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Phosphate-lanthanum coated sewage sludge biochar improved the soil properties and growth of ryegrass in an alkaline soil

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A R T I C L E I N F O

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A B S T R A C T

The reclamation of alkaline soils remains challenging while the application of biochar has been proposed as a viable measure to rehabilitate soil fertility. The objective of the current pot study was to evaluate the efficacy of various P-La modified sewage sludge biochars (SSBC, La-SSBC, SSBC-P, La-SSBC-P) on soil phosphate-retention and ryegrass (*Lolium perenne* L.) growth in an alkaline soil (excess $CaCO_3$). The results revealed that germination percentage, plant dry biomass, plant height, and the total amount of P in the ryegrass leaves were significantly ($P < 0.05$) improved under La-SSBC-P treatment as compared to other treatments. La-SSBC-P treatment significantly altered the chemical characteristics of post-harvest alkaline soil, such as pH, electrical conductivity (EC), cation exchange capacity (CEC), soil organic matter (SOM), limestone ($CaCO_3$), phosphate, and lanthanum contents. In comparison to the SSBC treatment, soil available phosphorous (AP) contents under La-SSBC-P were enhanced by 6.7 times after loading biochar with P and La (La-SSBC-P). After the plantation of ryegrass, concentration of lanthanum in the soil was negligible. The contents of $CaCO_3$ reduced by 76.2% after La-SSBC-P biochar treatment, compared to the cultivated control. This phenomenon clearly indicated that lanthanum was reduced due to the precipitation with limestone, which was proposed based on the data of X-ray diffraction (XRD) analysis. Overall, results showed that the P-loaded lanthanum decorated biochar (La-SSBC-P) could be used as a potential substitute for P-fertilizer under the experimental conditions. However, field experiments are required to confer the efficiency of La-SSBC-P as P fertilizer in different soils.

1. Introduction

The supply of an appropriate and adequate amount of nutrients and water without any hazardous substances (organic and inorganic) to various crop plants is a serious concern to ensure the food security worldwide (Havlin et al., 2013). The productive lands have been considered the essential sink for the sustainable agricultural production; however, the degradation of fertile soils is intensively increasing around

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the globe (Cai et al., 2019; Kamran et al., 2020b). Moreover, in arid and semi-arid region of the whole world, soil fertility is commonly constrained where the alkaline soil predominates, and rainfall is minimal. In alkaline soils, most of the essential nutrients are unavailable to the plants, having low amounts of organic matter and water holding capacity because of high soil pH (Ali et al., 2019). Moreover, it is well known that the availability (solubility) of plant nutrients is considerably affected by the soil pH along with other factors. Among all the essential nutrients, plants usually uptake fourteen mineral elements including primary and secondary nutrients from the soil after being dissolved in the soil solution to complete their life cycle. Most essential minerals elements are available at a pH range of 6.5–7.5 than acidic and alkaline soils (Singh et al., 2016).

Phosphorous (P) is a fundamental macronutrient which is responsible for enhancing the global crop production and is mainly supplied to the soil through the various sources (Jiang et al., 2021). Recently, it has been revealed that 5.7 billion hectors of agricultural soils are P deficient throughout the world (Ma et al., 2020). In contrast, around 3–4 million tons of applied inorganic P fertilizers (especially in China) have been leached into the surface/groundwater through infiltration, drainage, or surface runoff (Hong-ling et al., 2010; Jaisi et al., 2011), which in turn cause the eutrophication or red tide in the water ecosystems (Vohla et al., 2011; Niyungeko et al., 2018). It is estimated that around 80% of applied P becomes unavailable to plants due to its immobile nature in the soil and has ability to form complexes with other nutrients such as aluminum (Al) and iron (Fe) (Rana et al., 2020; Teng et al., 2020). The salt affected soils in China have higher pH, an excessive quantity of carbonates (CO_3^{2-}) and sulfates (SO_4^{2-}), and have less amount of organic matter (OM), which ultimately enhance the P leaching risks that led to reduce its retention and availability to plants (Xu et al., 2016; Wu et al., 2020). Besides, the P leaching process depends on various soil factors, including soil pH, Fe/Al oxides, clay minerals, CEC and organic matter (Luengo et al., 2007; Uchimiya et al., 2010). The reduction in P was observed in the alkaline soil conditions because of the significant decrease in P sorption on the bindings sites which is greatly influenced due to the greater electrostatic repulsion (Jiang et al., 2015). Additionally, P is also present in negatively charged form, which becomes unavailable to the plants because of strong complexation with Fe/Al oxides (Arai and Livi, 2013; Chen et al., 2018). The leaching and fixation of P has been considered an emerging issue and recognized as a global constraint that badly affects the efficiency of P fertilizers in sustainable production systems. Therefore, it is the need of time to understand the soil P dynamics (release and retention) in alkaline soils and development of novel organo-mineral fertilizers that can improve the soil fertility.

