.45 dS m^{-1} (1 biochar: 10 water), pH 8.2, total N 1.38%, total P 0.65 %, total K 1.18 % and cation exchange capacity (CEC) of 32.42 cmol kg^{-1} biochar.

Table (1): Chemical and Physical characteristics of studied soil.

Properties	Soil
pH	8.31
EC (dS m^{-1})	5. 47
Soluble ions (meq L^{-1})	
Ca^{++}	5.70
Mg^{++}	4.89
Na^{+}	39.00
K^{+}	0.10
Cl^{-}	31.25
HCO_3^{-}	10.20
SO_4^{--}	10.79
Exchangeable cations (c mol $_{(+)}$ kg $^{-1}$)	
Ca^{++}	12.20
Mg^{++}	4.03
Na^{+}	11.46
K^{+}	2.89
CEC	30.58
ESP (%)	37.47
NPK available (mg kg $^{-1}$)	
N	36.18
P	17.64
K	193.58
NPK total (%)	
N	0.98
P	0.198
K	0.20
O.M %	1.36
Particle size distribution	
Clay	24.99
Silt	41.23
Sand	33.78
Texture	Clay loam
Bulk density (g. cm $^{-3}$)	1.33
Total heavy metal (mg kg $^{-1}$)	
Pb	495
Cd	105
Zn	512
Ni	648

The compost (RC) used in this experiment was prepared from rice straw and animal wastes. Rice straw was mixed with animal wastes in turned piles to give a C/N ratio (30–35) as recommended for composting process. Composting piles were remained for 12 weeks after that produced compost. Its organic carbon ratio is 23.7%, and characterized by electrical conductivity (EC) of 4.36 dS m^{-1} (1 compost:10 water), pH 7.21, total of N 1.42 %, P 0.34 %, K 0.8 %, Ca^{++} 1.2%, and Mg^{++} 0.9% .

Set up of experiment

Canola (*Brassica napus*) was sown in plastic pots under greenhouse conditions in a completely randomized experimental design with five replicates. The treatments were untreated soil (CT) and soil treated with two rates of rice straw compost (RC) and rice straw biochar (RB), and RC+RB (1:1 wet weight ratio) applications. Soil was amended by mixing dry RC and RB with a mass fraction of 0.5 and 1.0 %. (w/w). Each plastic pot contained 4 kg soil from a composite soil sample after of air dried and passing through an 8 mm sieve to reflect natural soil conditions. The soil portions were uniformly mixed with the RC and RB, and packed in the plastic pots of 18 cm diameter and 15 cm height. Nitrogen fertilizer was added in two equal doses as after 20 and 45 days of planting NH_4NO_3 33.5% N at the rate of 143 kg ha^{-1} and a basal dose of phosphorus was applied as superphosphate 15% P_2O_5 at the rate of 357 kg ha^{-1}. The amount of irrigation water was measured by weighting the plastic pots to raise the moisture content to the field capacity of each treatment, with the addition to 10% as leaching requirement. Twenty days after planting, plants of each pots were thinned to three uniform plants per pot. Canola plant was harvested after 16 weeks from planting. Plants were washed and then dried at 65 °C for 72 h. The plant dry weight was recorded and the tissue ground to pass a 0.20-mm sieve prior to analysis.

Analysis of soil and amendments

The EC and pH were measured in the soil paste extract with a pH/conductivity meter using a 1:10 biochar or compost: water ratio after stirring for 1 h and. The cations (Na^+ Mg^{++}, Ca^{++}, K^+) and anions (HCO_3^- and Cl^-) were determined in soil paste extract as described by Rhoades (1954). Organic matter (OM) of soil was estimated by multiplying the OC value by Van Bemmelen of 1.724 based on the assumption that OM contains 58% OC (Nelson and Sommers, 1996). While, the organic matter of compost and biochar was determined by combustion method (Page *et al.,* 1982).

Analysis of total heavy metals

Total heavy metals concentration was measured by atomic absorption after wet digesting the air dried soil, compost and biochar digested in concentrated H_2SO_4 + H_2O_2 (Cotteine *et al. 1982*).

X-ray diffraction patterns of the samples of rice straw boichar (RB), rice straw compost (RC), and the soil treated with (RB+RC) at 1% were investigated using, (Defractometer APD 2000PRO) at 40 KV and 40 mA with Cu-Ka radiation source. Two grams of each sample were granulated for powder diffraction. Continuous scanning mode of 2 was conducted from 15 to 70 with interval of 2 second measurement an interval. The scattering was minimized using planer exposure.

The functional groups of the samples of rice straw boichar (RB), rice straw compost (RC), and the soil treated with (RB+RC) at 1% were examined by Fourier transmission infrared spectroscopy (FTIR) . These samples were mixed with KBr at a fixed ratio to form disks. FTIR was conducted in an atmosphere using

TENSOR 27- by Bruker. A spectrum (600-4000 cm-1) was collected with 4 cm^{-1} resolution.

The surface morphology of the biochar particles was studied using a scanning electron microscopy system JEOL (JSM-7610F FEG-SEM). Samples were first coated with a sputter coater with a conductive layer to minimize the charging. The characteristic X-rays were used to distinguish the element composition of the samples (using EDX, Energy Dispersive Spectroscopy by X-rays). The suitable detectors allow to analyze qualitatively and quantitatively the elemental composition of the spectra.

