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Full Length Article

Influence of Feedstock and Pyrolytic Temperature of Biochar on Physico-Chemical Characteristics and Sorption of Chromium in Tannery Polluted Soil

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Abstract

Leather industry of Pakistan has severely polluted the adjoining tannery area with heavy metal chromium (Cr). A survey of tannery area of Kasur (K) and Sialkot (S) was conducted to determine the Cr toxicity in different locations. In parallel, biochar were prepared at laboratory scale by using feedstocks of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) at 350 and 500°C pyrolytic temperatures. Furthermore, an incubation study was performed to evaluate the effect of biochar on physico-chemical characteristics and adsorption of Cr in tannery polluted soil. Plastic cups were filled with 400 g tannery soil and biochar were applied at rate of 1.5 and 3%. Soil pH, electrical conductivity (EC), cation exchange capacity (CEC) and organic carbon (OC) were affected by application of various kinds of biochar. However, SB-350°C biochar (3%) showed maximum decrease in soil pH (K=7.51, S=7.73), increased the soil CEC (K=22.17, S=27.20 $cmol_c$ kg^{-1}), OC (K=13.27, S=18.21 g kg^{-1}) and reduced the soil available Cr (K=5.45, S=8.94 mg kg^{-1}) observed after 30, 60 and 90 days. Whereas, less increased in soil EC were observed by SB-350°C biochar (1.5%). Conclusively, biochar reduced the Cr availability in tannery polluted K and S soils and SB-350°C biochar applied at the rate of 3% was found more effective in improving soil characteristics and remediation of tannery polluted soil.

Keywords: Chromium; Kasur; Sialkot; Soil; Biochar; Remediation

Introduction

Soil pollution with heavy metal is one of the most serious environmental problems in many places worldwide. Industrial activities have increased the use and extraction of heavy metals for manufacture of various products. The toxicity of these heavy metals and non-degradable nature threaten the soil quality, groundwater, plants survival and human health (Njar *et al*., 2012; Zhang *et al*., 2013; Ghorade *et al*., 2014). Leather industry is one of the most prominent sectors in Pakistan. It is 2nd largest export-oriented industry in the manufacturing sector contribute in GDP and overall export earnings (Ghafoor and Zafar, 2015; PTA, 2016; Pakistan Economic Survey, 2017–2018). There are more than 800 tanneries located on eastern fringe of Pakistan. However, District Kasur (K) (>300) and Sialkot (S) (>250) are the most noteworthy, concentrated with tannery clusters within and around residential area (Bhalli and Khan, 2006; Rafique *et al*., 2010; Syed *et al*., 2010). Lack of environmental management practices results discharge of untreated effluents from tannery industry, severely polluted the nearby soil, air, and underground water (Syed *et al*., 2010).

Chromium (Cr) is a toxic heavy metal declared as a mutagen, teratogen and carcinogen, exists in numerous oxidation states, however, Cr (III) and Cr (VI) are of great concern due to most stable and common form in the environment (Cervantes *et al*., 2001; Singh *et al*., 2013; Junaid *et al*., 2016). Chromium (III) is naturally occurring stable, insoluble and immobile form and it is considered relatively innocuous (Das and Mathew, 2011). Chromium (VI) is a product of industrial activities and it is considered highly toxic, soluble and mobile form of Cr (Costa and Klein, 2006; Razic and Dogo, 2011). Chromium, despite its adverse toxicities, is a widely used heavy metal in leather industry in order to make durable, finish and stable leather by stabilizing the animal hides against moisture, aging and decomposition (Wionczyk *et al*., 2006; Ahamed and Kashif, 2014). The leather industry released huge amount of untreated wastewater due to repeated tanning and washing (3–4 times) of raw hides (Chowdhury *et al*., 2015). A little fraction of Cr salt is used to tan the animal hides and repeated washing discharged the rest of the salt through

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wastewater (Kornhauser *et al*., 2002). Tannery waste when disposed off in soil, the risk of potential oxidation of Cr (III) to the hazardous Cr (VI) may results (Adeel *et al*., 2012; Agrafioti *et al*., 2014). Chromium (VI) accumulation in soil affects soil quality, biota and leached down into deeper soil layers results surface and ground water pollution (Mohan and Pittman, 2006; Ahamed and Kashif, 2014). Moreover, Cr accumulation in soil consequences removal of vegetation covers (Beesley *et al*., 2014). Poor soil structure and low organic matter may results erosion of soil (Ruttens *et al*., 2006; Beesley *et al*., 2014).

Various organic adsorbent materials are used now a day to remediate the polluted soil as well to maintain soil characteristics. Biochar is a porous fine grained charred organic material got remarkable attention to maintain soil structure as a recalcitrant product and could remediate the contaminated soil (Houben *et al*., 2013; Lucchinia *et al*., 2014; Aslam *et al.*, 2017). Source of feedstock and production process may usually regulate the characteristics of biochar (Park *et al*., 2014).

Though, it is even not understood which kind of biochar most efficiently decreases the heavy metals toxicity and what characteristics of biochar are most important in remediation of polluted soil. To the best of our knowledge, a limited work has been reported by individual and interactive effect of feedstock and pyrolysis temperature of biochar on adsorption of heavy metal particularly Cr. In the present study, a survey of tannery area of District Kasur and Sialkot was conducted to determine the Cr toxicity level at different locations (towards and away from tannery industry). Biochar was prepared from feedstock of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) at two pyrolytic temperatures (350 and 500°C). Furthermore, incubation study was conducted to evaluate the effect of different types of biochars on various physico-chemical properties and adsorption of Cr in tannery polluted Kasur and Sialkot soils.

Materials and Methods

Biochar Production

Maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) were used as feedstock for biochar production at 350°C and 500°C pyrolytic temperature. Feedstocks were pyrolyzed in a laboratory setup muffle furnace in anaerobic (oxygen limited) condition as described by Sanchez *et al*. (2009). The pyrolysis was carried out in Pyrex flask (2 Liter) and a bended (60°) glass rod of 2.3 feet basal length with 0.8 feet vertical height connected for the removal of gases and vapors from the muffle furnace. The temperature of the furnace was maintained/adjusted by temperature gauge and the increase was 8–10°C min^{-1}. After attaining the required temperature (350°C and 500°C), 20 min residence time was maintained. On cooling, the Pyrex flask was removed from furnace chamber and biochar was collected.

Characterization of Biochar

Conversion efficiency (yield) of biochar was calculated using the following equation:

Conversion efficiency (%) = (weight of biochar/weight of feedstock) × 100

The surface area and pore volume of the biochar was determined through a surface area analyser (NOVA 1200) using the Brunauer–Emmett–Teller (BET) nitrogen adsorption method at 77 Kelvin (Brunauer *et al*., 1938).