Among the different soil remediation amendments, biochar has been recently proposed as an efficient tool to rehabilitate the fertility of alkaline soils (Cai et al., 2020; Yang et al., 2021). However, the effect of biochar application on soil varies with the biochar induced feedstock, modification methods as well as soil types. The application of biochar can improve the soil fertility, retain nutrients and thereby enhance the plant growth (Bonanomi et al., 2017; Kamran et al., 2019), and affects the soil pH, electric conductivity (EC), organic carbon, and cation exchange capacity (CEC) of the soil (Wang et al., 2016; Saifullah et al., 2018). The positive effects of biochar on soil and plants might be due to the presence of plant-available nutrients, large surface area, porous structure, that could contribute to provide the habitat for microorganisms (Lehmann et al., 2006; Li et al., 2019; Kamran et al., 2020a). However, the production of biochar through conventional methods may limit its efficiency in terms of surface functional groups, anion exchange capacity, and specific surface area (Zheng et al., 2020; Zhu et al., 2020). To the fact, negatively charged surfaces of biochar provides the efficient binding sites for the adsorption of various anions such as phosphate and nitrate. It was previously reported that the traditional biochars have < 5 mg g^{-1} P adsorption capacity (Jung et al., 2017; Liao et al., 2018). Consequently, different suggestions were proposed to avoid the alkaline effects of biochar i.e., treatment of biochar with various chemicals and nutrients (Qayyum et al., 2020), composting of biochar (Steiner et al., 2010; Fischer and Glaser, 2012), change in the porous nature of biochar matrix with nutrients (Zheng et al., 2020), and increase in the biochar surface reactivity using enhanced oxidative aging (Cheng and Lehmann, 2009; Liu et al., 2020). Biochar surface decoration with oxides of metals/nutrients (Fe, Ca, Mg, Al, and La) can improve the phosphate retention efficiency of alkaline soils (Yin et al., 2018; Wu et al., 2019; Jia et al., 2020). In particular, lanthanum (La) has been found to be the cost-effective, harmless in the environment, and a novel candidate for P (PO_4^{3-}) adsorption from the wastewater (Pham et al., 2019; Jia et al., 2020). Moreover, the phosphate-doped biochar could consider a better strategy for slow-release P fertilizer in the soils for sustainable management of soil fertility (Zhang et al., 2020). Therefore, phosphate-loaded-$La(OH)_3$ modified biochar would be a win-win approach for enhancing nutrients availability, P retention, and sustainable management of alkaline soil.

Ryegrass (*Lolium perenne* L.) has been considered a perennial turf grass and forage species which is extensively cultivated in the temperate areas of the world (Xing et al., 2007). It would be of great importance to establish the perennial ryegrass in alkaline soils for the turf industry as well as soil compaction, which is an important characteristic of such soils (Wu et al., 2005). Keeping in view the above discussion, we hypothesized that sewage sludge biochar induced modification with P-La might be the suitable candidate for P availability in alkaline soil. Therefore, the prime objective of the current investigation was to assess the (i) surface characterization of sewage sludge induced biochars using synchrotron techniques (FTIR and SEM) before and after P-La-modification (ii) the impact of P-La modified biochar application on the growth of ryegrass as well as the induced alterations in the selected soil chemical characteristics, (iii) and the efficacy of the P-La modified biochar on nutrients uptake and bioavailability (especially P) in the alkaline soil.

2. Material and methods

2.1. Materials collection

Lanthanum nitrate [$La(NO_3)_3$], potassium dihydrogen phosphate (KH_2PO_4), isopropanol (C_3H_8O), hydrochloric acid (HCl), and ammonium acetate ($C_2H_7NO_2$) were acquired from Tianli Chemical Reagent located in Tianjin, China. All reagents were of analytical grade while the solutions were prepared in duly-deionized (DI) water. Similarly, sewage sludge as a feedstock was collected from the municipal wastewater treatment plant (Tangxun Lake) situated in Wuhan, Hubei, China.

2.2. Biochar production

Pristine biochar was obtained after the slow pyrolysis of dried sewage sludge at 400 °C for 2 h in a furnace tube in the presence of N_2 under limited oxygen supply. The resulted sewage sludge biochar (SSBC) was ground and passed through a sieve (0.3 mm) before modification (Ifthikar et al., 2017). Thereafter, La-coating of SSBC was performed by following the method of Jia et al. (2020) with some minor modifications. Briefly, uniformly suspended magnetic biochar was obtained after the stirring of 1.0 g SSBC in 25 mL de-ionized (DI) water for 30 min. Then, Lanthanum (III) nitrate [$La(NO_3)_3$] was dissolved in 25 mL of isopropanol and added to the above-mentioned magnetic biochar suspension. The resulting suspension was stirred for 18.5 h prior to changing the pH value to 9.0. Subsequently, magnetically stirred for 5 h and the resulting suspension was allowed to settle down for 24 h. After this, the powders were separated, washed with DI water and ethyl alcohol and dried out at 80 °C for overnight to obtain the adsorbent entitled Lanthanum-decorated sewage sludge biochar (La-SSBC). Eventually, phosphate adsorption was carried out on the surfaces of SSBC and La-SSBC which were entitled as phosphate loaded-sewage sludge biochar (SSBC-P) and phosphate loaded-La decorated sewage sludge biochar (La-SSBC-P), respectively.

2.3. Biochar characterization

Elemental composition (C, H, N, and S) of various biochar samples was detected by cube elemental analyzer (Vario MICRO, German). Pore width and pore volume of the biochar samples were measured using Brunauer-Emmett-Teller (BET, Micromeritics ASAP 2420, USA) to examine the physical characteristics. Chemical interaction was observed by Fourier transform infrared spectrometer spectra (FTIR, VERTEX 70, USA) using the KBr pellet technique. Surface morphology was observed using Quanta 200 ESEM (FET, Holland). The crystalline structure of biochar was characterized via X-ray diffraction spectra in the range of 0–90 theta degree (XRD, X′Pert PRO X-ray photoelectron spectrometer, PANalytical B.V, Holland) and the phase was identified by search-match approach using JCPDS (Joint committee of powder diffraction standard) database. The basic properties of all decorated biochars have been presented in Table (1).

2.4. Pot experiment and growth conditions

Soil samples were collected from the depth of 0–20 cm from the field area of Huazhong University of Sciences and Technology, Wuhan, P.R. China. The collected soil was packed into polyethylene bags and transported to the laboratory for further basic analysis and for the pot experiment. Then soil samples were passed through a sieve (2 mm) after air drying, grinding and removing the plant residues, litter and pebbles. A pot (height 12, bottom diameter 7, and upper diameter 10 cm) experiment was designed after cleaning the pots with DI water. Each pot was filled with 200 g natural alkaline soil. The pristine biochar (SSBC) and all modified biochars (La-SSBC, SSBC-P, La-SSBC-P) were mixed with the air-dried alkaline soil at 1% application rate (on dry weight basis; w/w), respectively. For control treatment, only alkaline soil without any biochar was used. After that, all pots were incubated for 7 days at 60% field capacity was maintained throughout the incubation period. The current study was carried out in a completely randomized statistical design (CRD) with four replications of each treatment. Later on, ten healthy seeds of ryegrass were sown per pot and placed them in a greenhouse under controlled environment i.e., temperature (18–20 °C) and humidity (55–60%). The soil moisture content was maintained in each experimental unit as per need of the seedlings depending on the climatic variations.