Statistical analysis

All treatments were conducted with three replicates. All of the data obtained were analyzed statistically using SAS software. Duncan's multiple range tests were used to compare the means of the treatments. Statistical significance level of P <0.05 was used in means comparison .

RESULTS AND DISCUSSION

I. Characters of soil amendments

a- Fourier Transmission Infra Red Spectroscopy (FTIR)

The FTIR spectrum of RB and RC shown in Fig. (1), contained absorption peaks represent many functional groups on their surface, which indicated potentially different capabilities for adsorption of heavy metals. The peaks at 756 cm^{-1} for RB and at 794 cm^{-1} for RC were assigned to C–H bending aromatic CH out-of-plane deformation (Wu *et al.,* 2012). Peak at 321 cm^{-1} is assigned to C–C–C deformation vibrations, appeared on the RB surface. Bands at 876 for RB and 878 cm^{-1} for RC were assigned to Al–OH-Fe and they represent stretching, res (Xu *et al.,* 2000). The peaks around 1100 cm^{-1} in the RB and RC were standing for out-of-plane bending of carbonates (Yuan *et al.,* 2011) or Si-O-Si, O-P-O, C–OH and C–C stretching, and the band around 1592 cm^{-1} to –COO− anti-symmetric stretching in RB (Yuan *et al.,* 2011) or aromatic C=C (Luo *et al.* 2011). The peaks at 1647 for RC and 1797 for RB indicated C=C stretching and C=O stretching, respectively. The bands at 2965 for RB and 2857 cm^{-1} for RC were assigned to –CH_2 and –CH_3 groups of long–chain aliphatic components, respectively (Uchimiya *et al.* 2010). The bands at 3418 and 3417 cm^{-1} were attributed to the stretching vibrations of hydrogen-bonded hydroxyl groups of BR and CR, respectively (Keiluweit *et al.,* 2010 and Chen *et al.,* 2008). BR, aromatic C=C ring stretching was observed at 1433 cm^{-1}. The sharp peak at 1090 cm^{-1} in RC was assigned to C-O stretching of polysaccharides or polysaccharide-like substances. This peak decreased at 1086 for RB, which indicated that polysaccharide was destructed with pyrolysis of rice straw compost. The peaks assigned to oxygenate and alkyl function groups decreased in the biochar while, the aromaticties increased (Harvey *et al.* 2011). Comparison of the FTIR spectrum of metal contaminated soil with FTIR spectrum of metal contaminated soil amended with RC+RB at 0.5% and 1.0% (Figure 2) shows a shit of Si-O stretching vibrations band at 1033 cm^{-1} to higher wave number at 526 cm^{-1} as a result of increasing Si content in the treatment owing to compost and biochar of rice straw addition. Also bands at 1653, 1435, 1033 and 792cm^{-1} were shifted to the higher wave numbers after metal contaminated soil amended with RC+RB at 1.0%. In the same figure new peaks at 2979-1796 cm^{-1} appeared in soil treated with RC+RB at 1.0% that is not found in the contaminated soil, which could be assigned to C=C in-line deformation vibration or carbon dioxide. The results indicated that Cd, Zn and Pb were adsorbed through the coordination

Fig 1

Fig 2

of metal electron to C=C (π-electron) bond of compost and biochar, which resulted in the immobilization of heavy metals in soil.

The oxygen-containing functional groups have been reported that play important roles in the capacity of organic sorbents in the adsorption of heavy metals (Chen *et al.* 2008). The main mechanisms affecting adsorption of heavy metals are most probably an electrostatic attraction and complexation. Electrostatic attraction occurs between the compost and biochar surfaces and heavy metals present in the contaminated soil. Biochar and compost of rice straw also contain surface functional groups (e.g. carboxylate, hydroxyl, P-O, Si-O) as shown in the respective FTIR section. These functional groups may interact with heavy metal ions and form surface complexes on biochar and compost (Liang *et al.,* 2006; Tong *et al.* 2011 and Xu *et al.* 2013). Han *et al.* (2013) reported that the removal of Cd^{2+} from aqueous solution by biochar of rice straw may be attributed to the formation of surface complexes between Cd and carboxylic-C and aromatic OH groups. These suggestions were confirmed as shown in the results of FTIR where in the soil treated with (RC+RB) at 1.0%, the contents of O, Si, and C were high. In the same sample, Al and Fe were presented in lesser quantities whereas K, Mg, P, Ca, and S show showed the lowest content.

b- Scanning Electron Microscopy system (SEM)

Figure (3) shows the SEM images of the soil treated with biochar and compost with two different magnification ratios to visualize the morphology of the surface and to show the homogeneous distribution of the additives in the soil. As shown in the images the surface seems to be comparatively rough and without cracks. Some beneficial porous texture is also observed due to thermal treatment in the biochar manufacturing process. The pores increase the capabilities of heavy metals adsorption (Jiang *et al.,* 2012a).

c-Energy Dispersive Spectroscopy by X-ray (EDX)

