



Original article

Pyrolytic and hydrothermal carbonization of date palm leaflets: Characteristics and ecotoxicological effects on seed germination of lettuce

Mohammad I. Al-Wabel^{a,*}, Muhammad Imran Rafique^a, Mahtab Ahmad^{a,b}, Munir Ahmad^a, Abid Hussain^a, Adel R.A. Usman^{a,c}

^a Soil Sciences Department, College of Food and Agricultural Sciences, King Saud University, P.O. Box 2460, Riyadh 11451, Saudi Arabia

^b Department of Environmental Sciences, Faculty of Biological Sciences, Quaid-I-Azam University, Islamabad 45320, Pakistan

^c Department of Soils and Water, Faculty of Agriculture, Assiut University, Assiut 71526, Egypt



ARTICLE INFO

Article history:

Received 21 August 2017

Revised 13 May 2018

Accepted 14 May 2018

Available online 26 May 2018

Keywords:

Biochar

Hydrochar thermal treatment

Polyaromatic hydrocarbons

Ecotoxicity

ABSTRACT

Biochar has vital importance as soil additives due to its characteristics, which are responsible for alleviating environmental problems and climate change. These additives should be evaluated to understand their physico-chemical properties and their ecotoxicological effects on plant growth. Therefore, this study aimed to (i) distinguish the properties of biochar produced from date palm and its derivative hydrochar, and (ii) investigate their ecotoxicological effects. Specifically, the biochar and hydrochar were produced from date palm leaflets by pyrolysis and hydrothermal carbonization, respectively. The produced chars were evaluated for their characteristics before and after water washing, and for their ecotoxicological effects on seed germination of lettuce (*Lactuca sativa* L.). The results show that water washing lowered biochar's pH and increased hydrochar's pH. Moreover, water washing of hydrochar caused a significant reduction in the total content of essential elements such as Ca, Mg, Mn, and Zn. Lettuce germination was significantly inhibited to 20% by hydrochar, whereas biochar enhanced lettuce growth by increasing shoot length (by 51%) and dry biomass (by 114%). Hydrochar toxicity was correlated ($R > 0.95$ at $p = 0.05$) with high contents of total polyaromatic hydrocarbons (98.8 mg kg^{-1}). Pre-treatment and assessment of hydrochar should be taken into account prior to application as a soil amendment.

© 2018 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Thermal carbonization of biomass is an expedient way of converting waste into valuable products of char, syngas, and bio-oil. It is considered as an environment-friendly technique of recycling waste biomass and generating energy. The open-air or uncontrolled burning of biomass creates serious environmental and health hazards by emitting obnoxious smoke, soot and greenhouse gases (Conesa et al., 2009). Hence, biomass combustion under

controlled conditions offers safe and effective treatment technology, also providing profitable byproducts.

Pyrolysis is one of the most favorable processes of controlled biomass carbonization via thermochemical decomposition at 200–900 °C temperature under no or limited oxygen (Demirbas and Arin, 2002). Products obtained in pyrolysis include gaseous (biogas), liquid (bio-oil) and solid (charcoal) materials, depending on fast and slow types of pyrolysis (Libra et al., 2011). Slow pyrolysis with a residence time of few minutes or several hours is generally recommended to obtain solid char material (Brown, 2009). The term “biochar” is now commonly used for the solid char material obtained during pyrolysis of biomass. Biochar has recently proved its potential applications in various fields such as climate change mitigation, carbon sequestration, soil quality improvement, plant growth, and contaminants remediation in soil and water. Hydrothermal carbonization is another process of controlled biomass carbonization via thermochemical decomposition at 180–300 °C under pressure in hot compressed water for several hours (Funke and Zeigler, 2010). The product obtained is a solid char

* Corresponding author.

E-mail address: malwabel@ksu.edu.sa (M.I. Al-Wabel).

Peer review under responsibility of King Saud University.



material known as “hydrochar”. Hydrochar has shown its potential applications in coal-power plants (possessing high heat calorific value), super capacitors industry (because of the high surface area), and soil amendment (containing essential nutrients) (Reza et al., 2014a). Recently, hydrochar has gained attraction in its application to soil as an amendment. For instance, Ro et al. (2016) suggested a great potential of hydrochar preventing the loss of soil nutrients via leaching to water bodies.

Substantial differences in the characteristics of biochar and hydrochar could produce anomalous results when applied as soil amendments. For example, Egamberdieva et al. (2016) reported increased growth of soybean in soil amended with hydrochar than the soil amended with biochar. Contrarily, Riebe et al. (2015) showed negative impacts of hydrochar and positive effects of biochar on wheat growth. Most of the recent literature support biochar as a potent soil amendment than hydrochar due to the little-known application of the latter as a soil amendment. Hydrochar may be superior to biochar in some ways such as the elimination of pre-dried biomass, reduction in a loss during transport, handling and application to the field, higher heating value and no atmospheric gaseous emissions during hydrothermal carbonization (Kambo and Dutta, 2015).

Another recent issue related with biochar and hydrochar is their toxicity. During thermochemical decomposition of biomass, cellulose and lignin are degraded and produce phenolic compounds including polyaromatic hydrocarbons (PAHs) and dioxins, thereby causing potential risk to soil biota (Garlapalli et al., 2016). PAHs toxicity in soil amended with biochar and hydrochar has recently been reported (Visioli et al., 2016; Oleszczuk et al., 2013; Busch et al., 2013). Therefore, it is important to determine ecotoxicological compositions of biochar and hydrochar before application as a soil amendment, in order to prevent negative effects on soil biota.

To remove ecotoxicological compounds from hydrochar and biochar, washing of the char material with water after carbonization is commonly practiced. However, washing may affect the char properties by removing soluble nutrients (Ca, Mg, K, N, and P), altering the surface morphology and chemical reactivity in terms of hydrolysis of aromatic compounds (Dieguez-Alonso et al., 2018). This study is proposed to produce biochar and hydrochar via pyrolysis and hydrothermal carbonization of date palm leaflets, respectively, and to examine the impact of different carbonization processes on their characteristics. Seed germination test with lettuce (*Lactuca sativa* L) was performed to evaluate the phytotoxicity of biochar and hydrochar. Furthermore, the effect of washing on chars' properties, seed germination, and plant growth parameters (including shoot and root lengths, and fresh and dry weights) were assessed.

2. Materials and methods

2.1. Biochar and hydrochar preparation

Date palm leaflets were collected from the agricultural farm of King Saud University. The leaflets were dried under the sunshine for two days, crushed, milled and sieved through 2 mm aperture to obtain homogeneous biomass (BM). To produce biochar (BC), a sufficient quantity of BM was pyrolyzed in a tube furnace (Carbolite Type 3216, England) at 600 °C for 3 h at a heating rate of 5 °C min⁻¹ under limited oxygen conditions. The produced BC was cooled in a desiccator and stored in air-tight container. Hydrochar (HC) was produced from the same BM via hydrothermal carbonization. A sufficient amount of BM was mixed with distilled water (1:3 w/v ratio) in an autoclave type steel container maintaining about 1-inch head space and heated in the furnace at 250 °C for 3 h.