Table 1
Basic physical and chemical properties of the alkaline-soil and various P-La decorated sewage sludge biochars used in the pot experiment.

Properties	Unit	Soil	SSBC	La-SSBC	SSBC-P	La-SSBC-P
Sandy	%	4	–	–	–	–
Clay	%	64	–	–	–	–
Silt	%	32	–	–	–	–
Soil Texture	–	Clay soil	–	–	–	–
pH	–	8.08 ± 0.02	9.0			
Available P	ppm	16.11 ± 1.37	39.31 ± 1.02	98.12 ± 0.95	141.52 ± 2.43	264.62 ± 1.55
Total C	%	1.91 ± 0.04	8.23 ± 0.01	7.01 ± 0.07	7.66 ± 0.03	6.22 ± 0.01
Total K	$cmol_c\ kg^{-1}$	–	2.05 ± 0.17	1.82 ± 0.05	1.69 ± 0.02	2.36 ± 0.03
Nitrogen	%	–	2.07	2.98	–	–
Sulfur	%	–	2.52	1.21	–	–
Specific surface area (BET)	($m^2\ g^{-1}$)	–	40.96	17.25	21.86	15.32
Pore volume	($cm^3\ g^{-1}$)	–	0.116	0.096	0.084	0.043
Pore width	Å	–	11.36	22.32	16.94	25.71

The given data is the average of 4 replications (n = 4) ± standard deviation (SD).

2.5. Determination of growth attributes

The germination rate (%) was computed by calculating the germinated seeds of ryegrass after one week of sowing using the following equation as explained by Sadaf et al. (2017):

$$Germinationrate(\%) = \frac{SE}{SS} \times 100$$

Where SE represents the count of seedlings germinated after a week and SS is the total count of the seeds sown in pots.

Finally, the height of ryegrass plants was recorded after 30 days of seed sowing and subsequently plants were harvested. The dry biomass of the ryegrass was calculated after the sample drying at 55 °C for about 24 h.

2.6. Soil and plant analysis

All the soil samples were air-dried and passed through a sieve (2 mm) before and after the plantation of ryegrass. The basic soil physico-chemical properties were determined with and without modified biochars application (before and after incubation) and in the post-harvest alkaline soil which were presented in Tables 1 and 3. Soil texture (sand, silt and clay contents) was determined using the pipet method as elaborated previously (Gee and Bauder, 1986). The chemical characteristics [pH, CEC, EC, $CaCO_3$, Total C, available P, exchangeable cations (Ca, Mg, Na, and K), phosphate and lanthanum] of the initial soil as well as the post-harvest soil were determined by using pH (Orion Versa Star Mmultiparameter) and EC meters (Thermo Scientific, USA), and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Soil organic matter (SOM) was estimated using the wet oxidation method as proposed by Walkley and Black (1934). The digestion of the soil samples was carried out through aqua regia consisting of HCl: HNO_3: $HClO_4$ (3:1: 1 ratio) using an open flask system (Chen and Ma, 2001). Similarly, the basic exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) were examined on ICP-MS. The cation exchangeable capacity (CEC) of the studied soil was measured using the method explained by Page et al. (1982). A soil to pure water mixture (1:5 ratio) was used for the measurement of soil available P by using ascorbic acid method with a spectrophotometer (Kuo, 1996). Both fresh and dried leaf samples were digested using di-acid mixture (HNO_3:$HClO_4$; 2:1 ratio) to determine various elements in samples (Jones and Case, 1990). Elemental concentration of La, phosphate, total P and total K (on fresh and dry biomass basis) in leaves of ryegrass were determined through a microwave plasma atomic emission spectroscopy (MP-AES 4200, USA).

2.7. Statistical analyzes

Statistically significant differences among treatments were done by SPSS v22.0®IBM opting one-way ANOVA along with Tukey's honest significant difference (HSD) test at $P < 0.05$. In addition, The Pearson's correlation coefficients (r values) were determined to evaluate the relationships between various characteristics of soil and plant. However, principal component analysis (PCA) was done by Minitab v16 software.

3. Results

3.1. Initial soil properties

The basic physical and chemical properties of the alkaline soil were as following: pH (8.08); sand contents 4%, clay contents 64%, and silt contents 32%; clayey soil texture; available P (16.11 ppm); total carbon (1.91%); 0.45 mS cm^{-1} electrical conductivity (EC); and 26.16% limestone ($CaCO_3$). The basic soil properties have been shown in Tables 1 and 3.

Table 2
Effect of P-La decorated sewage sludge biochar on growth, lanthanum and nutrients concentrations in the leaves of ryegrass along with post-harvest soil CEC, organic carbon and available phosphorous.