The moisture content of biochar was determined gravimetrically by measuring the difference between fresh weight and weight after being dried for 24 h in an oven (Eyela WFO-600ND, Tokyo Rikakikai, Tokyo, Japan).

Moisture content (%) = ((Fresh weight – Dry weight)/Dry weight) × 100

Volatile matter content (%) was determined as weight loss after combustion in a ceramic crucible with a loose ceramic cap at 850–900ºC for 6 min.

For ash content of biochar, 1 g samples of ground biochar (1-mm sieved) was heated at 200°C for 1 h and then at 750ºC for an additional 4 h in a muffle furnace with no ceramic cap according to method described by Slattery *et al*. (1991).

Ash content (%) = (Weight of ash/Weight of biochar) × 100

Fixed carbon was determined by difference method, as described by Crombie *et al*. (2013) after the determination of moisture, ash and volatile matter.

Fixed carbon (%) = 100 −(moisture + ash + volatile matter) %

The pH and electrical conductivity (EC) of biochar was measured using 1:20 (w/v) suspension ratio after shaking for 90 min in deionized water on mechanical shaker (Rajkovich *et al*., 2012). The CEC of the biochar was measured by a modified NH_4-acetate compulsory displacement method (Gaskin *et al.*, 2008).

The carbon (C), hydrogen (H) and nitrogen content were determined using CHN Elemental Analyzer (Carlo-Erba NA-1500) by a way of high-temperature catalysed combustion through a series of absorption columns selectively trapping CO_2, H_2O and NO_2 gases. Oxygen (O) content was determined by difference method.

Oxygen (%) = 100 −(Ash + C + H + N) %

Macronutrients *i.e*., phosphorus (P), potassium (K) calcium (Ca) and magnesium (Mg) as well as micronutrient *i.e*., zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn) were extracted from biochar samples by a modified dry-ashing method (Enders and Lehmann, 2012). Biochar was weighed to 200 mg and transferred to ashing vessels. Ashing was done for 8 h in a muffle furnace. Then 5 mL HNO_3 was added to each vessel and processed at 120°C on the digestion plate until dryness was reached. On cooling, 1

mL HNO_3 and 4 mL H_2O_2 were added. Samples were placed back into a preheated plate, processed at 120°C before dryness and solubilized. Filtered samples were analysed on inductively coupled plasma with optical emission spectroscopy (ICP–OES).

Soil Analysis

Tannery polluted soil for the experiment was collected from different locations of tannery area of District Kasur (K) and Sialkot (S). The subsamples of the sieved soils were analysed for various physico-chemical characteristics (Table 3). Soil texture was determined by hydrometer method (Gee and Bauder, 1986). The pH of saturated soil paste was measured by Calomel glass electrode assembly. Electrical conductivity (EC) was determined by EC meter of the saturated soil paste extract. Soil organic carbon was determined by TRL-TOC Model Analyzers. Soil cation exchange capacity (CEC) was determined following the method of Sumner and Miller (1996). Calcium carbonate of Kasur and Sialkot soil was determined by method described by Leoppert *et al*. (1984). Total Cr concentration in soil was analysed by atomic absorption spectrophotometer (Perkin Elemer Aanalyst-100) after aqua regia (HCl : HNO_3 = 3:1) digestion (Soon and Abboud, 1993). Chromium (VI) was determined from the soil samples by DTPA method, using 1,5-diphenylcarbazide (Bartlett and James, 1979) with modifications (Menden *et al*., 1990) on a spectrophotometer (Shimadzu UV-1800) at 540 nm wavelength. Chromium (III) was calculated by the difference between the total Cr and Cr (VI) concentration.

Experimental Setup

Soil samples were collected from different locations of tannery polluted areas of District Kasur and Sialkot as shown in Fig. 1 and 2, respectively. Homogenized soil (400 g) was filled in small plastic cups for incubation study. Treatment comprising of biochar prepared from three feedstock (maize stalk, sugarcane bagasse and eucalyptus twigs) at two pyrolytic temperatures (350 and 500°C) was applied at the rate of 0 (control), 1.5 and 3% (w/w). The soil in each plastic cups was thoroughly mixed. Soil pH, EC, CEC, Cr (VI), total Cr and Cr (III) was analyzed after 30, 60, and 90 days of incubation.

Statistical Analysis

Data obtained were analyzed through analysis of variance to estimate the differences among the mean (n=3) values by using standard error at 5% probability level (Little and Hills, 1978) using computer based software.

Results

A detailed survey was conducted in tannery polluted area of District Kasur (K) and Sialkot (S) and soil was collected from different sites to estimate the Cr concentration in major tannery area of the Pakistan.

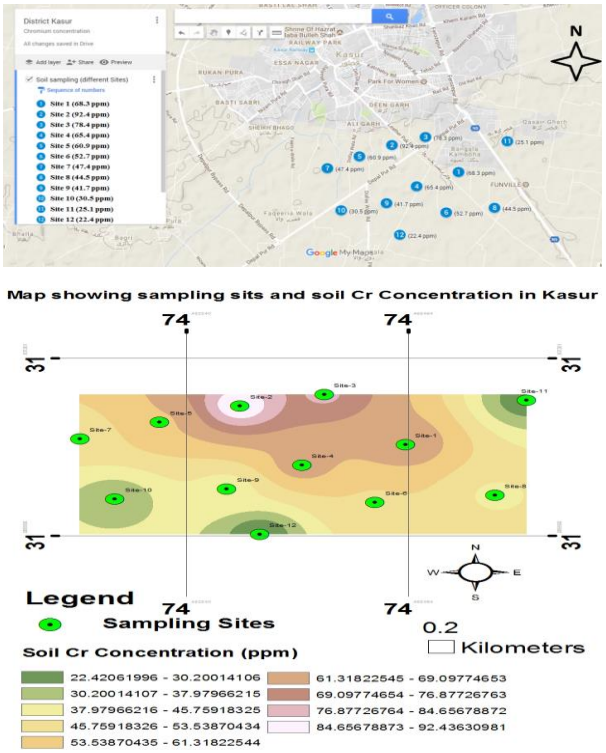

Fig. 1: Soil sampling and range of chromium concentration at different sites of District Kasur, Pakistan