The resulting HC was dried in an oven at 70 °C for 24 h, cooled in a desiccator and stored in air-tight container.

Washing of the dry BC and HC was carried out with distilled water in polypropylene tubes at the ratio of 1:10 (w/v). The suspensions were shaken on an orbital shaker at 120 rpm for 1 h, followed by centrifugation and filtration (Liu et al., 2015). The process was repeated thrice and the supernatant was combined and stored in polypropylene tubes as washed water of BC (WWB) and washed water of HC (WWH). The solid residue of washed BC (WBC) and washed HC (WHC) was dried at 70 °C for 24 h and stored in air-tight containers.

2.2. Biochar and hydrochar characterization

All the materials including BM, BC, HC, WBC, and WHC were subjected to proximate and ultimate analyses.

2.2.1. Proximate analysis

The production yield of BC and HC was calculated as the proportion of BC or HC weight to the weight of BM. All the produced biochar and hydrochar materials were subjected to proximate analysis (moisture, mobile matter, ash and resident matter) following the standard method of ASTM D1762-84 (ASTM, 1989). Moisture contents were determined by heating the materials at 105 °C for 24 h. Mobile matter and ash contents were measured by heating the materials at 450 °C for 30 min (in covered crucibles), and 750 °C for 1 h (in open top crucibles), respectively. The resident matter was calculated by taking the difference in moisture, ash and mobile matter.

2.2.2. Ultimate analysis

Elemental composition (C, H, N, and O) of the materials was determined by using an elemental analyzer (Euro EA, Germany), and their atomic ratios were calculated. Total elements contents (Cu, Fe, Mn, Zn, Ca, and Mg) were measured following microwave assisted digestion in concentrated nitric acid and hydrogen peroxide (USEPA method 3052, 1995), and analyzing on inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 4300 DV, USA).

The surface structure of the materials was determined by taking scanning electron microscope (SEM, EFI S50 Inspect, Netherlands) images by mounting the material on double coated adhesive carbon conductive tabs (12 mm; PELCO, UK) and placed on the aluminum stubs. Different images were captured at an acceleration voltage of 30 kV and a magnification of 6000x. Mineralogy of the materials was measured using X-ray diffractometer (MAXima_X XRD-7000, Shimadzu, Japan) with 30 mA Cu K α radiation at the scan speed of 2-degree min⁻¹ in continuous scan mode.

Electrical conductance (EC) and pH were measured in 1:10 solid/water suspensions using digital pH and EC meters. Cation exchange capacity (CEC) was measured following the method described in Takaya et al. (2016). Briefly, 1 g of material was mixed with 20 mL distilled water and the suspension was shaken on an orbital shaker at 150 rpm for 10 min. Subsequently, the suspension was filtered through Whatman 42 filter paper. The process was repeated thrice. The material was then saturated with 10 mL of 1 M sodium acetate at pH 7 (adjusted with glacial acetic acid), followed by shaking at 150 rpm for 15 min and filtration. The filtrate was discarded and the process was repeated again. The residual material was rinsed with ethanol thrice, and then mixed with 10 mL of 1 M ammonium acetate (to displace sodium cations), shaken at 150 rpm for 15 min and filtered. The process was repeated two more times, and the filtrates were combined and analyzed for sodium cations on a flame spectrometer (PerkinElmer AAnalyst 300, USA). Subsequently, CEC was calculated using the following equation:

$$\begin{aligned} \text{CEC (meq } 100 \text{ g}^{-1}) &= \text{Na (meq L}^{-1}) \\ &\times \text{ volume of extractant (mL)/soil weight (g)} \\ &\times 100/1000 \end{aligned}$$

2.2.3. PAHs analysis

Accelerated solvent extraction (ASE) was employed for PAHs extraction from biochar and hydrochar samples. Accurately weighed the amount of sample material was mixed with diatomaceous earth and anhydrous sodium sulfate, and transferred to pre-cleaned (with acetone + dichloromethane mixture) stainless steel ASE cell (35 mL, Dionex, Sunnyvale, CA, USA). Subsequently, extraction was made with 1:1 (v/v) mixture of acetone and dichloromethane (HPLC grade) in ASE unit operated at 100 °C, 1500 psi, 60% flush volume and 5 min of each cycle. The extract was collected in 100 mL round bottom flask and concentrated to 1.5 mL on a rotary evaporator (BUCHI, Germany). The concentrated extract was then purified by solid phase extraction through silica SPE cartridge. Finally, the collected fraction was transferred to amber colored GC vial and volume was made up to 1 mL with hexane and dichloromethane mixture (1:1 v/v). The PAHs in these extracts were then analyzed on a GC-MS-MS (Thermo Scientific™ TSQ™ 8000, Evo Triple Quadrupole, USA) by using TRACE™ TR-5MS GC column (30 m × 0.25 mm × 0.1 μm) in a splitless gas saver mode with 1 μL injection volume, and injector inlet temperature of 270 °C. The GC oven temperature was ramped from 50 °C to 310 °C (3 min) at the rate of 10 °C min⁻¹, and then to 325 °C (10 min) at the rate of 4 °C min⁻¹. SRM method was used with transfer line temperature 180 °C and ion source temperature 250 °C. A certified reference material (M-8100-QC-PAK, AccuStandard, USA) containing 17 PAHs was used to construct calibration curves and quantify the samples.

2.3. Germination test

To determine the toxic effects of produced chars (BC and HC), washed chars (WBC and WHC) and their washings (WWB and WWH), lettuce (*Lactuca sativa*) seeds were germinated on filter papers (Whatman 42). Briefly, filter papers were cut to the size of Petri plate (90 mm × 12 mm), soaked in 5 mL of distilled water and placed in Petri plates. 0.2 g of char (BC, HC, WBC and WHC) was sprinkled separately on the respective filter paper. In the case of WWB and WWH, the filter papers were wetted with the washed waters of BC and HC instead of distilled water. Subsequently, 20 seeds of lettuce were spread over each filter paper. The Petri plates were covered and placed in the dark for 48 h at 25 °C, followed by cycles of 16 h light and 8 h dark for the next 72 h. Afterward, the number of germinated seeds was counted in each treatment and percentage germination rate was calculated (Ahmad et al., 2012). Shoot and root lengths of the seedlings were also measured and recorded. Additionally, fresh and dry weights of lettuce seedlings were also determined. A control was also performed with only distilled water. All the treatments were triplicated.

2.4. Statistical analysis

All analyses were performed at least in duplicate. Mean values of replicates with standard deviations are reported. One-way analysis of variance (ANOVA) and Tukey's honestly significance difference (HSD) studentized range test was applied to mean values of all treatments, using the Statistical Analysis System (SAS, ver 9.2, SAS Institute Inc. Cary, NC, USA). Pearson's correlation coefficient (R) and probability (P) values were also calculated from SAS software.