Treatment	Germination %	Aboveground dry biomass (g pot^{-1})	Plant height cm	Lanthanum ppm	Phosphate ppm	Total leaf P-FB (cmol c kg^{-1})
Control	10.00	0.03 ± 0.00e	10.30 ± 0.16e	0.00 ± 0.00b	5.47 ± 0.00e	0.01 ± 0.00b
SSBC	33.33	0.09 ± 0.00d	12.69 ± 0.46d	0.00 ± 0.00b	18.90 ± 050d	0.29 ± 0.04ab
La-SSBC	50.00	0.14 ± 0.00c	17.63 ± 0.41c	0.00 ± 0.00b	46.40 ± 0.96c	0.19 ± 0.01ab
SSBC-P	60.00	0.21 ± 0.02b	18.29 ± 0.25b	0.00 ± 0.00b	68.26 ± 2.12b	0.26 ± 0.00ab
La-SSBC-P	66.66	0.85 ± 0.03a	26.34 ± 0.92a	0.01 ± 0.01a	112.59 ± 2.76a	0.43 ± 0.00a
Treatment	Total leaf K-FB (cmol c kg^{-1})	Total leaf P-DB (cmol c kg^{-1})	Total leaf K-DB (cmol c kg^{-1})	Soil CEC (cmol c kg^{-1})	Soil total organic carbon (%)	Soil avalable P (ppm)
Control	0.02 ± 0.00d	0.01 ± 0.00d	0.01 ± 0.00d	20.14 ± 2.08e	1.47 ± 0.19e	10.70 ± 1.61e
SSBC	0.14 ± 0.02a	0.04 ± 0.00d	0.12 ± 0.02a	33.49 ± 3.19a	6.97 ± 0.34a	34.08 ± 3.16d
La-SSBC	0.12 ± 0.01b	0.13 ± 0.00c	0.10 ± 0.00b	27.07 ± 2.82b	5.15 ± 0.49c	94.60 ± 3.14c
SSBC-P	0.09 ± 0.01c	0.23 ± 0.04b	0.07 ± 0.02c	25.89 ± 2.19c	6.31 ± 0.41b	126.51 ± 5.62b
La-SSBC-P	0.09 ± 0.00c	0.37 ± 0.06a	0.07 ± 0.01c	24.58 ± 3.34d	4.57 ± 0.27d	253.23 ± 8.89a

Note: FB: fresh biomass basis; DB: dry biomass basis; CEC: soil cation exchange capacity. The different lowercase letters indicate significant differences among the treatments at $P < 0.05$ according to Tuckey's HSD test. Data is the average of 4 replications (n = 4) ± standard deviation (SD).

Table 3
Effect of P-La decorated sewage sludge biochar on the physical and chemical characteristics of an alkaline-soil used in pot experiment before and after planting ryegrass.

Treatment	pH	EC	Exchangeable cations				SOM	La	$CaCO_3$
			Ca	Mg	K	Na			
		mS cm^{-1}	$cmol_c$ kg^{-1}				%	ppm	ppm
Before Planting									
Control	8.08 ± 0.02c	0.45 ± 0.01c	–	–	–	–	–	0.00 ± 0.00c	26.16 ± 0.56c
SSBC	8.26 ± 0.03ab	0.48 ± 0.02a	–	–	–	–	–	0.00 ± 0.00c	26.18 ± 0.04c
La-SSBC	8.32 ± 0.01a	0.47 ± 0.01a	–	–	–	–	–	4.72 ± 0.01b	25.44 ± 0.59d
SSBC-P	8.15 ± 0.02b	0.46 ± 0.02ab	–	–	–	–	–	0.00 ± 0.00c	26.45 ± 0.28b
La-SSBC-P	8.15 ± 0.01b	0.44 ± 0.03c	–	–	–	–	–	5.12 ± 0.08a	26.83 ± 0.07a
After Planting									
Control	7.22 ± 0.03c	0.43 ± 0.01 cd	0.51 ± 0.02e	0.08 ± 0.01d	0.05 ± 0.03e	0.02 ± 0.01d	2.53 ± 0.33e	0.00 ± 0.00a	19.75 ± 0.36b
SSBC	7.62 ± 0.03a	0.78 ± 0.02a	2.95 ± 0.09a	1.20 ± 0.11a	0.65 ± 0.02c	1.75 ± 0.02a	11.99 ± 0.25a	0.00 ± 0.00a	21.34 ± 0.04a
La-SSBC	7.53 ± 0.02ab	0.69 ± 0.03b	1.93 ± 0.10b	1.18 ± 0.14b	2.16 ± 0.12a	1.66 ± 0.00b	8.86 ± 0.32c	0.01 ± 0.01a	5.02 ± 0.07c
SSBC-P	7.26 ± 0.05c	0.48 ± 0.01c	1.28 ± 0.01c	1.12 ± 0.06b	0.51 ± 0.01 cd	1.43 ± 0.02 BCE	10.85 ± 0.70b	0.00 ± 0.00a	20.85 ± 0.05a
La-SSBC-P	7.05 ± 0.05d	0.66 ± 0.02b	1.04 ± 0.04d	0.65 ± 0.07c	1.17 ± 0.03b	1.32 ± 0.03c	7.86 ± 0.01 cd	0.01 ± 0.00a	4.70 ± 0.43 cd

Different lowercase letters indicate significant differences among the treatments at P < 0.05 according to Tuckey's HSD test. Data is the average of 4 replications (n = 4) ± standard deviation (SD). The abbreviations are as following: EC, electrical conductivity; La, lanthanum; CaCO3, limestone; and SOM, soil organic matter.

3.2. Biochar characterization

The findings of Brunauer-Emmett-Teller (BET) analysis showed high specific surface area of SSBC compared to that of La-SSBC, SSBC-P, and La-SSBC-P biochars (Table 1). It was noticed that the surface area (m^2 g^{-1}) of SSBC decreased from 40.96 to 17.25, 21.86, 15.32 after alone or combined with La and phosphate (PO_4^{3-}), respectively. It was revealed that the pore volume (0.116 cm^3 g^{-1}) of SSBC was the highest which was decreased in La-SSBC (0.096 cm^3 g^{-1}), SSBC-P (0.084 cm^3 g^{-1}), and La-SSBC-P (0.043 cm^3 g^{-1}) after decoration with La and P on the surface of SSBC. Moreover, compared to the SSBC, the available phosphorous (AP) and total potassium (TK) contents of La-SSBC-P were increased by 6.73 and 1.15 times, respectively. In addition, total carbon (TC) contents were reduced by 14.82% in La-SSBC, 6.93% in SSBC-P, and 24.42% in La-SSBC-P biochar when compared with the SSBC biochar (8.23%). These results have been presented in Table 1.