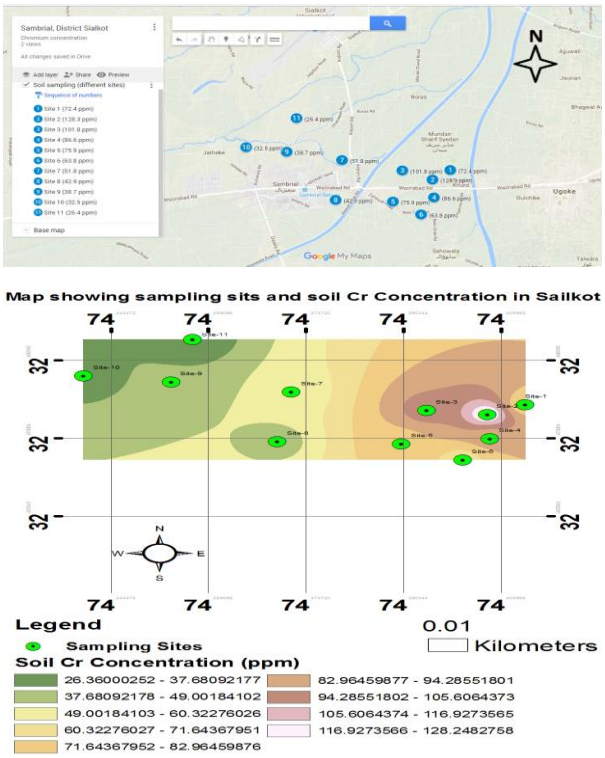

Fig. 2: Soil sampling and range of chromium concentration at different sites of Sambrial, District Sialkot, Pakistan

Table 1: Elemental composition of biochar produced from different feedstock and pyrolytic temperature

Elements	Units	Biochar types					
		Maize stalk		Sugarcane bagasse		Eucalyptus twigs	
		350°C	500°C	350°C	500°C	350°C	500°C
Carbon	%	46.0 ± 0.45	R ± 0.36	54.8 ± 0.40	65.4 ± 0.11	48.2 ± 0.55	59.1 ± 0.27
Hydrogen	%	2.9 ± 0.03	1.4 ± 0.03	2.6 ± 0.13	1.3 ± 0.06	3.1 ± 0.02	2.5 ± 0.03
Oxygen	%	27.6 ± 2.11	20.7 ± 0.35	19.9 ± 1.70	8.3 ± 0.63	27.6 ± 1.80	14.8 ± 1.80
Nitrogen	%	1.5 ± 0.01	1.3 ± 0.01	1.9 ± 0.01	1.7 ± 0.01	1.7 ± 0.01	1.5 ± 0.01
Phosphorous	g kg^{-1}	1.9 ± 0.42	3.8 ± 0.30	2.3 ± 0.62	4.6 ± 0.86	1.3 ± 0.63	2.6 ± 0.41
Potassium	g kg^{-1}	8.6 ± 2.86	15.7 ± 2.68	12.4 ± 1.48	19.4 ± 1.74	9.4 ± 1.94	17.8 ± 3.72
Sulfur	g kg^{-1}	2.3 ± 0.56	3.7 ± 1.35	3.7 ± 0.88	5.3 ± 1.16	2.0 ± 0.15	3.7 ± 1.67
Calcium	g kg^{-1}	8.1 ± 2.91	13.2 ± 1.14	13.7 ± 3.16	18.8 ± 2.78	11.4 ± 2.45	16.7 ± 3.56
Magnesium	g kg^{-1}	4.4 ± 1.43	5.7 ± 0.89	7.9 ± 2.79	10.4 ± 1.99	5.0 ± 2.24	8.6 ± 2.55
Zinc	mg kg^{-1}	57.1 ± 3.56	71.9 ± 2.53	84.5 ± 4.27	98.7 ± 3.85	66.5 ± 3.76	79.5 ± 3.43
Iron	mg kg^{-1}	66.6 ± 2.74	86.7 ± 3.31	88.4 ± 3.38	96.8 ± 3.32	71.9 ± 3.52	85.5 ± 2.29
Manganese	mg kg^{-1}	56.5 ± 2.13	75.5 2.65	81.5 1.84	92.4 2.32	68.7 1.76	84.3 2.02
Chromium	µg kg^{-1}	0.05 ± 0.09	0.08 ± 0.13	0.06 ± 0.03	0.08 ± 0.02	0.07 ± 0.01	0.09 ± 0.02

The values are mean ± S.E. (n=3)

Table 2: Physical/chemical characteristics of biochar produced from different feedstock and pyrolytic temperature

Properties	Unit	Biochar types					
		Maize stalk		Sugarcane bagasse		Eucalyptus twigs	
		350°C	500°C	350°C	500°C	350°C	500°C
pH (1:20)		7.2 ± 0.04	8.4 ± 0.06	6.5 ± 0.04	7.3 ± 0.04	7.5 ± 0.06	9.8 ± 0.09
EC (1:20)	dS m^{-1}	2.2 ± 0.03	4.1 ± 0.05	1.6 ± 0.03	3.2 ± 0.02	3.50 ± 0.02	4.6 ± 0.03
CEC	$cmol_c$ kg^{-1}	54.3 ± 1.20	44.6 ± 0.95	86.9 ± 1.60	66.5 ± 0.70	42.2 ± 0.45	32.2 ± 0.65
Moisture	%	3.2 ± 0.34	2.8 ± 0.08	3.4 ± 0.19	3.0 ± 0.11	4.5 ± 0.28	3.1 ± 0.31
Ash	%	23.0 ± 0.54	25.3 ± 0.43	21.8 ± 0.44	24.3 ± 0.89	20.4 ± 0.85	23.2 ± 0.75
VM*	%	22.5 ± 0.56	18.4 ± 0.48	17.3 ± 0.64	12.5 ± 0.47	21.5 ± 0.32	15.7 ± 0.41
FC**	%	51.4 ± 1.30	53.5 ± 1.50	57.5 ± 1.50	60.2 ± 2.20	53.5 ± 1.40	58.1 ± 1.30
Yield	%	39.1 ± 0.15	27.1 ± 0.20	51.6 ± 0.13	39.7 ± 0.08	54.9 ± 0.07	43.2 ± 0.09
SA***	m^2 g^{-1}	<2 ± 0.00	12.3 ± 0.02	<5 ± 0.01	18.5 ± 0.11	<4 ± 0.04	15.3 ± 0.34
DFT-PV	cc g^{-1}	ND	0.01 ± 0.00	ND	18.9 ± 0.16	0.01 ± 0.00	1.1 ± 0.07

The values are mean ± S.E. (n=3)
* Volatile matter, ** Fixed carbon, *** Surface area

Table 3: Physical/chemical characteristics of tannery polluted Kasur and Sialkot soils

Characteristics of soils	Units	Kasur	Sialkot
Electrical conductivity (EC)	dS m^{-1}	1.469	1.969
Soil texture		Silty loam	Silty clay loam
Organic carbon (OC)	g kg^{-1}	3.41	4.16
Cation exchange capacity (CEC)	$cmol_c$ kg^{-1}	11.56	15.72
Calcium carbonate	%	2.96	3.23
Cr (VI)	mg kg^{-1}	12.45	18.62
Cr (III)	mg kg^{-1}	40.02	54.94
Total Cr	mg kg^{-1}	52.47	73.56

The values are mean ± S.E. (n=3)

Both soils were quite different in their characteristics and Cr concentration (Table 3). The level of Cr toxicity also varied at different locations toward and away from tannery industry in K and S soils (Fig. 1 and 2).