EDX spectrum of the control and the soil treated with RB+RC are shown in (Fig. 4). In the soil treated with (RC+RB) at 1.0%, elements as O, Si, and C have high content. In the same sample, Al and Fe have lesser quantities whereas K, Mg, P, Ca, and S have the lowest content. EDX has shown the dominant elements to be C, O, and Si whose percentage compositions are 41.19, 21.99, and 11.35%, respectively. This analysis indicated that the mineral composition in the study areas was silica (SiO_2), alumina (Al_2O_3), and iron (III) oxide (FeO_3). According to the previous studies, the presence of P, Si, Al, and O in soil may be associated with the immobilization of Pb (Ahmad *et al.,* 2012a and Moon *et al.,* 2013). This fits well with the noticeable reduction in the content percentage of the Cd and Pb elements as shown in (Fig. 4) where the Cd is reduced by 35%, while Pb is reduced by 82%.

d- X-Ray Diffraction (XRD)

X-ray diffraction pattern of the samples of rice straw biochar (RB), rice straw compost (RC), and the soil treated with RB+RC are shown in (Fig. 5). The crystalline structure of the three samples is observed from the sharp peaks. The phase identity of the soil treated with RB+RC confirms the homogeneous mixing and show a dominant crystals form of quartz (SiO_2), and calcite ($CaCO_3$) which existence may relate to the alkalinity of the rice straw products. Also the presence of sylvite (KCl), struvite ($KMgPO_4.6H_2O$), and whitelokite Ca_9 (MgFe) $(PO_4)6PO_3OH$ were confirmed.

Fig 3

Fig 4

Fig 5

Some organic components were observed at lower diffraction angles; as crystalline cellulose and at some extent of such degrees the development of aromatic order in the carbonized samples was existed. Moreover, the crystalline peaks reveal the presence of Cd composites as cadmium sulfide (CdS) and cadmium carbonate ($CdCO_3$) as well as Pb composites in the form of anglesite ($PbCO_3$), cerussite ($PbSO_4$) and hydroxypyromorphite ($Pb_5 (PO_4)_3(OH)$) in the soil treated with biochar and compost.

II. Dry weight of canola plants

Application of compost, biochar individually and incommbination had a significant effect on dry weight of canola plants (Table 2). Dry weight of canola plants was increased by RC and RB, although differences between the 0.5% and 1.0% rate were not statistically significant. The additive ratio of 0.5% compost +0.5% biochar gives the highest increase in the dry weight. The application of compost or biochar improved soil chemical and physical properties, which together were reflected on the dry weight and this effect was increased when compost was combined with biochar. Compost and biochar provide both NPK and other nutrients for growing canola plants (Asagi *et al.,* 2007).

III. Metal Phytovailability

Lead (Pb) and cadmium (Cd) uptake (mg/kg) by canola roots significantly decreased with biochar and compost mixtures addition at percentage of 1% (Table 2), Also, Cd and Pb of biochar and compost uptake by canola roots decreased with increasing addition rates of biochar and compost , where Pb uptake of the roots decreased by 15.7 and 22.4 % for RB, and by 30.8 and 42.9 % for RC with addition ratios of 0.5 % and 1.0 %, respectively, compared to the control (Table 2). Similar results were obtained by Zheng *et al.* (2017) who found that the addition of rice straw biochar reduced uptake of Cd in lettuce shoots in the polluted soils. Ni and Zn uptake in the root of canola plants varied between the treatments, to reach its lowest values with the addition of biochar and compost mixtures. Treatments of RB or RC, uptake of Zn and Ni was not significantly influenced. As compared to control treatment, reduction of Ni and Zn uptake of the canola roots were significantly enhanced with the addition ratio of 1.0% of (RC+ RB) treatment. However, no significant decreases were obtained in Ni and Zn uptake of the canola roots following the application of RC and RB at 0.5% (Table 2). Ni uptake of the roots decreased by 8.6 and 30.1% for RB, and 6.9 and 11.2% for RC by 0.5 and 1.0 % of applications, respectively, compared to the control.

The treatments of RC, RB and their mixtures show remarkable reduction effect of Cd and Pb uptake by canola shoots (Table 2), this effect increases with the increase of application. Reduction in Pb accumulation by canola shoots was 46.5 and 48.4% for rice straw compost, and 15.5 and 36.2% for rice straw biochar at 0.5 and 1.0% addition, respectively. Similar results agree with Lu *et al.* (2014), who found that the application of rice straw biochar reduced the concentration of Cd, Pb and Zn in the shoots of *Sedum plumbizincicola* plant growth in a sandy loam paddy soil naturally co-contaminated with Cd, Cu, Pb and Zn.

The results showed that, the addition of 1% mixture of RC and RB gives the most effective immobilizing metals as 100% and 74.2%, reduction in Cd and Pb accumulation by canola shoots, respectively (Table 2).