The findings of the SEM-EDX analysis have been presented in Fig. 1. The results showed that SSBC and La-SSBC exhibited a tube-shaped mesoporous structure along with rough surfaces. On contrary, the La-SSBC-P showed a bit smooth surface after adsorption of P on the La-SSBC. The EDX elemental mapping of the SSBC displayed relatively lower contents of C, while higher contents of silicon (Si) and Al. Whereas, the La-SSBC showed a successful integration of $La(OH)_3$ on the coarser cavities of SSBC, which was obvious in the EDX mapping results. Due to the fact, there was an increment in the pore width of La-SSBC, as compared to SSBC (Table 1). The detected signals represented C, oxygen (O), Al, calcium (Ca) and Si elements in the SSBC sample. In addition to C and O elements, La-SSBC also showed a significant peak for La in the EDX mapping (Fig. 1).

The FTIR spectra of SSBC, La-SSBC and La-SSBC-P samples have been presented in Fig. 2. The spectra revealed that the band at the 3427 cm^{-1} wavenumber is attributed to the stretching rings of O-H and N-H functional groups for SSBC (Li et al., 2016). Me–H) were found in the SSBC induced FTIR spectra (Fig. 2a) at the wavenumbers of 1628 cm^{-1}, 1034 cm^{-1}, and 796 cm^{-1}, respectively. Moreover, the FTIR spectrum of La-SSBC sample (Fig. 2b) was quite similar to that of SSBC sample. The additional peaks in the La-SSBC at 1384 cm^{-1} and 472 cm^{-1} were corresponded to the NO^{3-} stretch which was might be originated from lanthanum nitrate and La-O active group, accordingly. Similarly, La-SSBC-P also carried additional functional groups i.e., P–O and O–P–O indicating the successful impregnation of SSBC with La and phosphate adsorbents (Fig. 2b).

3.3. Effect of decorated biochars on the growth characteristics of ryegrass

The results related to the growth performance of ryegrass under various modified biochars under alkaline soil conditions have been presented in Table 2. The results depicted that the biochar amendments showed a great enhancement in the germination percentage and plant height under La-SSBC (50.02% and 38.92%), SSBC-P (80.02% and 44.13%), and La-SSBC-P (100.0% and 107.57%), when compared with the alone SSBC treatment. Moreover, the aboveground dry biomass of