Meanwhile, biochar prepared from feedstock of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) at pyrolytic temperature 350 and 500°C varied in their elemental composition (Table 1). Hydrogen (H), oxygen (O) and nitrogen (N) contents were decreased with increasing pyrolysis temperature of biochar. Maximum content of H (3.1%), O (27.6%) and N (1.9%) were observed in ET, MS and SB biochar, respectively. Carbon (C), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), magnesium (Mg), zinc (Zn), iron (Fe) and manganese (Mn) contents were increased with increasing pyrolysis temperature of biochar and SB biochar have highest content. Similarly, pH, electrical conductivity (EC), ash content, fixed carbon, surface area (SA) and pore volume (PV) of biochar were increased with increasing pyrolysis temperature (Table 2) and SB biochar have lowest pH (6.5), EC (1.6 dS m^{-1}) and highest fixed carbon (60.2%), SA (18.5 m^2 g^{-1}) and PV

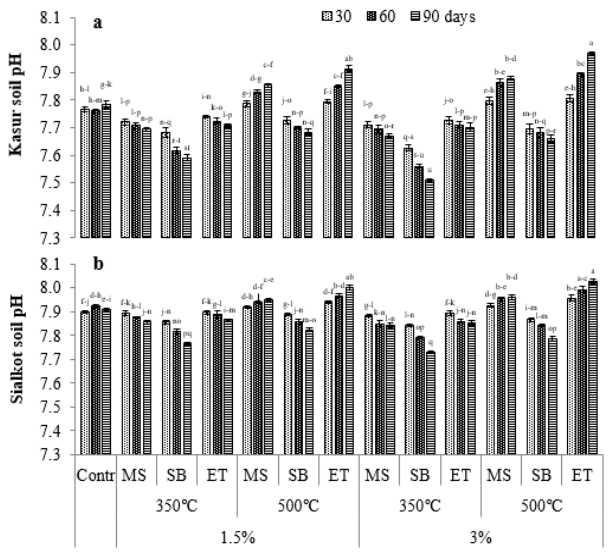

Fig. 3: Effect of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) feedstock and pyrolytic temperature (350 and 500°C) of biochar applied at rate of 1.5 and 3% on temporal change in soil pH of tannery polluted Kasur (a) and Sialkot (b) soil after 30, 60 and 90 days. Columns show mean values and bars show the S.E. of means

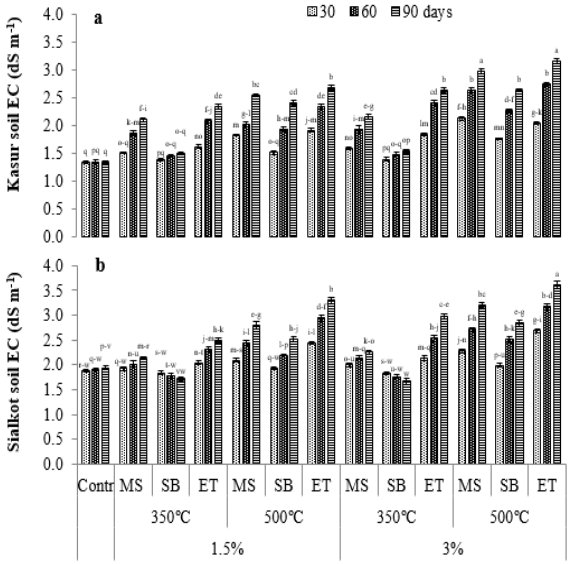

Fig. 4: Effect of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) feedstock and pyrolytic temperature (350 and 500°C) of biochar applied at rate of 1.5 and 3% on temporal change in soil electrical conductivity (EC) of tannery polluted Kasur (a) and Sialkot (b) soil after 30, 60 and 90 days. Columns show mean values and bars show the S.E. of means

(18.9 cc g^{-1}). However, ash contents were highest observed in MS biochar (25.3%). Cation exchange capacity (CEC), moisture content, volatile matter and conversion efficiency was decreased with increasing pyrolysis temperature. Maximum CEC (86.9 $cmol_c$ kg^{-1}) and lowest loss of volatile matter (12.5%) were observed in SB biochar. Whereas, moisture content (4.5%) and conversion efficiency (54.9%) were maximum found in ET biochar.

Influences of various kinds of biochar applied at 1.5 and 3% rate were observed after 30, 60 and 90 days on soil characteristics of tannery polluted K and S soils. Soil pH was increased and decreased depending upon type and characteristics of biochar (Fig. 3). The effects of days were most significantly observed after 90 days as considered to 30 and 60 days. Low temperature biochar (350°C) applied at rate of 1.5% decreased the soil pH. Sugarcane bagasse biochar after 90 days greater decreased the soil pH to 7.59 and 7.77 in K and S soils, respectively as considered to MS and ET biochar. Biochar (350°C) applied at rate of 3% greater reduced the soil pH after 30, 60 and 90 days as considered to biochar (350°C) applied at rate of 1.5%. Sugarcane bagasse biochar (350°C) applied at rate of 3% showed maximum decrease in soil pH to 7.51 and 7.73 in K and S soils, respectively. Biochar prepared at high temperature (500°C) showed variable response on soil pH after 30, 60 and 90 days. Sugarcane bagasse biochar prepared at 500ºC, applied at rate of 1.5% after 90 days, decreased the soil pH to 7.68 and 7.82 in K and S soils, respectively. Whereas, MS and ET biochar (500°C) applied at rate of 1.5% increased the soil pH. Biochar (500°C) applied at rate of 3% after 90 days also showed varying results on soil pH as regarded to biochar (500ºC) applied at rate of 1.5%. Sugarcane bagasse biochar prepared at 500ºC applied at rate of 3% decreased the soil pH to 7.66 and 7.79 in K and S soils, respectively. Whereas, MS biochar (500°C) applied at rate of 3% increased the soil pH after 90 days to 7.88 and 7.96 in K and S soils, respectively. Eucalyptus twigs biochar (500°C) applied at rate of 3% showed maximum increase in soil pH *i.e.*, 7.97 and 8.03 in K and S soils, respectively.