3. Results and discussion

3.1. Biochar and hydrochar characteristics

3.1.1. Effect of production process

The proximate and ultimate characteristics of biochar (BC) and hydrochar (HC) were clearly distinguished (Table 1). The results showed that HC had a higher yield (65.47%) than BC (41.32%). The lower yield of BC can be explained by the higher loss of volatile matter and a greater weight loss from biomass during pyrolysis under limited oxygen conditions than those of HC during hydrothermalization in an airtight container. In this context, our results showed clear evidence that volatile matter decreased from 62.22% in the feedstock to 8.93% and 53.04% in BC and HC, respectively. This result indicates that HC had greater volatile matter content (53.04%) than BC (8.93%). However, BC contained a greater percentage of fixed carbon (51.39%) compared to HC (24.00%), indicating that BC had high recalcitrant carbon potential. Higher stability of BC as compared to HC is according to other works that attributed this fact to greater polyaromatic carbon contents in BC (Busch and Glaser, 2015). The results showed that ash percentage increased from 8.33% in the feedstock to 38.66% and 16.65% in BC and HC, respectively. As indicated by several other researchers, higher ash content in the pyrolyzed materials than that of its feedstock can be mainly attributed to the formation and condensation of mineral constituents and elements in biochar samples under pyrolysis conditions (Ronsse et al., 2013). Ash contents in BC (38.68%) were 2.4 times greater than HC (16.15%), showing thermal oxidation of organic compounds through pyrolysis process. The pH value of feedstock accounted for 5.94, while this value increased to 10.23 in BC and decreased to 5.32 in HC, indicating an alkaline nature of BCs. Overall, the highest alkaline pH values of BC samples could be attributed to liming effects stimulated by decreasing acidic functional groups and increasing basic functional groups as well as due to high ash contents of BC having alkali salts (Mukherjee et al., 2011; Fuertes et al., 2010). The decrease in pH value during HC could be due to hydrolysis and breakdown of biomass compositions. However, slight increase in the pH of WHC (6.03) was observed compared to HC (5.32), which could be attributed to the removal of water soluble acidic compounds and salts. Washing could introduce more hydroxyl groups, leading also to increase in pH of WHC. The HC possesses less EC value (3.47 dS m⁻¹) than BC (5.55 dS m⁻¹), which is again related to the ash contents, i.e. accumulation of recalcitrant ionic species. Likewise, CEC of BC (39.86 cmol kg⁻¹) was higher than HC (13.46 cmol kg⁻¹) attributing to the concentration of exchangeable cations in BC during pyrolysis (Inyang et al., 2010). Moreover, tar accumulation on the surface of HC during hydrothermal carbonization may also cause a reduction in its CEC (Takaya et al., 2016).

Elemental composition and their atomic ratios are presented in Table 2. Total C contents in HC (80.27%) were much higher than feedstock (48.46%) and slightly higher than BC (76.23%), which could be due to the retention of volatile hydrocarbons in HC during hydrothermal carbonization. For the same reason, total H and N contents in HC (6.56 and 2.50%, respectively) were also higher than BC (3.36 and 0.00%, respectively). While due to higher mobile contents (62.22%), H and N contents (9.73 and 3.20%, respectively) in feedstock were higher than HC and BC. Contrarily, BC contained ~2 times more O contents (20.40%) than HC (10.66%), consequently resulting in higher O/C ratio (0.20). Low O/C value of HC (0.10) indicated the presence of less polar groups on HC surface. As compared to feedstock, O contents in BC and HC are much lower due to the environment of limited O supply. In other words, BC surfaces are more hydrophilic, while HC surfaces are more hydrophobic (Fang et al., 2014). Greater hydrophobicity of HC could also be

Table 1
Yield, proximate and chemical analyses results of date palm leaflets biomass (BM) and its derived biochar (BC), hydrochar (HC), washed biochar (WBC) and washed hydrochar (WHC).

	Yield, %	Moisture, %	Mobile matter, %	Resident matter, %	Ash, %	pH, 1:10	EC ^a , dS m ⁻¹	CEC ^b , cmol kg ⁻¹
BM	–	4.98 ± 0.04	62.22 ± 2.32	24.47 ± 2.36	8.33 ± 0.01	5.94 ± 0.00	10.46 ± 0.54	70.30 ± 1.07
BC	41.32 ± 0.61	1.01 ± 0.09	8.93 ± 1.13	51.39 ± 0.70	38.68 ± 0.34	10.23 ± 0.01	5.55 ± 0.01	39.86 ± 0.71
HC	65.47 ± 4.19	6.81 ± 0.29	53.04 ± 3.43	24.00 ± 3.58	16.15 ± 0.14	5.32 ± 0.14	3.47 ± 0.41	13.46 ± 3.47
WBC	37.39 ± 0.07	5.00 ± 1.41	17.91 ± 1.75	46.55 ± 5.12	30.54 ± 1.93	8.46 ± 0.04	0.55 ± 0.04	19.75 ± 2.99
WHC	46.95 ± 0.33	3.00 ± 1.41	45.34 ± 2.35	38.26 ± 2.10	13.4 ± 1.27	6.03 ± 0.24	0.09 ± 0.06	14.81 ± 5.98

^a Electrical conductivity.

^b Cation exchange capacity.

Table 2
Elemental composition and ratios (ash and moisture free) of date palm leaflets biomass (BM) and its derived biochar (BC), hydrochar (HC), washed biochar (WBC) and washed hydrochar (WHC).

	C, %	H, %	N, %	O, %	O/C	H/C
BM	48.46	9.73	3.20	38.61	0.60	2.40
BC	76.23	3.36	0.00	20.40	0.20	0.53
HC	80.27	6.56	2.50	10.66	0.10	0.98
WBC	89.79	2.13	2.55	5.53	0.05	0.28
WHC	76.53	6.64	1.08	15.44	0.15	1.04

caused by tar accumulation during hydrothermal carbonization. The lower value of molar H/C for BC (0.53) than HC (0.97) and feedstock (2.39) indicated greater carbonization and high aromaticity of BC. High aromaticity of BC also implicated its high stability than HC that has previously been reported (Busch and Glaser, 2015).

Distinctive surface morphology of BC and HC was observed because of different production processes. SEM images (Fig. S1a and b in the supplementary material) clearly showed porous surface of BC, whereas HC surface was irregular having microspheres probably originating from the hydrothermal decomposition of cellulose (Sevilla et al., 2011). Similarly, a substantial difference in the mineralogy of BC and HC was observed, as shown in (Fig. S2). XRD spectra indicated amorphous nature of BC and HC. The peaks at 29.2° and 46.9° 2θ suggested calcite (CaCO₃) as the dominant mineral in BC, which is also reported by Usman et al. (2015) who produced BC from the similar date palm tree waste material. On the other hand, XRD spectra of HC showed the presence of Carletonite (KNa₄Ca₄Si₈O₁₈(CO₃)₄ (OH. F). H₂O), anorthite (CaAl₂Si₂O₈), bayerite (α-Al(OH)₃), iron (Fe) and steropesite (Ti₃-BiCl₆). The appearance of the various minerals peaks in XRD spectra of HC could be attributed to chemical reactions occurred in a closed container under pressure during hydrothermal carbonization of biomass.