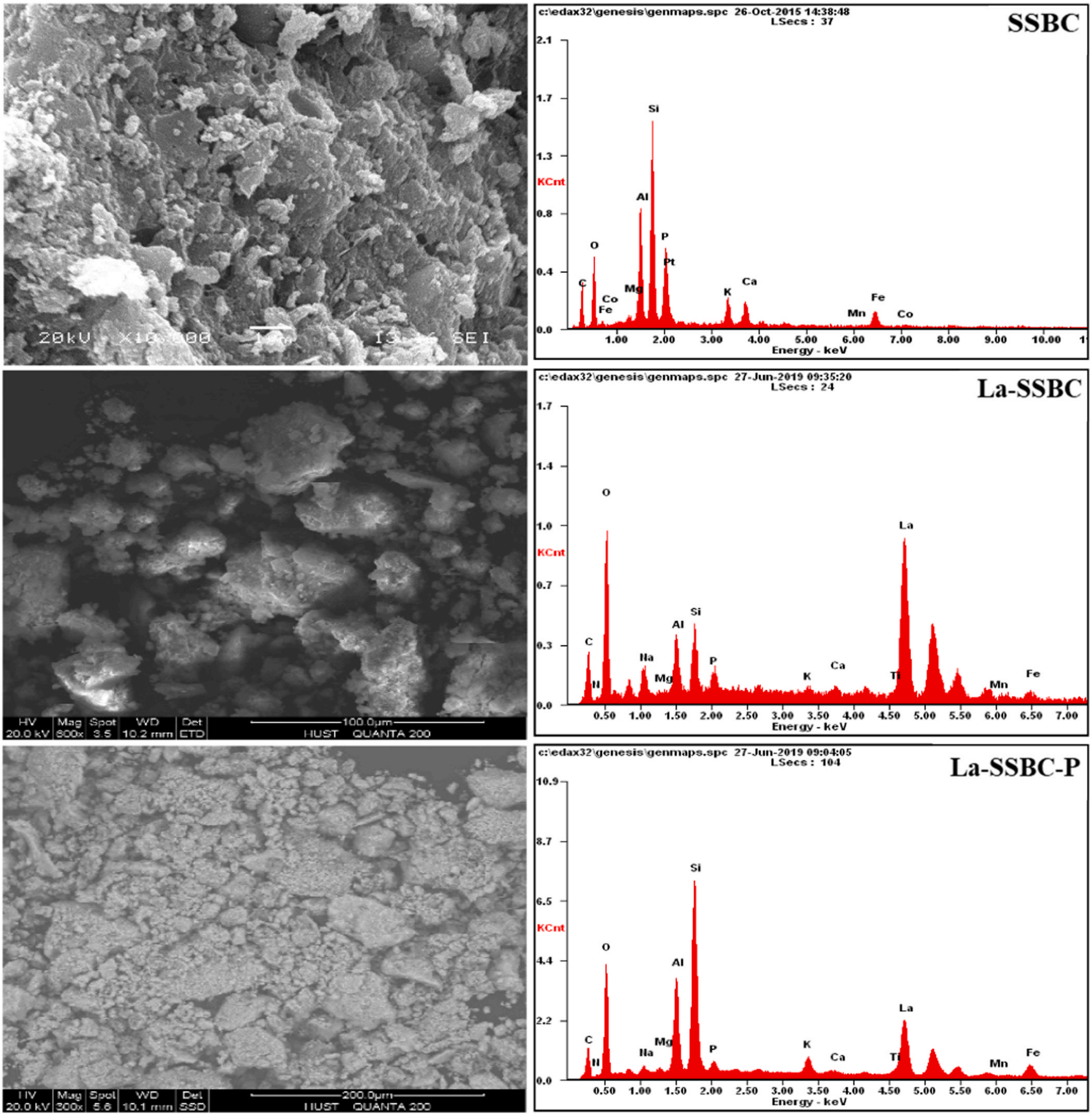

Fig. 1. SEM-EDX analysis of the surfaces of SSBC, La-SSBC, and La-SSBC-P decorated sewage sludge induced biochars. phosphate loaded-La decorated sewage sludge biochar (La-SSBC-P). phosphate loaded-La decorated sewage sludge biochar (La-SSBC-P).

ryegrass seedlings was increased by 844.44% under La-SSBC-P, 55.56% under La-SSBC, 133.33% under SSBC-P, as compared to SSBC alone.

3.4. Effect of decorated biochars on lanthanum and nutrients uptake in ryegrass leaves

The results showed that ryegrass leaves accumulated higher amount ($P < 0.05$) of total P (on fresh and dry biomass bases) under SSBC-P (24.8- and 33.2-times) and La-SSBC-P (41.0- and 52.0-times), respectively, compared to the control treatment. Besides, total leaf potassium (TK) concentration on the bases of fresh and dry biomass was increased by 7.6- and 11.4-folds under SSBC treatment compared to the control treatment, respectively. However, the concentration of TK in the ryegrass leaves was significantly reduced under the phosphate and/or La decorated biochars as compared to the SSBC alone (Table 2). The highest increase in the concentration of phosphate was found in the leaves of ryegrass under SSBC-P (261.2%) and La-SSBC-P (495.7%) treatments as compared to the SSBC treatment alone (18.90 ppm), respectively. Moreover, the La concentration was not detected under all biochar treatments which was due to its immobilization with $CaCO_3$ under alkaline soil conditions (Table 2).

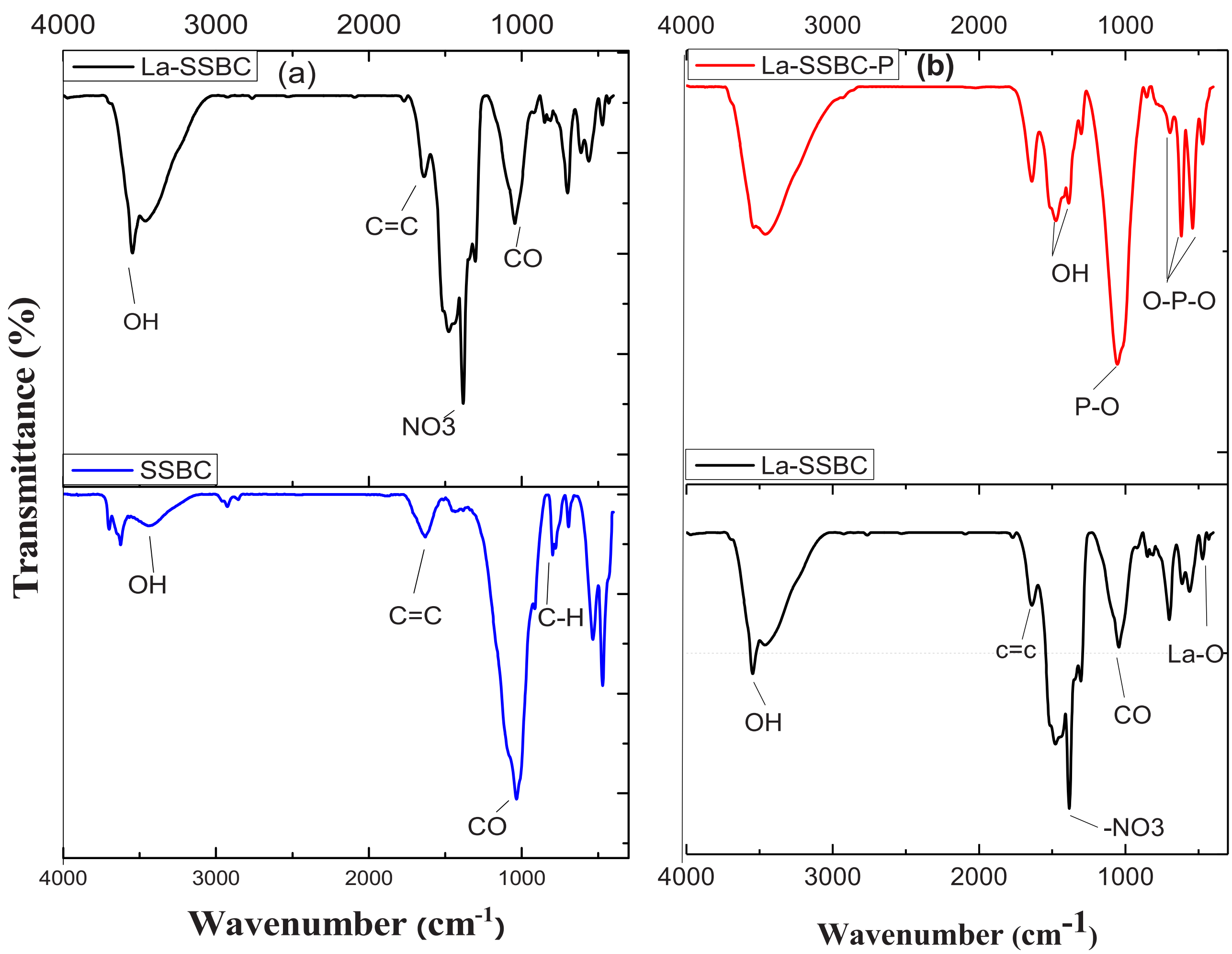

Fig. 2. The comparison of the FTIR spectra of La-SSBC and SSBC (a) and of La-SSBC-P and La-SSBC (b) biochar samples.