Similarly, soil EC was also altered by application of biochar prepared from different feedstocks and pyrolysis temperatures after 30, 60 and 90 days as shown in Fig. 4. Soil EC in control (0% biochar) treatment was 1.34 and 1.94 dS m^{-1} in K and S soils, respectively. After 90 days, maize stalk and ET biochar (350°C) applied at rate of 1.5% increased the soil EC whereas, SB biochar prepared increased the soil EC (1.51 dS m^{-1}) in K soil and decreased the soil EC (1.72 dS m^{-1}) in S soil as compared to control (0% biochar) treatment. Biochar (350°C) applied at rate of 3% greater altered the soil EC as examined to biochar (350°C) applied at rate of 1.5% after 90 days. Maize stalk and ET biochar (350°C) applied at rate of 3% increased the soil EC after 90 days in K as well in S soil, however, SB (350°C) increased the soil EC (1.54 dS m^{-1}) in K soil and maximum decreased the soil EC (1.67

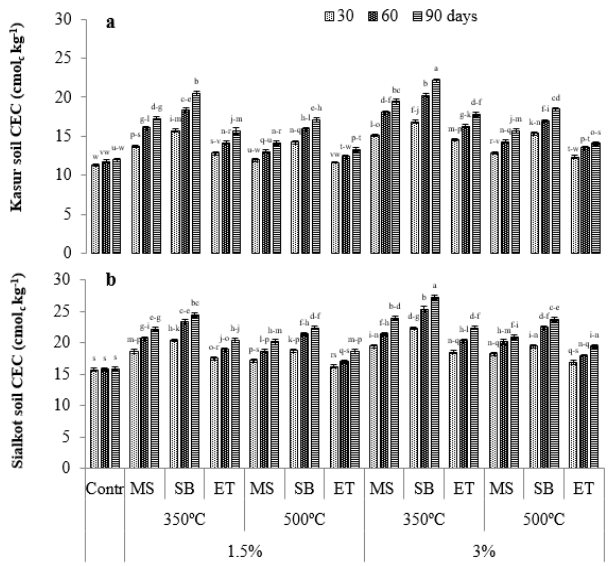

Fig. 5: Effect of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) feedstock and pyrolytic temperature (350 and 500°C) of biochar applied at rate of 1.5 and 3% on temporal change in soil cation exchange capacity (CEC) of tannery polluted Kasur (a) and Sialkot (b) soil after 30, 60 and 90 days. Columns show mean values and bars show the S.E. of means

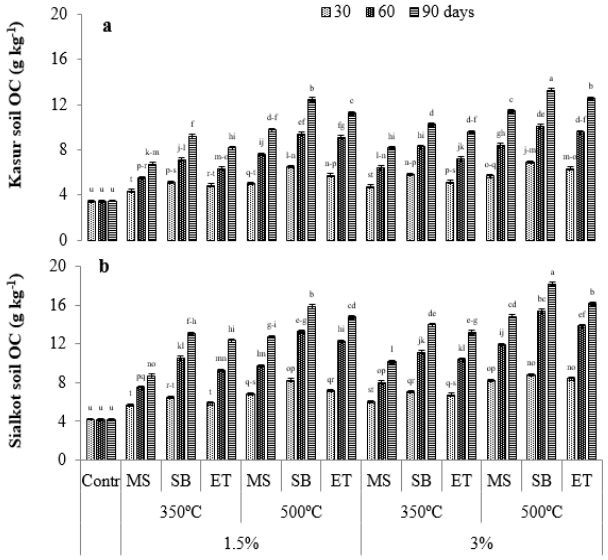

Fig. 6: Effect of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) feedstock and pyrolytic temperature (350 and 500°C) of biochar applied at rate of 1.5 and 3% on temporal change in soil organic carbon (OC) of tannery polluted Kasur (a) and Sialkot (b) soil after 30, 60 and 90 days. Columns show mean values and bars show the S.E. of means

dS m^{-1}) in S soil as related to control (0% biochar) treatment. Biochar prepared at high temperature (500°C) after 30, 60 and 90 days generally increased the EC in K and S soils. Sugarcane bagasse, MS and ET biochar prepared at 500°C applied at rate of 1.5% showed increased in soil EC after 90 days. Biochar (500°C) applied at rate of 3% greater raised the EC as related to biochar (500°C) applied at rate of 1.5% in both K and S soils after 90 days. Eucalyptus twigs biochar (500°C) applied at rate of 3% showed maximum increase in soil EC *i.e.*, 3.15 and 3.61 dS m^{-1} in K and S soils, respectively after 90 days.

Soil cation exchange capacity (CEC) was generally enhanced by application of various types of biochar after 30, 60 and 90 days (Fig. 5). Soil CEC in control (0% biochar) treatment of K and S soils was 11.96 and 15.82 cmol$_c$ kg^{-1}, respectively. Addition of biochar (350ºC) at rate of 1.5% enhanced the soil CEC, however, 3% greater improved. Considered to MS and ET biochar, SB biochar (350°C) applied at rate of 3% maximum increased the soil CEC and it was found 22.17 and 27.20 cmol$_c$ kg^{-1} in K and S soils, respectively. Biochar prepared at high temperature (500°C) showed less increase in soil CEC as regarded to biochar prepared to low temperature biochar (350°C). Biochar (500°C) applied at rate of 1.5% raised the soil CEC, however, 3% application showed greater alteration. Application of 3% ET and MS biochar (500°C) improved the soil CEC after 90 days, whereas, SB biochar greater enhanced the soil CEC in K and S soils and it was detected 18.44 and 23.68 cmol$_c$ kg^{-1}, respectively.

Data regarding soil organic carbon (OC) was increased in general by application of various kinds of biochar after 30, 60 and 90 days (Fig. 6). Soil OC in control (0% biochar) treatment of K and S soils was 3.45 and 4.22 g kg^{-1}, respectively. Maize stalk and ET biochar prepared at 350°C, applied at rate of 1.5% to K and S soils were increased the soil OC. Sugarcane bagasse biochar (350°C) applied at rate of 1.5% after 90 days greater improved the soil OC and it was observed 9.19 and 13.07 g kg^{-1} in K and S soils, respectively. Addition of biochar (350°C) at rate of 3% greater enhanced the soil OC associated to biochar (350°C) applied at rate 1.5%. Biochar prepared at high pyrolytic temperature (500°C) led to more increased in soil OC as regarded to biochar prepared at low pyrolytic temperature (350°C). Maize stalk, SB and ET biochar prepared at 500°C, applied at rate of 1.5% were increased the soil OC in K and S soils after 90 days, whereas, 3% greater improved the soil OC. Considered to MS and ET biochar, SB biochar (500°C), applied at rate of 3% were highest increased the soil OC to 13.27 and 18.21 g kg^{-1} in K and S soils, respectively.