Total metal contents in BC and HC are given in Table 3. Relatively high contents of Cu and Zn were observed in HC (183.7 and 257.4 mg kg⁻¹, respectively) as compared to BC (47.1 and 44.8 mg kg⁻¹, respectively). The hydrothermal process resulted in greater enrichment of these metals in HC than pyrolytic process. According to IBI (2015), total contents of Cu in HC were higher than the lower maximum allowed threshold values of 143 mg kg⁻¹ for Cu. All other metals were below the lower maximum allowed thresholds. These results suggested that pyrolysis process could be safer than the hydrothermal process in terms of toxic metals enrichment. However, the bioavailability of metals should be

assessed in BC and HC for determining the toxic levels of metals. Nevertheless, both hydrothermal and pyrolysis processes are reported to reduce the bioavailability of toxic metals (Huang and Yuan, 2016).

Biomass combustion is considered as one of the major anthropogenic sources of PAHs (Abdel-Shafy and Mansour, 2016). PAHs contents in HC and BC were, therefore, measured to examine the retention of PAHs in the two materials as a result of different combustion processes of hydrothermal carbonization and pyrolysis. Results of PAHs are presented in Table 4. HC showed greater contents for most of the PAHs than BC. About 2 times higher contents of acenaphthylene, acenaphthene, fluorine, phenanthrene, fluoranthene, chrysene, benzo[a]pyrene, indeno [1,2,3-c, d] pyrene, dibenz [a,h]anthracene, 7H-dibenzo[c,g]carbazole and dibenzo[a,e]pyrene were observed in HC as compared to BC. These results are in agreement with other studies indicating that HC contains larger amounts of PAHs than BC (Wiedner et al., 2013). Condensation of tar on HC surface during hydrothermal carbonization of biomass results in retention of PAHs as compared to dry pyrolysis process (Libra et al., 2011). Nevertheless, ∑ 14 PAHs contents (sum of 16 US EPA PAHs, except naphthalene and benz[a]anthracene) in both BC (53.36 mg kg⁻¹) and HC (98.80 mg kg⁻¹) were much higher than the threshold value (6–20 mg kg⁻¹) provided by the IBI (2015). On the basis of a number of aromatic rings, 2 and 3 rings PAHs were dominant in BC and HC followed by 5, 4 and 6 rings PAHs. Comparatively, HC contained high proportions of 2 and 3 ring PAHs than BC, while BC contained high proportions of 5 and 4 ring PAHs (Fig. 1). A plausible reason for high proportions of low molecular weight (2 and 3 ring) PAHs in HC could be due to their retention in the condensed tar during hydrothermal carbonization and atmospheric emission during pyrolysis. Contrarily, more heat is required for the generation of high molecular weight (>3 rings) PAHs during pyrolysis of biomass (Sharma and Hajjaligol, 2003).

Table 3
Total elements (Cu, Fe, Mn, Zn, Ca and Mg) contents (mg kg⁻¹) in biochar (BC), washed biochar (WBC), hydrochar (HC) and washed hydrochar (WHC).

	Cu	Fe	Mn	Zn	Ca	Mg
BC	47.1 ± 6.7	1252.7 ± 66.3	76.7 ± 3.0	44.8 ± 5.9	39720 ± 198	6589.0 ± 123.0
HC	183.7 ± 71.1	1163.1 ± 91.5	47.2 ± 3.1	257.4 ± 8.2	17457 ± 1515	2906 ± 248.9
WBC	84.4 ± 0.8	1177.8 ± 55.2	77.2 ± 1.7	43.7 ± 3.3	36040 ± 1075	6390 ± 152.7
WHC	116.7 ± 3.0	1392.9 ± 78.5	11.7 ± 0.1	126.0 ± 2.8	4722 ± 472	594.4 ± 19.2

Table 4Polycyclic aromatic hydrocarbons (PAHs) contents ($\mu\text{g kg}^{-1}$) in biochar (BC), hydrochar (HC), washed biochar (WBC) and washed hydrochar (WHC).

PAHs	BC	HC	WBC	WHC
Acy ^a	10950 ± 5	21858 ± 6	12412 ± 1783	21850 ± 0
Ana ^a	10544 ± 77	20260 ± 110	11976 ± 834	20139 ± 8
Flu ^a	11208 ± 213	20526 ± 221	13816 ± 2102	20504 ± 58
Phe ^a	12119 ± 73	24242 ± 141	12118 ± 84	23997 ± 4
Ant ^a	1533 ± 891	538 ± 6	3521 ± 2120	493 ± 6
Flt ^a	782 ± 464	1002 ± 27	997 ± 239	1003 ± 23
Pyr ^a	1869 ± 831	2716 ± 85	1873 ± 272	2790 ± 91
Chr ^a	621 ± 124	1065 ± 7	570 ± 49	1059 ± 0.3
BbF ^a	131 ± 32	107 ± 2	117 ± 92	100 ± 4
BkF ^a	51 ± 37	52 ± 3	92 ± 0	50 ± 2
BaP ^a	932 ± 62	1795 ± 17	1023 ± 169	1782 ± 4
Ipy ^a	923 ± 161	1628 ± 14	807 ± 1	1614 ± 2
DbA ^a	1031 ± 2	2065 ± 4	1057 ± 35	2089 ± 24
Bpe ^a	665 ± 281	950 ± 5	503 ± 58	934 ± 10
DbC	1767 ± 48	3728 ± 1485	1434 ± 156	2841 ± 280
Mca	6426 ± 8029	1542 ± 89	773 ± 0	1640 ± 94
DbP	931 ± 57	1817 ± 35	925 ± 71	1768 ± 0
∑ total PAHs	62,483	105,891	64,014	104,653
∑ 14 PAHs of 16 US-EPA PAHs	53,359	98,804	60,882	98,404

^a US-EPA PAHs, PAHs are acenaphthylene (Acy), acenaphthene (Ana), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (Ipy), dibenz[a,h]anthracene (DbA), benzo[g,h,i]perylene (Bpe), 7H-dibenzo[c,g]carbazole (DbC), methylochloranthene (Mca) and dibenzo[a,e]pyrene (DbP). Values are the mean value ± standard deviation from at least two replicates.

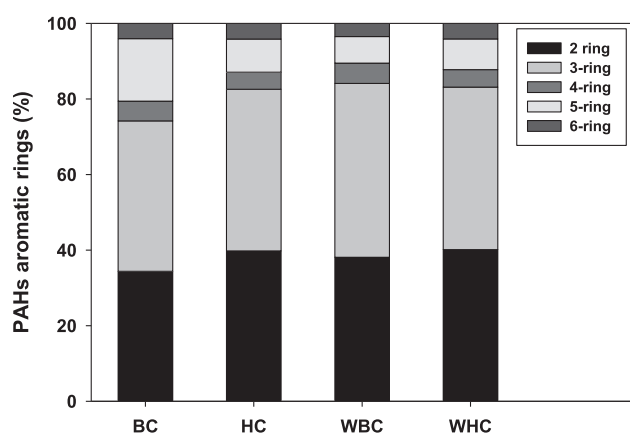


Fig. 1. Relative contribution of 2–6 rings PAHs in biochar (BC), hydrochar (HC), washed biochar (WBC) and washed hydrochar (WHC).