Table (2): Effect of compost and biochar on heavy metals uptake (mgkg^{-1}) in root and shoot canola plants

Treatments	Dry weight g pots^{-1}	Shoots				Roots			
		Ni	Zn	Cd	Pb	Ni	Zn	Cd	Pb
CT	5.35 ^{c}	132.0 ^{a}	232.0 ^{a}	3.85 ^{b}	177.5 ^{a}	62.5 ^{a}	237.33^{a}	41.83 ^{a}	197.5 ^{a}
RB 0.5%	6.69 ^{abc}	130.0 ^{a}	229.53^{a}	4.46 ^{ab}	113.3 ^{b}	57.1 ^{a}	233.5 ^{a}	25.16 ^{b}	167.0 ^{b}
RB 1.0%	5.54 ^{bc}	120.53 ^{b}	219.0 ^{b}	4.06 ^{b}	150.0 ^{a}	43.67^{b}	233 ^{ab}	18.0 ^{bc}	153.33^{bc}
RC 0.5%	8.01 ^{a}	116.35^{bc}	228.5^{ab}	4.60 ^{ab}	95.01 ^{b}	58.16 ^{a}	232.17^{ab}	14.83^{c}	136.66^{cd}
RC 1.0 %	7.51^{ab}	111.0 ^{c}	223.5 ^{ab}	4.35 ^{ab}	91.66 ^{b}	55.5 ^{a}	230.5 ^{ab}	18.5 ^{bc}	112.67^{d}
RC +RB 0.5%	6.85 ^{abc}	69.0 ^{d}	223.5 ^{ab}	5.40 ^{a}	85.0 ^{b}	34.5 ^{b}	238.17 ^{a}	12.48 ^{c}	151.66^{bc}
RC+RB 1.0%	8.38 ^{a}	42.67 ^{e}	228.5 ^{ab}	3.89 ^{b}	45.73 ^{c}	20.25 ^{c}	224 ^{b}	11.5 ^{c}	115.0 ^{d}
L.SD 0.05	0.23	7.082	10.36	1.25	30.30	12.32	9.44	11.28	25.45

Heavy metal uptake by canola plants was decreased by the application of RB, RC and the mixtures of RB and RC as compared with the untreated soil. The clear interaction between the RB and RC enhances heavy metal immobilization. Mahmoud (2011) found that the reduction of Cd, Pb and Zn uptake in the root and shoot of canola plants with the addition of rice straw compost to contaminated soil. The organic matter was the most effective for heavy metal immobilization by surface complexion and adsorption. The decrease in the phytoavailability of metals in the presence of organic amendments is often attributed to the increased complexation of the metal by organic constituents (Adriano 2001and Bolan *et al.,* 2003). Addition of compost to contaminated soils has been used for many centuries to enhance revegetation, improve soil fertility, and decrease the plant availability of toxic metals (de Souza *et al.,* 2013). The addition of organic amendments to soils can decrease the heavy metal bioavailability by transforming them from bioavailable forms to the fractions associated with OM or metal oxides or carbonates (Walker *et al.,* 2004).

CONCLUSION

The results of this study have confirmed the ability of RB when used alone or mixed with RC to decrease the heavy metals uptake by canola plants grown in the contaminated soils. The soil treated with mixtures of RB + RC gave the highest canola growth. The addition of the mixtures of RB + RC resulted in more pronounced immobilize heavy metals as compared with RB and RC only. Therefore, it is proposed that a RB + RC application to contaminated soils might be a promising method for remediation of heavy metals contaminated soils. The use of spectroscopic analysis observed the precipitation, inner-sphere complex reaction and electrostatic attraction are the dominating mechanism for heavy

metals immobilization with organic amendments.

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تأثير إضافة كلا من البيوشار والكمبوست المصنوع من قش الأرز بنسب مختلفة على تثبيت المعادن الثقيلة في التربة الملوثة المنزرعة بها نبات الكانولا.

عيسوى قاسم محمود(١) ، محمود محمد محمد إبراهيم(١) ، نهال على (٢) ، حنان محمد على(١)

(١) قسم علوم الأراضى والمياه – كليه الزراعة – جامعة طنطا.
(٢) قسم الفيزيقا و الرياضيات الهندسية – كلية الهندسة – جامعة طنطا.

الملخص

تساهم الأنشطة الصناعية في تراكم المعادن الثقيلة في التربة ، والتي يمكن أن تهدد صحة الإنسان وإنتاجية المحاصيل الزراعية والبيئة. وأجري هذا البحث لمعرفة مدى امتصاص المعادن والتحليل الطيفي بواسطة أشعة أكس (XRD)، والتحليل الطيفي المتشتت للطاقة بواسطة الأشعة السينية (EDX) ، والتحليل الطيفي بالأشعة تحت الحمراء (FTIR) لتقييم تأثير كل من البيوشار والكمبوست من قش الأرز بنسب مختلفة على تثبيت المعادن الثقيلة في تربة ملوثة منزرع بها نبات الكانولا . وأظهرت النتائج أن تركيزات الكادميوم والرصاص والنيكل والزنك في الجذور والأوراق فى نبات الكانولا إنخفضت بشكل ملحوظ مع إضافة الكمبوست والبيوشار وكذلك إضافة خليط بنسبة ١٪ من الكمبوست والبيوشار أعطى أكثر تأثيراً معنوياً لخفض الكادميوم بنسبة ١٠٠٪ والرصاص بنسبة ٧٤.٢٪ مما أدى ذلك الى خفض تراكم الكادميوم والرصاص فى أوراق الكانولا .وأظهرت النتائج أن البيوشار والكمبوست المصنوع من قش الأرزيحتوى على نسبة عالية من الكربون والسيليكا مما يدل ذلك على قدرته العالية على امتصاصه للمعادن الثقيلة . وأن ألية تثبيت المعادن الثقيلة مع المحسنات العضوية هى الترسيب و inner–sphere complex reaction, electrostatic attraction .