Soil available Cr in the form of Cr (VI) of tannery polluted K and S soils after 30, 60 and 90 days displayed in Table 4. Chromium (VI) concentration in control (0% biochar) treatment of K and S soils were not affected and after 90 days, it was observed 13.01 and 18.87 mg kg^{-1} in K and S soils, respectively. Application of biochar decreased the soil Cr (VI) concentration in both K and S soils. Eucalyptus twigs and MS biochar prepared at 350°C applied

Table 4: Effect of biochar produced from different feedstock and pyrolytic temperature on soil available chromium (Cr (VI)) of tannery polluted soils

Biochar Rate	Pyrolysis Temperature	Feedstock	Cr (VI) Concentration (mg kg^{-1})																	
			Kasur soil									Sialkot soil								
			30 days			60 days			90 days			30 days			60 days			90 days		
		Control	12.8	± 0.12	a-c	12.8	± 0.10	ab	13.0	± 0.15	a	18.5	± 0.12	ab	18.7	± 0.16	a	18.9	± 0.17	a
1.5%	350°C	MS*	11.2	± 0.17	e-j	9.7	± 0.14	n-q	8.8	± 0.14	rs	16.8	± 0.13	c-g	14.4	± 0.33	l-n	12.4	± 0.23	q
		SB**	10.6	± 0.19	i-m	8.4	± 0.11	s	6.7	± 0.11	t	16.2	± 0.17	e-i	13.1	± 0.21	o-q	10.4	± 0.18	s
		ET***	11.8	± 0.22	d-g	10.5	± 0.13	j-n	9.6	± 0.17	n-r	17.1	± 0.18	c-f	15.2	± 0.17	i-m	14.3	± 0.21	l-n
	500°C	MS	11.9	± 0.14	c-f	11.0	± 0.17	f-j	9.8	± 0.11	m-p	17.3	± 0.31	c-e	15.8	± 0.25	g-j	14.5	± 0.16	k-n
		SB	11.5	± 0.23	d-i	9.9	± 0.14	l-o	8.9	± 0.12	q-s	17.7	± 0.19	a-c	16.4	± 0.22	d-i	12.6	± 0.22	q
		ET	12.2	± 0.18	a-d	11.5	± 0.13	d-h	10.6	± 0.15	h-m	17.7	± 0.26	a-c	17.0	± 0.23	c-f	16.0	± 0.26	f-j
3.0%	350°C	MS	10.7	± 0.11	h-l	9.0	± 0.12	p-s	7.5	± 0.16	t	16.1	± 0.20	f-i	13.8	± 0.16	n-p	11.1	± 0.16	rs
		SB	10.1	± 0.10	k-n	7.4	± 0.16	t	5.5	± 0.13	u	15.4	± 0.23	h-l	12.3	± 0.25	qr	8.9	± 0.27	t
		ET	11.3	± 0.16	e-j	9.6	± 0.14	n-r	8.6	± 0.15	s	16.5	± 0.28	d-h	14.2	± 0.21	m-o	12.4	± 0.23	q
	500°C	MS	11.4	± 0.11	d-i	10.0	± 0.13	k-o	9.2	± 0.18	o-s	17.1	± 0.27	c-f	14.8	± 0.23	j-n	12.8	± 0.24	pq
		SB	10.9	± 0.24	g-k	8.7	± 0.21	s	7.3	± 0.16	t	17.2	± 0.21	c-f	15.5	± 0.14	h-l	10.9	± 0.16	s
		ET	11.9	± 0.24	b-e	10.8	± 0.23	h-k	9.9	± 0.17	l-o	17.5	± 0.21	b-d	15.7	± 0.25	g-k	14.6	± 0.26	k-n

*Maize stalk, **Sugarcane bagasse *** Eucalyptus twigs, the values are mean ± S.E. (n=3)

at rate of 1.5% after 90 days decreased the soil Cr (VI) concentration and SB biochar (350°C) were more decreased the Cr (VI) concentration in K (6.67 mg kg^{-1}) and S (10.38 mg kg^{-1}) soil. Biochar (350°C) applied at rate of 3% after 30, 60 and 90 days greater decreased the Cr (VI) concentration as associated to biochar (350°C) applied at rate of 1.5%. After 90 days, ET and MS biochar prepared at 350°C, applied at rate of 3% declined the Cr (VI) concentration in K and S soils. Sugarcane bagasse biochar (350°C) applied at rate of 3% maximum decreased the Cr (VI) concentration to 5.45 and 8.94 mg kg^{-1} in K and S soils, respectively. Biochar prepared at high temperature (500°C) showed less decreased in the soil Cr (VI) concentration as related to biochar prepared at low temperature (350°C). Considered to 1.5% biochar (500°C) applied, 3% biochar greater decreased the Cr (VI) concentration. Eucalyptus twigs biochar (500°C) applied at rate of 3% decreased the Cr (VI) concentration to 9.87 and 14.58 mg kg^{-1} in K and S soils, respectively. As well, MS biochar (500°C) applied at rate of 3% also declined the Cr (VI) concentration in soil to 9.17 and 12.83 mg kg^{-1} in K and S soils, respectively. Sugarcane bagasse biochar (500°C) applied at rate of 3% more declined the Cr (VI) concentration in K (7.30 mg kg^{-1}) as well S (10.92 mg kg^{-1}) soil.

Discussion

Industrial development has improved the living standards of human beings. Lack of implementation of legislative management and no pollution control measures have caused release of heavy metals and recalcitrant pollutants in an exponential amount from various industries which creating severe environment related issues, increasing ecological and global public health concerns. In Pakistan, leather industry is considered one of the oldest and major foreign exchange earner sectors. However, it has severely polluted air, water and nearby land with wide varieties of high strength harmful chemicals. Chromium (Cr) is a toxic heavy metal used in tanning process and discharged out into the soil through waste water (Adeel *et al*., 2012; Nigussie *et al*., 2012). Low soil fertility and accumulation of Cr in soil affect the soil structure and crop growth (Ruttens *et al*., 2006). Biochar is a carbon rich recalcitrant charred organic material produced by process of pyrolysis (Lucchinia *et al*., 2014; Patra *et al*., 2017). It could enhance soil structure, fertility and ameliorate the Cr polluted tannery soil (Choppala *et al*., 2012; Houben *et al*., 2013; Beesley *et al*., 2014).

In present study, a survey of tannery area of Districts Kasur (K) and Sialkot (S) was conducted. The level of Cr toxicity varied with respect to change in location towards and away from tannery industry (Fig. 1 and 2). This variation could be associated to distance from tannery industry and dilution of Cr probably have reduced Cr accumulation (Chowdhury *et al*., 2015; Homa *et al*., 2016). Similarly, the variation in soil characteristics also exists which most likely associated to difference in climatic condition and soil texture (Oyinlola and Jinadu, 2012; Karmakar *et al*., 2016). In addition, the level of Cr toxicity also varied, and S soil have high amount of Cr concentration associated to K soil. Tannery waste water treatment plant at Kasur, in general, remove the Cr in the form of solid particles and sludge which perhaps have reduced the accumulation in soil (Syed *et al*., 2010). Whereas, at Sialkot there is lack of treatment plant facility and tannery industry waste water is directly discharged into sewerage drains, ponds and open agricultural lands (Bhalli and Khan, 2006; Rafique *et al*., 2010).