Overall, very clear discrepancies were observed between BC and HC characteristics because of different carbonization processes. Both of the pyrolytic and hydrothermal carbonization processes have their own advantages and disadvantages. For instance, hydrothermal carbonization produces HC with greater yield, acidic pH, more hydrophobicity and greater crystallinity as compared to BC. Contrarily, dry pyrolysis produces BC with high CEC, greater carbon stability, high aromaticity and more porosity than HC. Hydrothermal carbonization could be better option preventing gaseous (CO , CO_2 , NO_2 , etc.) and PAHs emissions into the environment, which are obvious during uncontrolled pyrolysis. The solid product of both processes must be very carefully applied to soil in order to avoid their negative impacts.

3.1.2. Effect of washing

Washing of the carbonized material produced from biomass combustion is a common practice. However, it may affect nutrients leaching and addition or removal of surface functional groups. In this study, the BC and HC were washed with distilled water and characterized again for all the parameters as did for the unwashed materials. A significant decrease in yields of WBC (3.93%) and WHC (18.52%) was observed after washing, indicating removal of soluble

material (Table 1). Likewise, EC and CEC of WBC were decreased by 90.18% and 50.45%, respectively, while of WHC were decreased by 97.55% and 10.03%, respectively. These results indicated that washing could have a significant effect on ionic properties of char materials. Washing with water can remove the soluble cations and anions, consequently decreasing the availability of essential ions to plant when applied to soil. It has been reported that increase in soil cationic (Ca, Mg, K) and anionic (Cl , SO_4 , PO_4) contents are directly related to the release of these ions from char material (Ahmad et al., 2017). Therefore, depending on soil deficiency in essential ions, unwashed char could serve as the main source of replenishing the soil ionic properties. pH of WBC was decreased by about 2 units than BC, whereas increased by about 1 unit in WHC than HC. The decrease in pH of WBC could be attributed to the removal of soluble basic salts (e.g. carbonates) during washing with water. On the other hand, increase in pH of WHC could be due to the removal of water soluble acidic salts (e.g. phosphates, etc.). These results are in line with the obvious decrease in ash contents of WBC (21.04%) and WHC (17.03%) after washing. It was interesting to note 100.56% increase and 14.52% decrease in a mobile matter of WBC and WHC, respectively. Contrarily, the resident matter was decreased by 9.42% in WBC and increased by 59.42% in WHC. This phenomenon could occur due to the hydrolysis of organic matter in BC producing organic acids (that also resulted in a decrease in WBC pH), thereby increasing the mobile matter contents in WBC. However, in the case of WHC, reduction in the mobile matter could be related to removal of tar from HC surface during water washing (Phuphuakrat et al., 2011). These results are further supported by an increase in total C of WBC (17.79%) and decrease in total C of WHC (4.66%) (Table 2). Total O contents in WBC were decreased by 72.89%, while increased by 44.84% in WHC after washing. The decrease in total O contents in WBC could be due to the removal of O-containing functional groups with water. Huang et al. (2016) also reported removal of O-containing functional groups with steam while synthesizing activated carbon from sawdust. On the contrary, removal of tar from WHC surface after washing made it more hydrophilic, as can be seen from relatively high O/C atomic ratio (0.15) than HC (0.10). Washing lowered the O/C ratio of WBC to 0.05 from 0.20 in BC, indicating its low polarity or high hydrophobicity.

Surface morphology of BC and HC was also affected by water washing. SEM micrographs showed partial blockage of pores and

rough surface appearance of WBC and WHC (Fig. S1c and d), respectively, which could be due to the accumulation of remnants of water soluble compounds (Kumar et al., 2011). No significant changes in the mineralogy of BC and HC were observed before and after water washing (Fig. S2). Generally, HC showed high contents of total metals than BC (Table 3). However, after washing, total Cu, Mn, Zn, Ca and Mg were significantly decreased in WHC. This speculated that HC contained more labile metals that were washed out in WHC. This further implicated that dry pyrolysis can cause metals immobilization to a greater extent than hydrothermal carbonization. Because of insolubility of PAHs in water, washing did not show any significant impact on PAHs contents in WBC and WHC (Table 4).

In general, washing of the char material demonstrated some changes in their properties. Washing step can lower BC pH (up to 2 units), thus facilitating its use in alkaline soils (such as arid regions). However, loss of essential elements such as Ca, Mg, Mn, and Zn (particularly from HC) by washing could lessen its potential of soil quality and crop productivity enhancement. Washing can increase the hydrophobicity of BC and hydrophilicity of HC making them more suitable for absorption of non-polar and polar compounds, respectively. Therefore, it is suggested to be selective in adopting washing of the char depending on its application to specific soil types.

3.2. Seed germination

3.2.1. Effect of char type

Results of the germination test on lettuce (*Lactuca sativa* L) are shown in Fig. 2. In control (CK) treatment 95% germination of lettuce was observed. There was no significant effect on lettuce germination between BC, WBC and WWB treatments. More than 85% germination occurred in all these treatments, indicating that BC did not show any toxic effect on lettuce germination. On the other way, HC treatment significantly decreased the germination of lettuce to only 20%. Washing slightly (but non-significantly) improved the germination to 38%. WWH treatment resulted in 77% germination of lettuce, which was compatible with CK treatment. These results noticeably pointed out that HC caused toxic effects on lettuce germination. Furthermore, it was revealed that water insoluble compounds in HC could be responsible for causing toxicity to lettuce germination. These findings are in agreement with other studies (Bargmann et al., 2013; Busch et al., 2013) showing phytotoxicity of HC. Comparatively, BC proved to be safe for soil application to enhance plant production without any phytotoxic effect.

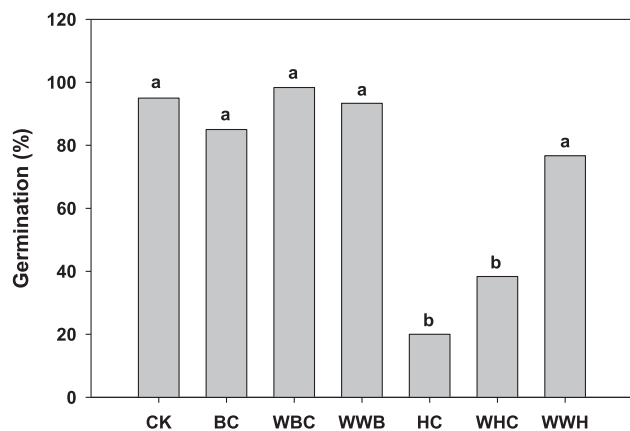


Fig. 2. Germination of lettuce (*Lactuca sativa*) affected by biochar (BC), washed biochar (WBC), washed water of biochar (WWB), hydrochar (HC), washed hydrochar (WHC) and washed water of hydrochar (WWH). Same letters on bars indicate non-significant differences between treatments.