وأتضح من ذلك أن تثبيت المعادن الثقيلة فى التربة بواسطة المحسنات العضوية من الطرق الحيوية والفعالة فى معالجة الأراضى الملوثة .

أسماء السادة المحكمين

أ.د/ سناء عبدالمنعم السيد عثمـــان   معهد بحوث الأراضى والمياه والبيئة
أ.د/ الحسينى عبدالغفار أبو حسين   كلية الزراعة – جامعة المنوفية

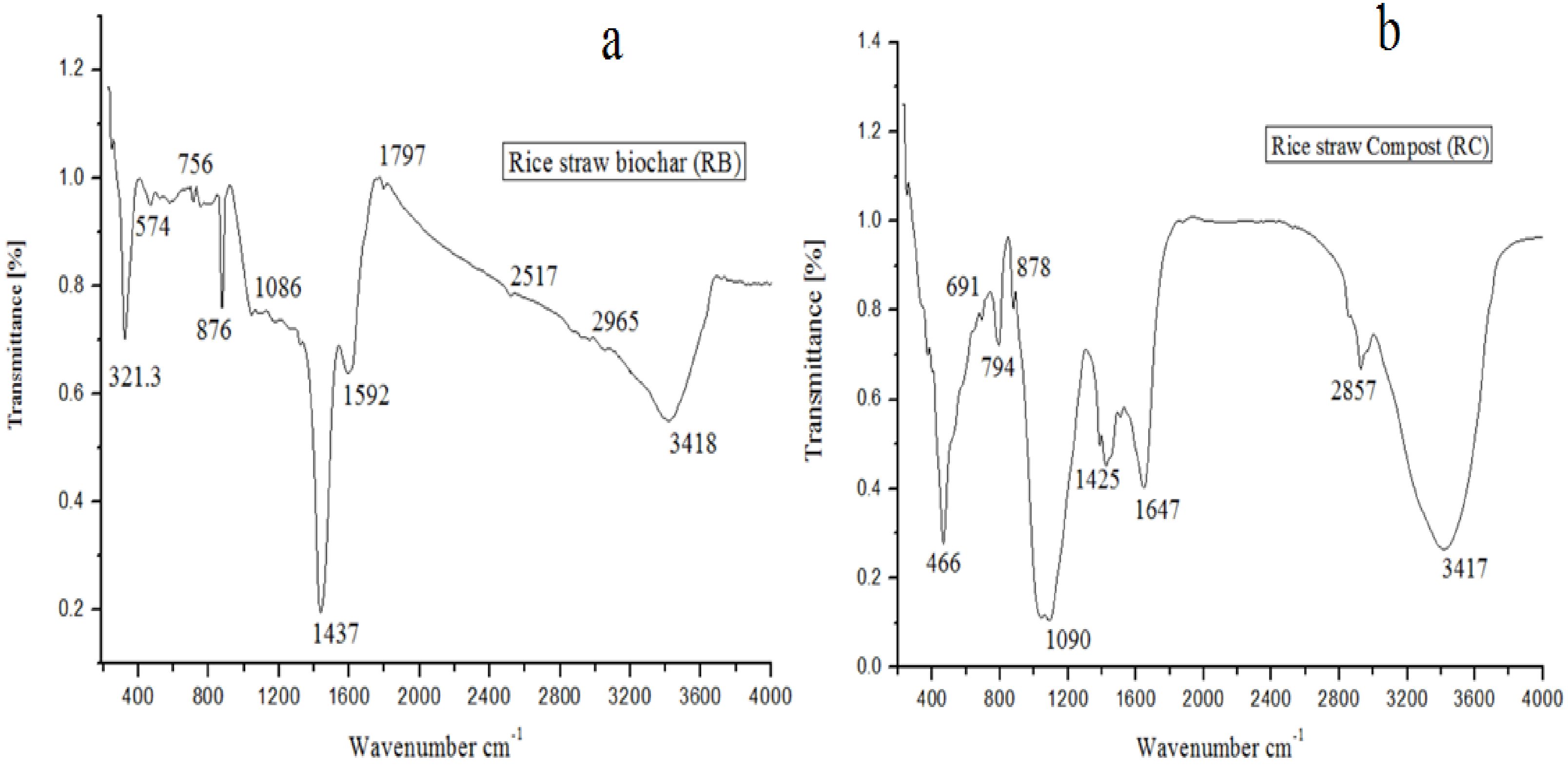


Figure (1): The FTIR spectrum of the rice straw biochar (RB) and rice straw compost (RC).