Elemental composition of biochar especially carbon (C) hydrogen (H) and oxygen (O) is quite complex and relate to kind of feedstock and pyrolysis temperature (Bourke *et al*., 2007; Masek *et al*., 2013). The content of nitrogen, hydrogen, oxygen and yield of biochar were decreased with the increase of pyrolysis temperature which may related to low volatilization temperature and increase in loss of volatile matters (Baldock and Smernik, 2002; Gai *et al*., 2014). Whereas, accumulation of carbon and other

elements (P, K, S, Ca, Mg, Zn and Fe) in biochar with increased in pyrolysis temperature associated to high volatilization temperature and concentrated these elements due to loss of volatile elements (Al-Wabel *et al*., 2013; Suliman *et al*., 2016). Similarly, the increased in pH, electrical conductivity (EC) and ash content of biochar might be associated to the fact of loss of weight (yield) and accumulation of recalcitrant ionic species in the residue (Inyang *et al*., 2010; Suliman *et al*., 2016; Shah and Shah, 2017). Removal of volatile matter and conversion of aliphatic carbon into complex aromatic carbon could be a possible reason of increased in carbon content of biochar (Joseph *et al*., 2010; Sun *et al*., 2017). Similarly, kind of feedstock also control the characteristics of biochar *i.e*., herbaceous and woody materials give rise more carbon content as regarded to animal manure or sludge (Novak *et al*., 2009; Bruun *et al*., 2011). Feedstock with high mineral and lignin content usually increased the yield of biochar (Antal and Gronli, 2003). Functional groups formation determines the cation exchange capacity of biochar (Rajkovich *et al*., 2012; Jien and Wang, 2013). In the present study, the cation exchange capacity was high in biochar prepared at low temperature (350ºC) and it was decreased by increasing pyrolysis temperature. Decomposition of cellulose and lignin by increasing pyrolysis temperature may results loss of functional groups of biochar and it could be a possible reason of decline in cation exchange capacity (Novak *et al*., 2009; Kloss *et al*., 2012). Similarly, pore volume and surface area of biochar also correlate with pyrolysis temperature and kind of feedstock (Ogawa *et al*., 2006; Chen *et al*., 2008). Formations of micro pores during pyrolysis of biochar contribute to surface area (Bird *et al*., 2008). In current study, increasing pyrolysis temperature of biochar enhanced the surface area and pore volume of biochar. Increased in surface area of biochar most likely be associated to formation of dense graphene layer with aromatic carbon leads to inordinate micro and nano pores (Gray *et al*., 2014; Song *et al*., 2014). Large surface area and functional groups of biochar may also serve as an adsorbent material for pollutants (Beesley and Marmiroli, 2011; Jiang *et al*., 2012).

Furthermore, effect of maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) biochars prepared at 350 and 500°C, applied at rate of 1.5 and 3% were observed on soil physico-chemical characteristics after 30, 60 and 90 days. Biochar application significantly ameliorated the tannery polluted K and S soils and 3% application rate of biochar showed better results as compared to 1.5%. Similarly, increasing incubation period (30, 60 and 90 days) improved the soil characteristics and decreased Cr availability. Soil pH was significantly altered by application of different types of biochar after 90 days of incubation. Biochar prepared at low temperature (350ºC) usually have low pH and addition of biochar in K and S soils were useful to decrease the soil pH. The difference in pH values of biochar and pH of soils might be the main reason of decreasing the soil pH from one to two units (Lehmann, 2007; Wu *et al*., 2014). The decrease in soil pH might also be associated to decomposition of organic materials (Dias *et al*., 2010; Luo *et al*., 2011). Acidic material formation in biochar treated soil could be involved in decreasing the soil pH (Cheng *et al*., 2006; Zavalloni *et al*., 2011; Liu and Zhang, 2012). Biochar in soil is not at all inert, it is slowly oxidized at surface by chemical and microbial action in the soil. Carboxylic functional groups perhaps have produced in soil by slowly oxidization of biochar and it could be entangled in lowering soil pH (Cheng *et al*., 2008). Production of biochar at high temperature (500°C) generally have high pH (>8) except SB biochar and its application has raised the pH in K and S soils. The increase in soil pH could be because of high accretion of biochar ash or disintegration of carbonates and hydroxide of biochar (Lucchinia *et al*., 2014; Kamara *et al*., 2015).

Similarly, to soil pH, the soil EC is a general measure of the amount of soluble salts content in soil solution (Hossain *et al*., 2011). The soil EC of the K and S soils altered to the greater magnitude which may also relates to the nature of feedstock and pyrolysis temperature. High EC may disturb soil characteristics and consequently led to detrimental impacts with ions imbalance (Tag *et al*., 2016). Our results showed that addition of SB biochar prepared at 350°C increased the soil EC in K soil whereas, in S soil, it decreased the soil EC. This increased in soil EC of K soil might be associated to greater EC of biochar as related to EC of K soil. Similarly, low EC of biochar might also be associated to decrease in soil EC in S soil. Biochars (SB, MS and ET) prepared at 500°C generally have raised the EC of K and S soils which might be attributed to high EC of biochars as considered to EC of soil. Salts such as carbonate, sulphate and chloride of calcium, magnesium, potassium and sodium perhaps have accumulated in soil through addition of biochar (Yadav *et al*., 2016). These salts mostly present in ash content of biochars which could be main cause of increase in soil EC (Nigussie *et al*., 2012; Abrishamkesh *et al*., 2015).

Soil cation exchange capacity (CEC) is one of the most important characteristics expressing the ability of soil to hold and exchange cations and thus their availability in soil (Singh *et al*., 2010; Peng *et al*., 2011). In the present study, addition of biochar into K and S soils enhanced the soil CEC with passage of incubation period and reached to highest value after 90 days. Sugarcane bagasse biochar prepared at 350°C maximum raised the soil CEC. As a result, it is quite reasonable that biochar remarkably have greater intrinsic CEC than the corresponding soils (K and S). It is evidenced that high CEC of biochar into soil keeps the nutrients from losses (Tag *et al*., 2016). Aging of biochar may develop negative exchange sites on biochar surfaces and could involve in enhancement of soil CEC (Cheng *et al*., 2008). Oxygenated functional groups (Carboxylic, lactonic and phenolic) formation on the

biochar surfaces could also be associated in improvement of soil CEC (Nelissen *et al*., 2014; Suliman *et al*., 2016). Similarly, high surface area and pore volume of biochar may also accompany to the enhancement in soil CEC (Gundale and DeLuca, 2006; Cornelissen *et al*., 2013).