Shoot and root lengths of the lettuce seedlings were also measured to assess the impact of different char materials; results are shown in Fig. 3. The BC, WBC and WWB treatments significantly enhanced the growth of lettuce as compared to CK. Specifically; BC treatment increased the shoot length of lettuce seedling by 50.76% than CK treatment. These results confirmed the potential of BC in improving plants growth. BC has already been reported to facilitate plants growth and crops productivity by releasing nutrients (Ahmad et al., 2012; Liu et al., 2013). Contrarily, HC and WHC significantly decreased the shoot length of lettuce by 40.5% than CK treatment, which was obviously related to the toxicity of HC as was observed in seed germination. No significant effect of any treatment was observed on the root length of lettuce seedlings. Fresh and dry weights of lettuce seedlings as affected by different char materials are shown in Fig. 4. As aforementioned, similar results were observed for these growth parameters. BC increased fresh and dry weights of lettuce by 33% and 114%, respectively, while HC decreased the fresh and dry weights of lettuce by 48% and 42%, respectively.

The seed germination and growth parameters reflected positive effects of BC and negative effects of HC on lettuce growth. It is, therefore, strongly suggested to carefully examine the toxicity of HC before applying it to the soil for plant productivity.

3.2.2. Toxicity effect of PAHs

Based on the characterization of BC and HC, it was observed that HC contained about 2 times higher contents of PAHs than BC. This provided a plausible reason of HC toxicity to lettuce germination. Toxicity of PAHs is well known to animals and plants. Particularly, anthracene, fluoranthene, fluorene, phenanthrene, and their derivative compounds have previously been reported to cause phytotoxicity (Somtrakoon and Chouychai, 2013; Pasakova et al., 2006). In this study, the lettuce seed germination was correlated with selected PAHs contents in char materials (Fig. 5). Significantly negative correlations were observed for benzo[a]pyrene, dibenzo[a,h]anthracene, chrysene, indeno pyrene, benzo[g,h,i]perylene,

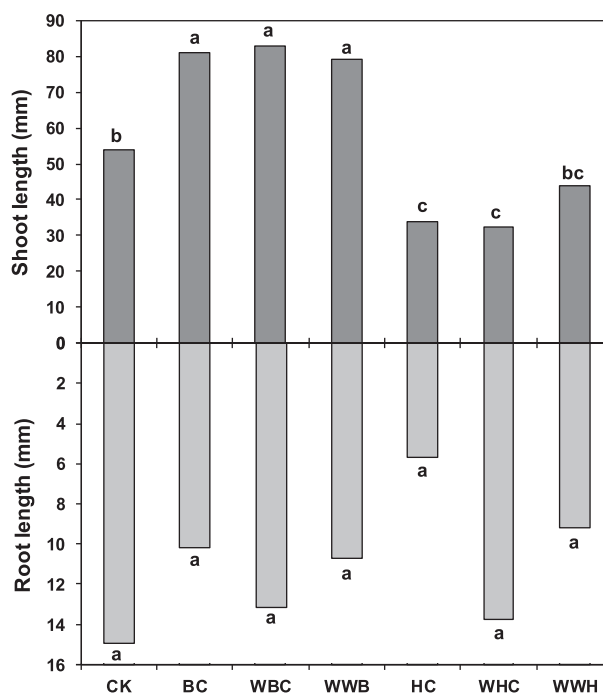


Fig. 3. Shoot and root elongation of lettuce (*Lactuca sativa*) affected by biochar (BC), washed biochar (WBC), washed water of biochar (WWB), hydrochar (HC), washed hydrochar (WHC) and washed water of hydrochar (WWH). Same letters on bars indicate non-significant differences between treatments.

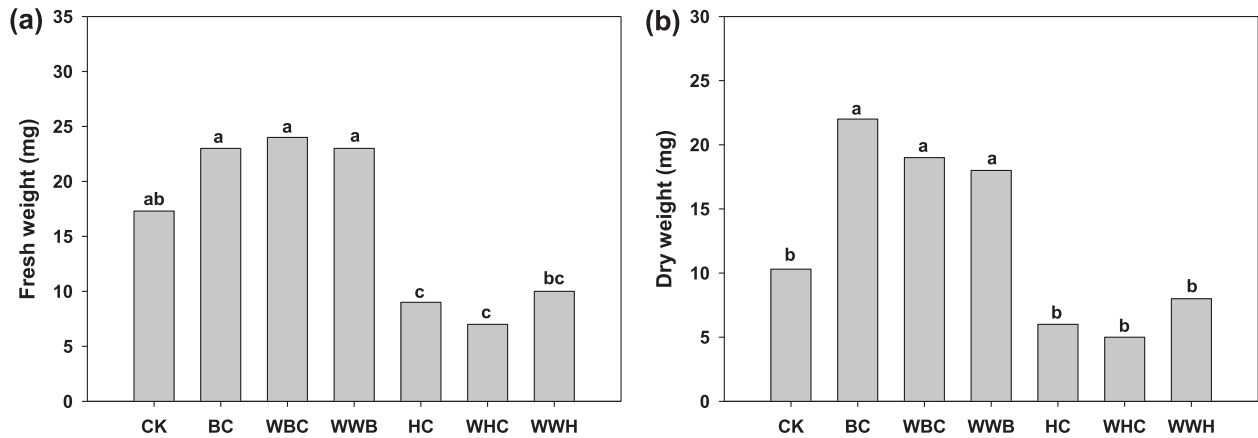


Fig. 4. Fresh (a) and dry (b) weights of lettuce (*Lactuca sativa*) affected by biochar (BC), washed biochar (WBC), washed water of biochar (WWB), hydrochar (HC), washed hydrochar (WHC) and washed water of hydrochar (WWH). Same letters on bars indicate non-significant differences between treatments.

pyrene, phenanthrene, dibenzo[c,g]carbazole and dibenzo[a,e]pyrene with lettuce germination at $P < 0.05$. This further affirmed that toxicity to lettuce from char materials was directly related to PAHs contents. Most of these PAHs are reported to be highly toxic and carcinogenic in animals and humans (ASTDR, 1995). However, their acute toxicity to plants is rarely reported. Somtrakoon and Chouychai (2013) stated that combined PAHs' toxic effect on plants could be more severe than individual PAH due to different toxic mechanisms such as cell wall modification, expansion, and acidifi-

cation. Generally, during hydrothermal carbonization of biomass, lignin is hydrolyzed to produce phenolic substances (mainly PAHs), thereby causing an ecotoxicological hazard by inhibiting plant germination (Reza et al., 2014b). Hence, HC is more prone of decreasing the lettuce germination in this study. Other researchers also reported toxic effects of HC on plants (cress, barley, and salad) and animals (earthworms) growth (Busch et al., 2012). It is therefore suggested that HC may not be used for soil application as an amendment without prior analysis and pretreatment to avoid pos-