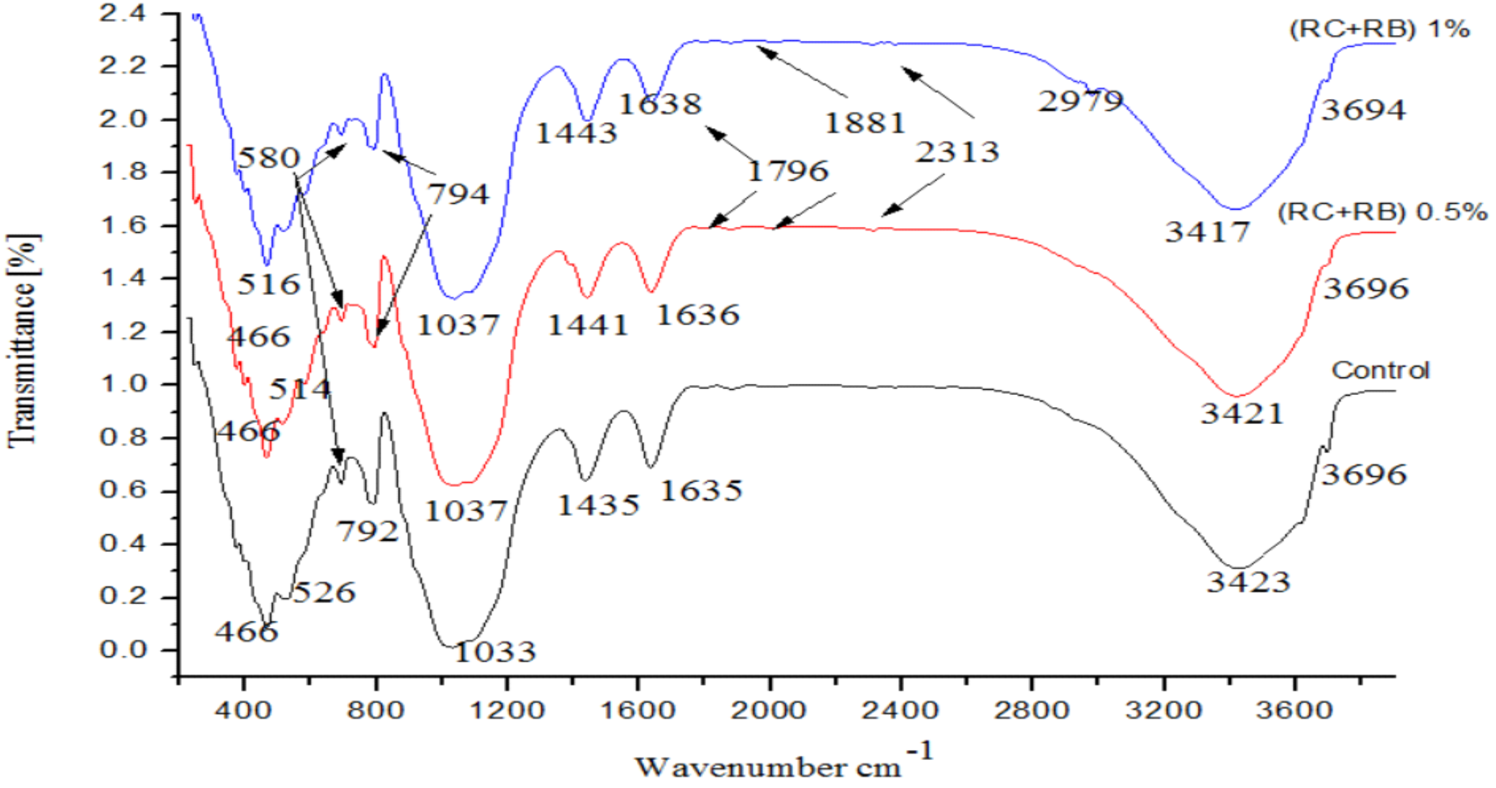
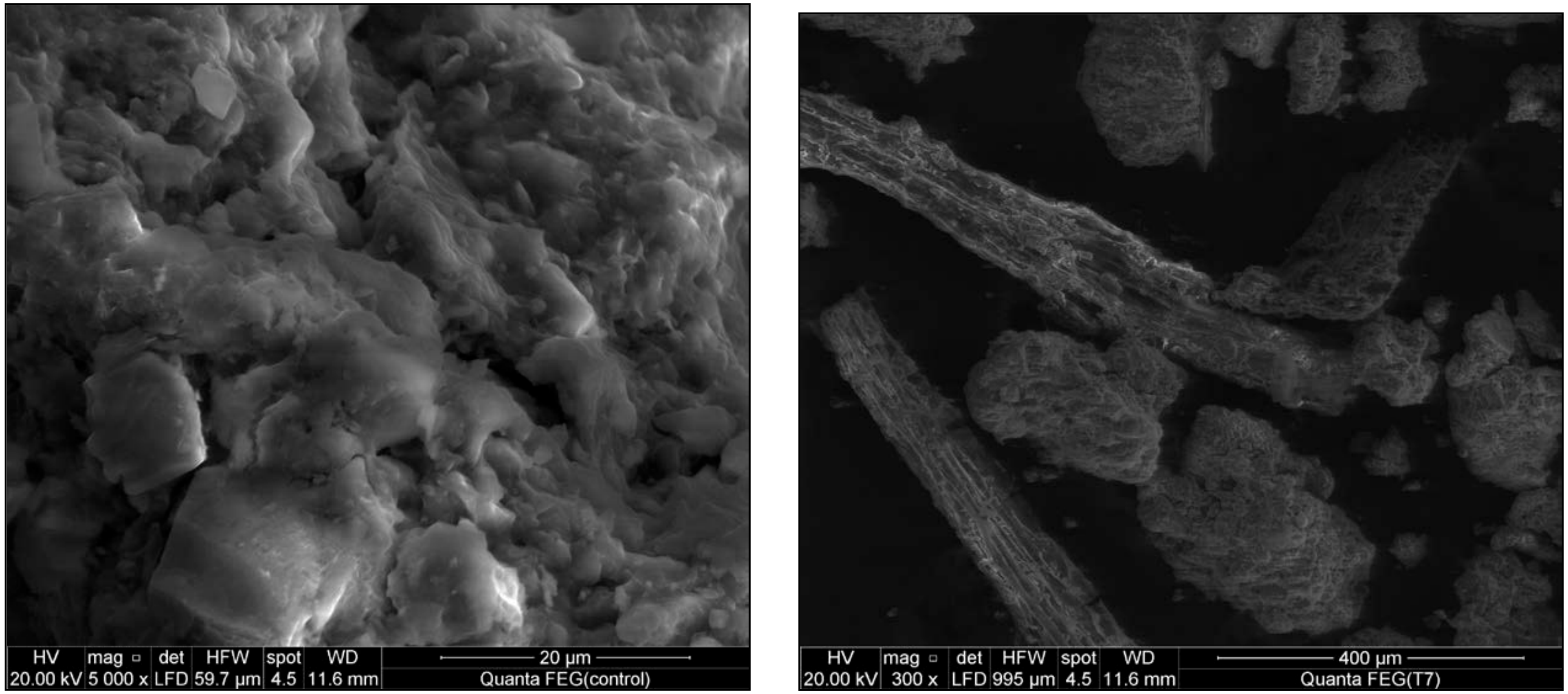