Soil organic carbon (OC) is most important constituents mainly contribute the mineral nutrition, CEC and source of energy for microorganisms in soil (Warnock *et al*., 2007). Its availability relates to fraction of soil organic matter in which it resides. An increased in soil OC was observed during the 90 days of incubation which suggests that the biochar contains high carbon content and have great potential for carbon sequestration in soil and could decrease the mineralization rate (Hammes and Schmidt, 2009; Nigussie *et al*., 2012). Biochar can stimulate microbial activity by providing easily decomposed carbon (Bruun *et al*., 2011). In current study, biochar probably has adsorbed the native soil OC on its surfaces and suppress its degradation (Kasozi *et al*., 2010; Zimmerman *et al*., 2011). High temperature (500°C) biochar more enhanced the soil OC which might be attributed to high carbon content and resistant against microbial degradation and chemical oxidation due to aromatic structure (Joseph *et al*., 2010; Sun *et al*., 2017). Similarly, increased in soil OC may also relates to feedstock characteristics (Novak *et al*., 2009; Bruun *et al.*, 2011) since SB biochar were greater enhanced the soil OC in K and S soils.

Soil available Cr in the form of Cr (VI) was decreased in K and S soils by usage of biochars prepared from different feedstocks and pyrolytic temperatures. This decreased in Cr (VI) concentration might be attributed to adsorption on biochar surfaces or it may reduce to Cr (III). High surface area and pore volume of biochar could act as an adsorbent material for pollutants on its surface or retained inside the pores (Patra *et al*., 2017). Sorption of Cr may take place by adsorption or adsorption coupled with reduction on biochar surfaces (Park *et al*., 2006). Biochar possess charged surfaces and could sorb Cr (VI) on biochar by electrostatic attraction (Tang *et al*., 2013; Lopez-Capel *et al*., 2017). Biochar might also have formed the precipitates of chromium with various mineral compounds like oxidates, carbonates or phosphates present on biochar surfaces (Beesley *et al*., 2011; Park *et al*., 2011; Tang *et al*., 2013). Moreover, Cr might also have formed complexes with different acidic (hydroxyl, carbonyl, phenol, carboxylic and lactonic) and basic (ketone, pyrone and chromene) functional group exist on biochar surfaces and therefore a decrease in its availability and toxicity was evidenced in our results (Uchimiya *et al*., 2011; Choppala *et al*., 2012; Ahmad *et al*., 2013). These functional groups may increase by oxidation of biochar in soil over time (Chen *et al*., 2008). Furthermore, soil pH and redox potential could play an important role of solubility and mobility of Cr (Razic and Dogo, 2011; Houben *et al*., 2013). In soil, iron, sulfur or organic matter are considered the principal source to donate electron and can reduce Cr (VI) into Cr (III) (Kotas and Stasicka, 2000; Choppala *et al*., 2012). Biochar might have also altered the oxidation state of Cr by adsorption of Cr (VI) initially on its surfaces and then sorbed Cr (VI) might have reduced to Cr (III) (Hsu *et al*., 2009). In another way, polycyclic aromatic hydrocarbon sheet of biochar most likely has donated the electron and reduced the Cr (VI) into less soluble Cr (III) (Saha and Orvig, 2010; Wang *et al*., 2010) and then adsorption of Cr (III) on biochar surfaces (Choppala *et al*., 2012; Liu *et al*., 2014). Alteration in soil pH could also change the oxidation state of Cr. In addition, Cr (VI) species usually dominate at high pH and it might be also reduced to Cr (III) by lowering of soil pH (Agrafioti *et al*., 2014; Liu *et al*., 2014). Increasing incubation period (30, 60 and 90 days) decreased the Cr (VI) concentration and maximum declined in Cr (VI) was observed after 90 days. Moreover, in the beginning all adsorbent sites on the biochar surfaces might be vacant and metal adsorption efficacy on adsorbent material may increase over time (Okoli and Ezuma, 2014; Mellis *et al*., 2017). Considering to high temperature biochar (500°C), low temperature biochar (350°C) were found more effective in declining the Cr (VI) concentration may be due to processing low (neutral) pH, high cation exchange capacity and greater amount of functional groups (Kloss *et al*., 2012; Gai *et al*., 2014). Chromium (VI) compound is an anion and has negative charge on its surface and increasing pyrolysis temperature of biochar have increased the pH and decreases positive charges on biochar surfaces, therefore, it might have decreased the adsorption of Cr (Lou *et al*., 2016). Similarly, declines in exchange capacity of biochar with pyrolysis temperature have also lowered the retention of Cr on its exchange sites (Wang *et al*., 2015). Most of the functional groups of biochar were lost or modified into recalcitrant aromatic structure at high charring temperature and may describe the lowering of biochar cation exchange capacity (Yuan and Xu, 2011; Domingues *et al*., 2017). In our results, 3% biochar application showed more decrease in Cr (VI) concentration as regarded to addition of 1.5% biochar in K and S soils. Increasing biochar application rate provides more adsorption sites and it might have immobilized the heavy metal Cr and lowered its availability. Sugarcane bagasse biochar were highest decreased the Cr (VI) concentration as regarded to MS and ET biochar in both K and S soils. This reduction of Cr concentration was found by SB biochar which might be associated to its basic characteristics like low pH, EC, high surface area, pore volume, cation exchange capacity, carbon fraction and mineral percentage and may results precipitation or complex formation with abundant mineral and functional groups (Beesley *et al*., 2011; Choppala *et al*., 2012).

Conclusion

Biochar prepared from maize stalk (MS), sugarcane bagasse (SB) and eucalyptus twigs (ET) at 350 and 500°C pyrolytic temperature, applied at rate of 1.5 and 3% were affected the

soil pH, EC, CEC, soil OC and Cr (VI) concentration after 30, 60 and 90 days of Kasur (K) and Sialkot (S) soils. Soil pH of K and S soils were generally decreased by low temperature (350°C) biochar, whereas, it were increased by application of biochar prepared at high temperature (500°C) (except sugarcane bagasse). Similarly, soils EC were normally increased by application of various types of biochars (except sugarcane bagasse prepared at 350°C in S soil). Soil CEC were more increased by low temperature biochar (350°C) associated to high temperature biochar (500°C) in K and S soils. Organic carbon of K and S soils were more accumulated by high temperature (500°C) biochar. Chromium (VI) was decreased by application of biochar in K and S soils and low temperature biochar (350°C) showed better results. Biochar application at rate of 3% were more influenced the soil pH, EC, CEC, OC and Cr (VI) concentration and SB biochar gave better results and reduced the Cr (VI) concentration.

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