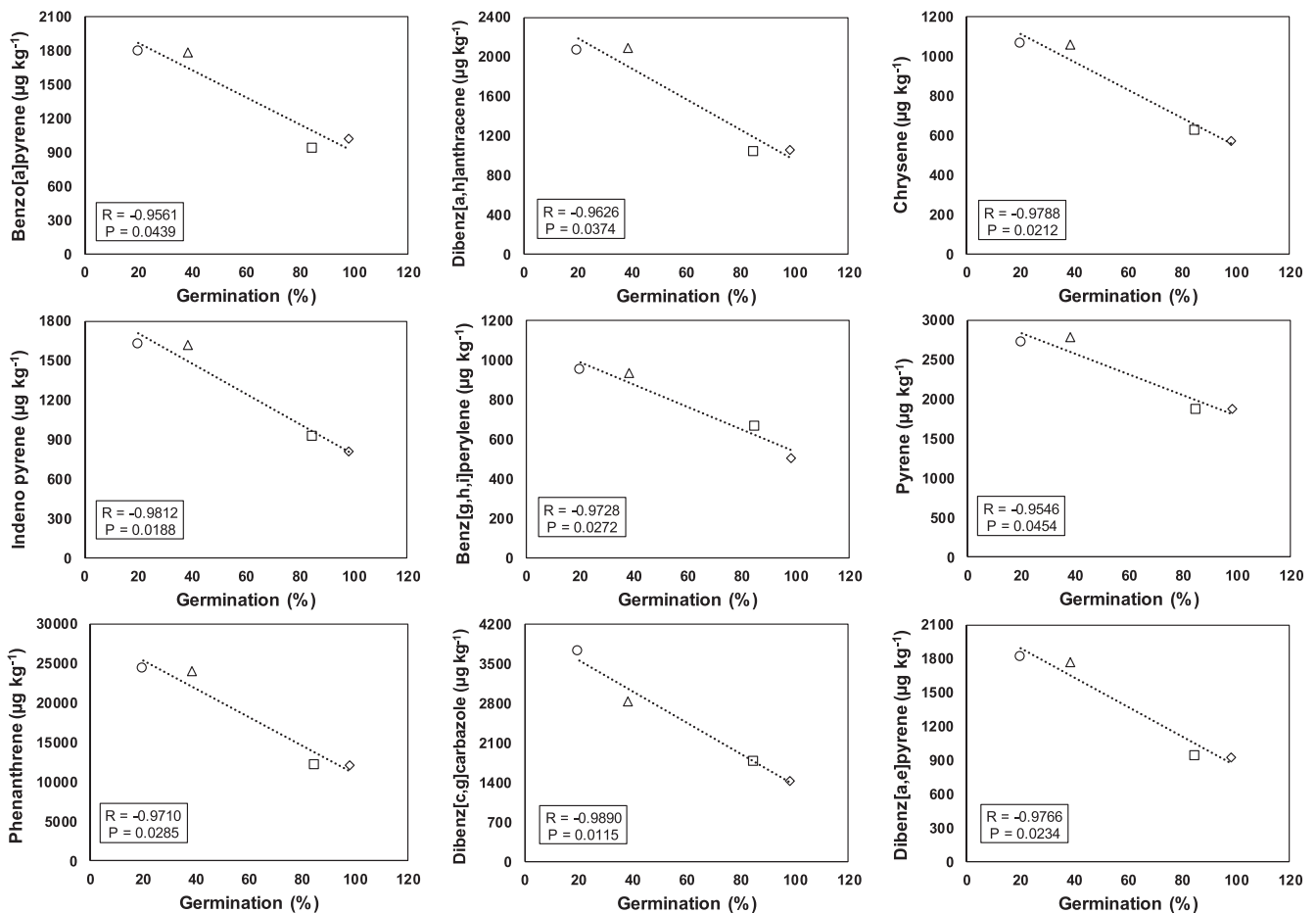


Fig. 5. Correlations between germination of lettuce (*Lactuca sativa*) and selected PAHs in biochar (\square), washed biochar (\diamond), hydrochar (\circ), and washed hydrochar (Δ). R is the Pearson's correlation coefficient and P is the probability.

sible toxic effects of PAHs present in HC. These findings are in good support of other recent studies (Garlapalli et al., 2016).

4. Conclusions

Biochar showed early and rapid growth and overall production was more than control treatment, which showed its potential as an effective soil additive. Contrarily, hydrochar had negative effects on germination and overall germination was less than control. Washing of char materials did not significantly boost germination for BC, for HC germination was slightly increased with WHC while WWH germination was compatible with control treatment. It showed water insoluble toxic substances like PAHs in HC which inhibited germination. Aforementioned BC has already been claimed as an effective soil amendment but for HC special pre-treatment condition is required to use it for agricultural purpose.

Acknowledgement

The authors extend their appreciation to the Deanship of Scientific Research, King Saud University – Saudi Arabia for funding this work through the international research group project RG-1439-043.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.sjbs.2018.05.017>.