3.5. Effect of decorated biochars on alkaline soil properties

The contents of total carbon (TC) and CEC of the post-harvest soil was enhanced under all biochar treatments with a maximum increase under SSBC by 374.15% and 66.28%, La-SSBC by 250.34% and 34.41%, and SSBC-P by 329.25% and 28.55% respectively, as compared to the control. Contrarily, the soil available P contents were greatly increased by 11.82- and 23.67-folds after the application of decorated biochars i.e., SSBC-P and La-SSBC-P respectively, compared to the soil under control treatment (Table 2).

The findings showed that pH of the alkaline soil was significantly ($P < 0.05$) reduced from 8.08 (absolute control) to 7.05 units after ryegrass plantation under various modified biochars with a maximum reduction under La-SSBC-P. Moreover, the application of La-SSBC and La-SSBC-P prominently enhanced the soil (EC by 60.47% and 53.49% and SOM by 250.20% and 210.67%, while limestone ($CaCO_3$) contents were reduced by 74.58% and 76.20% in post-harvest alkaline soil respectively, as compared to the cultivated control. The soil exchangeable nutrient cations were significantly improved after various decorated biochars application, when compared to the control treatment. The increments were as following: Ca (5.8- and 3.8-times), Mg (15.0- and 14.8-times), and K (13.0- and 43.2-times) under SSBC and La-SSBC, accordingly (Table 3).

The Fig. 3 showed the X-Ray diffraction (XRD) patterns of the alkaline soil before and after the treatment with La-SSBC. The results revealed the appearance of new peaks ($La_2O_2CO_3$) after the application of La-SSBC which corresponds to the precipitation and/or immobilization of La with limestone in alkaline soil, as compared to the peaks of limestone ($CaCO_3$) before the biochar treatment.

3.6. Major controlling factors of biochar-induced changes in soil and plant properties

The principal component analysis (PCA) was conducted to determine the association between the plant properties and the controlling factors in the soils treated with different biochar treatments (Fig. 4). The total variance in the results was 77.2%, which was explained by two primary components (Component 1 (PC1): 43.8% and component 2 (PC2): 33.4%). The plant height and contents of P and La were associated with the changes in soil P and La as indicated by large positive loading scores of both PC1 and PC2. This relation was very clear in the soils treated with La-SSBC-P followed by SSBC-P.

The soil pH had an inverse relationship with the P availability in soil and its uptake by plants as indicated by negative correlation between soil pH and soil available P ($r = -0.613$, $P < 0.01$), P-PO_4^{3-} ($r = -0.586$, $P < 0.01$), and total P in plant dry biomass ($r = -0.6127$, $P < 0.01$) (Supplementary Table 1). Meanwhile, the soil pH had a positive correlation with total K on plant fresh biomass ($r = +0.649$, $P < 0.01$), and dry biomass ($r = +0.607$, $P < 0.01$). The enhanced plant weight was also positively correlated with the improvement in soil fertility parameters such as soil EC ($r = +0.725$, $P < 0.01$), TC ($r = +0.505$, $P < 0.05$), Ca ($r = +0.483$, $P < 0.05$), K ($r = +0.523$, $P < 0.05$), and CEC ($r = +0.605$, $P < 0.01$). The biochar-induced improvement in the soil fertility led to higher uptake of P and K which enhanced the plant

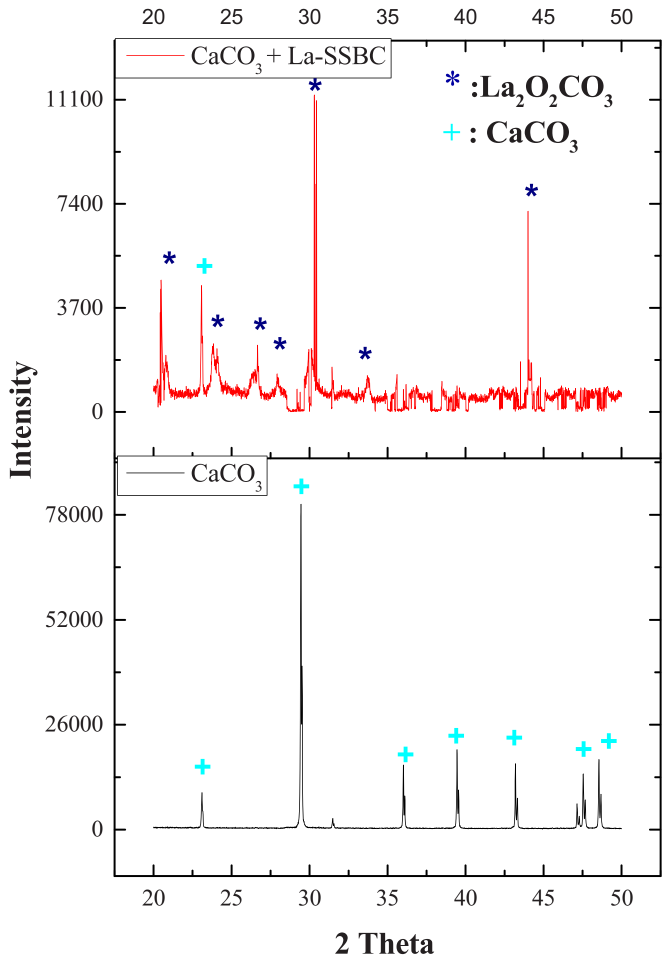

Fig. 3. X-Ray Diffraction patterns of the alkaline soil ($CaCO_3$) before cultivation of ryegrass and after treating the alkaline soil with La-SSBC biochar ($CaCO_3$ + La-SSBC) sampled after harvesting of ryegrassX-Ray Diffraction.