Figure (2): The FTIR spectrum of the control and the treated soil with RB+RC at 0.5% and 1.0% .



(a) **(b)**

Figure (3): SEM images of the control (a) and soil treated with biochar and compost at 01% (b).

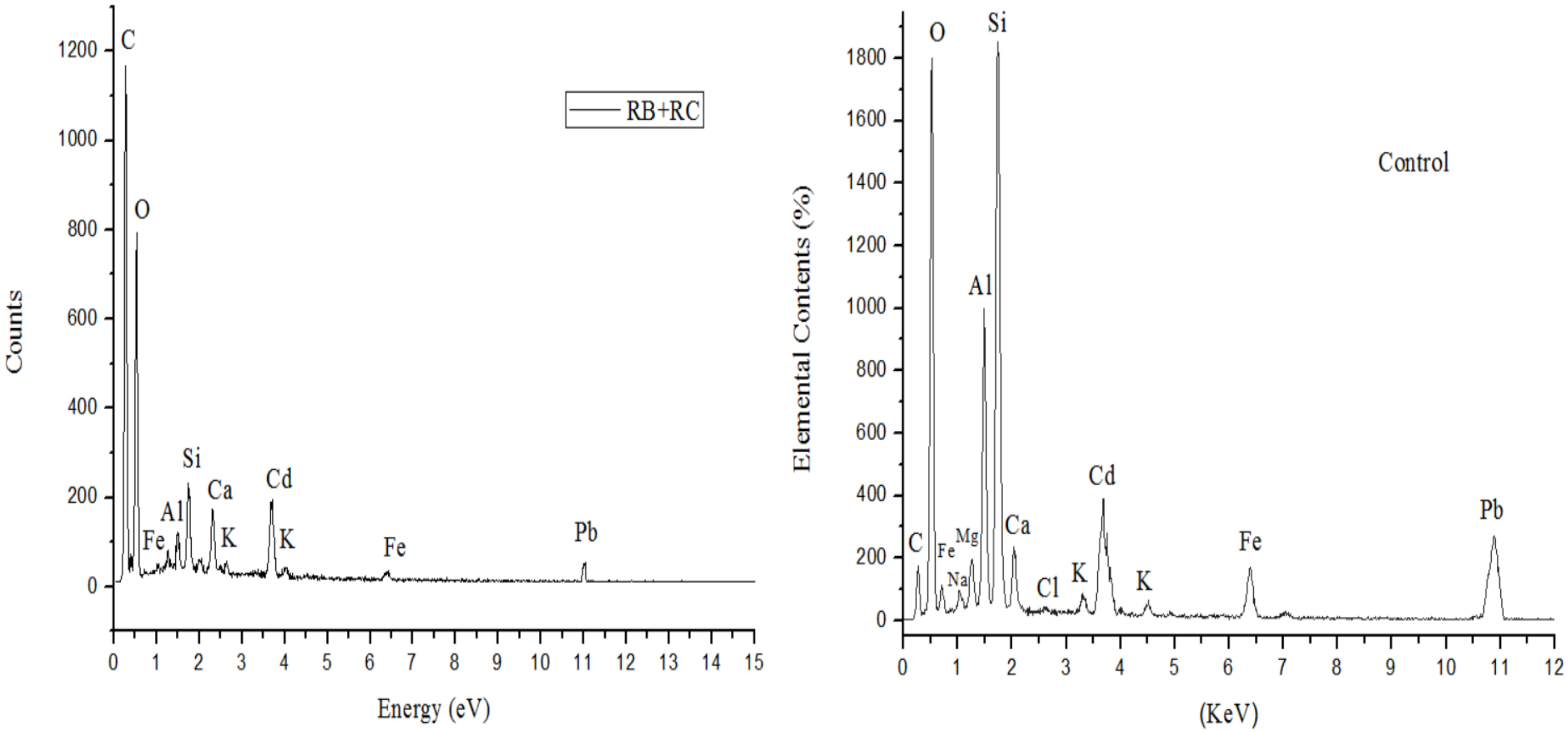


Figure (4): EDX spectrum of the control and the soil treated with RB+RC.