References

- Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egypt. J. Petro.* 25, 107–123.
- Ahmad, M., Lee, S.S., Lee, S.E., Al-Wabel, M.I., Tsang, D.C.W., Ok, Y.S., 2017. Biochar-induced changes in soil properties affected immobilization/mobilization of metals/metalloids in contaminated soils. *J. Soils Sediments* 17, 717–730.
- Ahmad, M., Lee, S.S., Yang, J.E., Ro, H.M., Lee, Y.H., Ok, Y.S., 2012. Effects of soil dilution and amendments (musselshell, cowbone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. *Ecotoxicol. Environ. Saf.* 79, 225–231.
- ASTM, D 1762–84, (1989). Standard method for chemical analysis of wood charcoal. Philadelphia, Pa, U.S.A.
- ASTDR, 1995. Public Health Statement, Polycyclic Aromatic Hydrocarbons (PAHs). Agency for Toxic Substances and Disease Registry, <<https://www.atsdr.cdc.gov/ToxProfiles/tp69-cl-b.pdf>>.
- Bargmann, I., Rilling, M.C., Buss, W., Kruse, A., Kuecke, M., 2013. Hydrochar and biochar effects on germination of spring barley. *J. Agron. Crop. Sci.* 199, 360–373.
- Brown, R., 2009. Biochar production technology. *Biochar for environmental management: Science and technology*. pp.127–146.
- Busch, D., Glaser, B., 2015. Stability of co-composted hydrochar and biochar under field conditions in a temperate soil. *Soil Use Manage.* 31, 251–258.
- Busch, D., Kammann, C., Grünhage, L., Müller, C., 2012. Simple biotoxicity tests for evaluation of carbonaceous soil additives: establishment and reproducibility of four test procedures. *J. Environ. Qual.* 41, 1023–1032.
- Busch, D., Stark, A., Kammann, C.I., Glaser, B., 2013. Genotoxic and phytotoxic risk assessment of fresh and treated hydrochar from hydrothermal carbonization compared to biochar from pyrolysis. *Ecotoxicol. Environ. Saf.* 97, 59–66.
- Conesa, J.A., Font, R., Fullana, A., Martín-Gullón, I., Aracil, I., Gálvez, A., Mólto, J., Gómez-Rico, M.F., 2009. Comparison between emissions from the pyrolysis and combustion of different wastes. *J. Anal. Appl. Pyrolysis* 84, 95–102.
- Demirbas, A., Arin, G., 2002. An overview of biomass pyrolysis. *Energy Source* 24, 471–482.
- Dieguez-Alonso, A., Funke, A., Anca-Couce, A., Rombolà, A.G., Ojeda, G., Bachmann, J., Behrendt, F., 2018. Towards biochar and hydrochar engineering—influence of process conditions on surface physical and chemical properties, thermal stability, nutrient availability. *Toxic. Wetta. Energies* 11 (3), 496.
- Egamberdieva, D., Wirth, S., Behrendt, U., Abd_Allah, E.F., Berg, G., 2016. Biochar treatment resulted in a combined effect on soybean growth promotion and a shift in plant growth promoting rhizobacteria. *Front. Microbiol.* 7, 209.
- Fang, Q., Chen, B., Lin, Y., Guan, Y., 2014. Aromatic and hydrophobic surfaces of wood-derived biochar enhance perchlorate adsorption via hydrogen bonding to oxygen-containing organic groups. *Environ. Sci. Technol.* 48, 279–288.
- Fuertes, A.B., Arbestain, M.C., Sevilla, M., Maciá-Agulló, J.A., Fiol, S., López, R., Smernik, R.J., Aitkenhead, W.P., Arce, F., Macias, F., 2010. Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover. *Aust. J. Soil, Res.* 48, 618–626.
- Funke, A., Zeigler, F., 2010. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. *Biofuel. Bioprod. Bior.* 4, 160–177.
- Garlapalli, R.K., Wirth, B., Reza, M.T., 2016. Pyrolysis of hydrochar from digestate: effect of hydrothermal carbonization and pyrolysis temperatures on pyrochar formation. *Bioresour. Technol.* 220, 168–174.
- Huang, H.J., Yuan, X.Z., 2016. The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge. *Bioresour. Technol.* 200, 991–998.
- IBI, 2015. Standardized Product Definition and Product Testing Guidelines for Biochar that is used in Soil, version 2.1. International Biochar Initiative. <<http://www.biochar-international.org/characterizationstandard>>.
- Inyang, M., Gao, B., Pullammanappallil, P., Ding, W., Zimmerman, A.R., 2010. Biochar from anaerobically digested sugarcane bagasse. *Bioresour. Technol.* 101, 8868–8872.
- Kambo, H.S., Dutta, A., 2015. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sustain. Energy Rev.* 45, 359–378.
- Kumar, S., Loganathan, V.A., Gupta, R.B., Barnett, M.O., 2011. An Assessment of U (VI) removal from groundwater using biochar produced from hydrothermal carbonization. *J. Environ. Manage.* 92, 2504–2512.
- Libra, J., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici, M.M., Fühner, C., Bens, O., Kern, J., Emmerich, K.H., 2011. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels* 2, 89–124.
- Liu, X., Zhang, A., Ji, C., Joseph, S., Bian, R., Li, L., Pan, G., Paz-Ferreiro, J., 2013. Biochar's effect on crop productivity and the dependence on experimental conditions—a meta-analysis of literature data. *Plant Soil* 373, 583–594.
- Liu, Z., Hoekman, S.K., Balasubramanian, R., Zhang, F.S., 2015. Improvement of fuel qualities of solid fuel biochars by washing treatment. *Fuel Process. Technol.* 134, 130–135.
- Mukherjee, A., Zimmerman, A.R., Harris, W., 2011. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma* 163, 247–255.
- Oleszczuk, P., Joško, I., Kuśmeirz, M., 2013. Biochar properties regarding to contaminants content and ecotoxicological assessment. *J. Hazard. Mater.* 260, 375–382.
- Pasakova, V., Hilscherova, K., Feldmannova, M., Blaha, L., 2006. Toxic effects and oxidative stress in higher plants exposed to polycyclic aromatic hydrocarbons and their n-heterocyclic derivatives. *Environ. Toxicol. Chem.* 25, 3238–3245.
- Phuphuakrat, T., Namioka, T., Yoshikawa, K., 2011. Absorptive removal of biomass tar using water and oily materials. *Bioresour. Technol.* 102, 543–549.
- Reza, M.T., Andert, J., Wirth, B., Busch, D., Pielert, J., Lynam, J.G., Mumme, J., 2014a. Hydrothermal carbonization of biomass for energy and crop production. *Appl. Bioenerg.* 1, 11–29.
- Reza, M.T., Wirth, B., Lüder, U., Werner, M., 2014b. Behavior of selected hydrolyzed and dehydrated products during hydrothermal carbonization of biomass. *Bioresour. Technol.* 169, 352–361.
- Riebe, K., Götz, K.P., Döring, T.F., Roß, C.L., Ellmer, F., 2015. Impact of hydro-biochars on root morphology of spring wheat. *Arch. Agron. Soil Sci.* 61, 1041–1054.
- Ro, K.S., Novak, J.M., Johnson, M.G., Szogi, A.A., Libra, J.A., Spokas, K.A., Bae, S., 2016. Leachate water quality of soils amended with different swine manure-based amendments. *Chemosphere* 142, 92–99.
- Ronsse, F., Van Hecke, S., Dickinson, D., Prins, W., 2013. Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. *Gcb Bioenergy* 5 (2), 104–115.
- Sevilla, M., Maciá-Agulló, J.A., Fuertes, A.B., 2011. Hydrothermal carbonization of biomass as a route for the sequestration of CO₂: chemical and structural properties of the carbonized products. *Biomass Bioenergy* 35, 3152–3159.
- Sharma, R.K., Hajaligol, M.R., 2003. Effect of pyrolysis conditions on the formation of polycyclic aromatic hydrocarbons (PAHs) from polyphenolic compounds. *J. Anal. Appl. Pyrolysis* 66, 123–144.
- Somtrakoon, K., Chouychai, W., 2013. Phytotoxicity of single and combined polycyclic aromatic hydrocarbons towards economic crops. *Russ. J. Plant. Physiol.* 60, 139–148.
- Takaya, C.A., Fletcher, L.A., Singh, S., Anyikude, K.U., Ross, A.B., 2016. Phosphate and ammonium sorption capacity of biochar and hydrochar from different wastes. *Chemosphere* 145, 518–527.
- USEPA, (1995). Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices, Method 3052, third ed. Test Methods for Evaluating Solid Waste, US Environmental Protection Agency, Washington DC.
- Usman, A.R.A., Abduljabbar, A., Vithanage, M., Ok, Y.S., Ahmad, M., Ahmad, M., Elfaki, J., Abdulazem, S.S., Al-Wabel, M.I., 2015. Biochar production from date palm waste: charring temperature induced changes in composition and surface chemistry. *J. Anal. Appl. Pyrolysis* 115, 392–400.
- Visioli, G., Conti, F.D., Menta, C., Bandiera, M., Malcevski, A., Jones, D.L., Vamerli, T., 2016. Assessing biochar ecotoxicology for soil amendment by root phytotoxicity bioassays. *Environ. Monit. Assess.* 188, 166–176.
- Wiedner, K., Rumpel, C., Steiner, C., Pozzi, A., Maas, R., Glaser, B., 2013. Chemical evaluation of chars produced by thermochemical conversion (gasification, pyrolysis and hydrothermal carbonization) of agro-industrial biomass on a commercial scale. *Biomass Bioenergy* 59, 264–278.