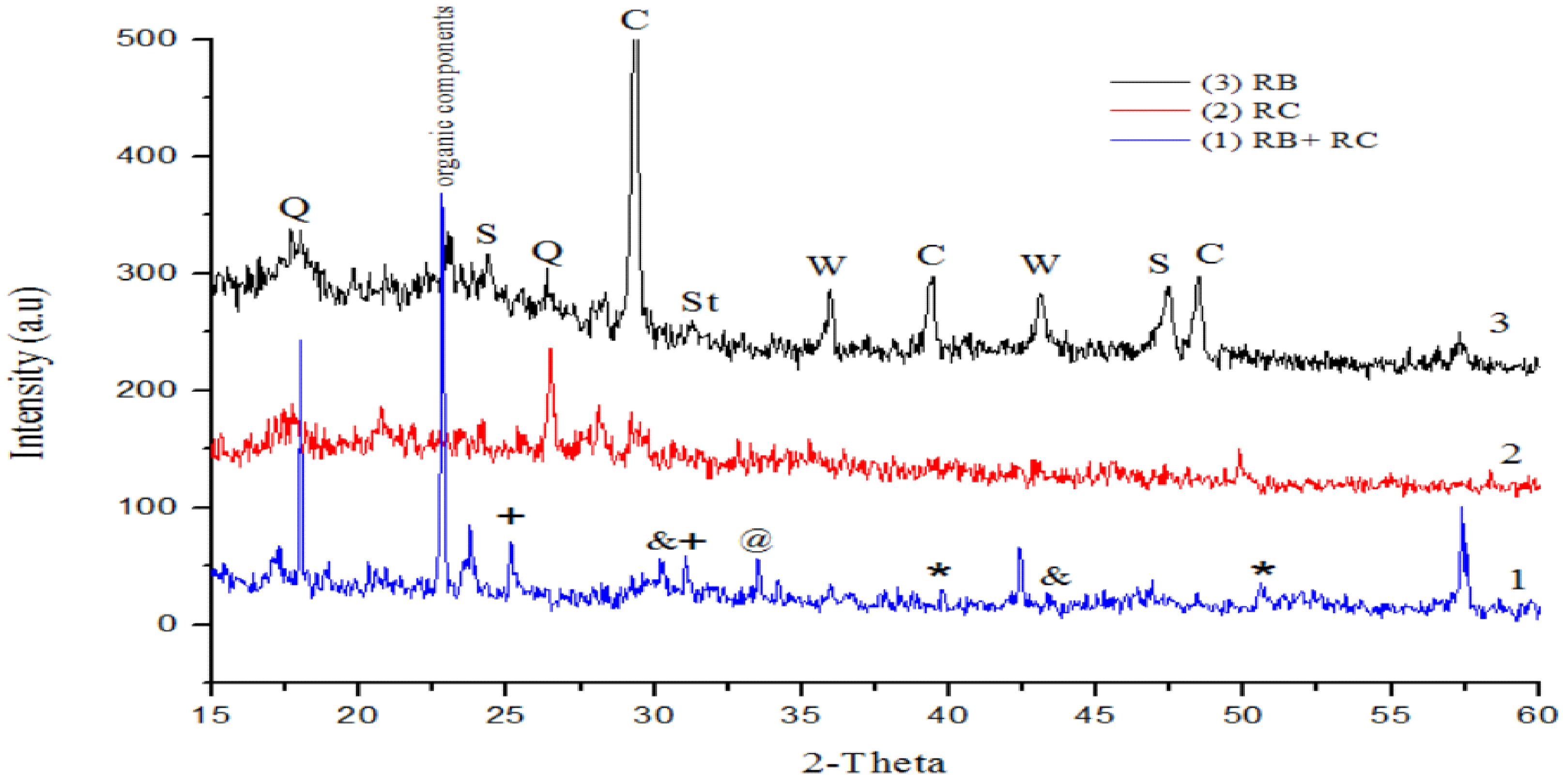


Figure (5) : X-Ray pattern of rice straw biochar (RB), rice straw compost (RC), and th treated soil with RB+RC (denoted as Q is Quartz; C is Calcite; S is Sylvite; W is whitelokite; St is Struvite; * is CdS; & is $Pb_5(PO_4)_3OH$; @ is $PbSO_4$; + is $PbCO_3$) .