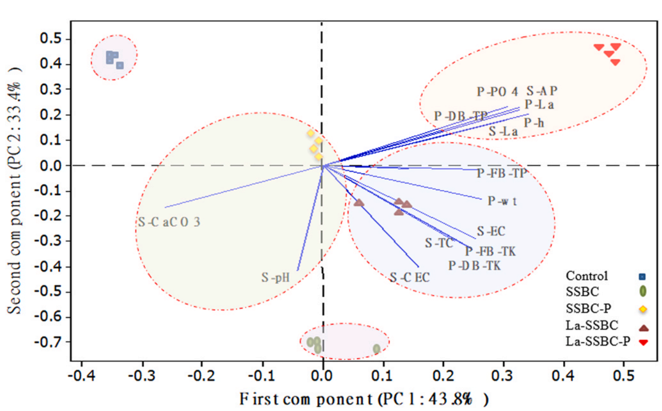

Fig. 4. Principal component analysis based on the soil and plant properties in different treatments. S, soil; P, plant, TC, total carbon, AP, available phosphorus; wt., weight; h, height; FB, fresh biomass; DB, dry biomass; TP, total phosphorus; TK, total potassium.

growth; hence, the plant weight correlated positively with the total P on plant fresh biomass bases ($r = +0.531$, $P < 0.05$), and total K on plant dry biomass bases ($r = +0.588$, $P < 0.01$) and fresh biomass ($r = +0.553$, $P < 0.05$). The results explaining the relationships between various measured variables are presented in.

4. Discussion

Modified biochars have shown rough and porous structure, which could contribute to reclaim the P from the aqueous environment and thereby reducing the eutrophication and P leaching potential of the medium (Ngatia et al., 2017; Li et al., 2020). The incorporation of biochar into the soil can alters the soil chemical properties, i.e., pH, EC, and efficiently improved plant growth (Cai et al., 2017). According to the current findings, the soil pH decreased after the ryegrass plantation under the addition of various types of biochar containing phosphate, because of the effective release of H^+ from the biochars (Table 3). However, the significant increase in EC of biochar was occurred due to the increase in thermal cracking temperature and thermal cracking time (Rehrah et al., 2014). The present study confirmed that the application of various decorated biochars showed the prominent improvement in soil organic matter due to the organic carbon dissolution in biochar amended soils (Table 3). It is interested to mention that, according to the findings of FTIR spectra (Fig. 2) the presence of carboxyl and aliphatic C bearing functional groups on the pristine as well as on the surface of modified biochars might have great contribution to the sharp increase of OM and total C contents in the modified biochar amended alkaline soil (Zhu et al., 2017).

The results revealed a sharp increment in P concentration in the soil when P-La modified biochar was incorporated (Table 2) which might have great role to reduce of the soil pH after ryegrass plantation. It has been attributed that P availability increased with the application of various biochars to the soil due to the sufficient amount of P related minerals present in the studied biochars (Xu et al., 2014; Li et al., 2016). It has been demonstrated that the P availability in the biochar-treated soil may be influenced with the significant change in soil pH and the exchange rate of P from the biochar surface (Table 3). The modification of biochar with La efficiently decreased the limestone contents that leads to overcome the immobilization of phosphate ions in the alkaline soil, which might have greater role to facilitate the P solubility in alkaline soils as well as improves the P availability to the plants. The exchangeable calcium contents were decreased in the decorated biochars as compared to the non-modified SSBC (Table 3). It might be due to the transformation of phosphate with precipitated calcium (CaP_2O_6) to the plant root zone along with the precipitated La with limestone in alkaline soil (Abolfazli et al., 2012). It was observed that limestone concentration was efficiently decreased after the plantation of ryegrass followed by the prominent reduction in La concentration in alkaline soil under the La-SSBC and La-SSBC-P amended soil relative to SSBC and SSBC-P amended soil which might be due to the precipitation of La with limestone. The previous study reported by Wang et al. (2015) confirmed that the adsorption of PO_4^{3-} could contribute to the increase in the formation of La_2CO_3 due to the presence of various functional groups on the phosphate-lanthanum loaded biochar. Moreover, XRD spectrum evidenced that the generation of new peaks corresponding to lanthanum dioxycarbonate ($La_2O_2CO_3$) confirmed the reduction of $CaCO_3$ in alkaline soil after treatment with La-SSBC. The precipitation mechanism can be interpreted as given in the following equation:

$$La(OH)_3\text{-SSBC} + \text{Alkaline soil-}CaCO_3 \rightarrow 2LaOHCO_3 \rightarrow La_2O_2CO_3 + CO_2 + H_2O$$

In addition, the exchangeable nutrient cations except K^+ were greatly enhanced under the SSBC than the modified biochars. It can be attributed that the release of nutrients from the SSBC which might be due to the presence of higher concentrations of these nutrients on the all the amended treatments (Angst and Sohi, 2013), which was confirmed by SEM-EDX analysis (Fig. 1). Generally, soil CEC is directly proportional to pH; as pH value increased (as observed in the SSBC and La-SSBC treated clay soil in this study), pH-dependent charges might have great contribution to enhance soil CEC. The positive relationship between pH and CEC could explain the increase of CEC in SSBC. Modified biochar could alter soil physicochemical properties such as pH, nutrient enrichment, soil aggregation, and retention, which indeed increase the yield of agricultural products (Rehrah et al., 2014; Wu et al., 2019). The uptake of phosphate can be enhanced by electrostatic attraction with protonation of Lanthanum biochar towards the $CaCO_3$. After the modification of biochar with La, soil CEC was decreased which indicated that La has no significant influence in alkaline soil which might be due to its stabilization with limestone. Therefore, SSBC-P, La-SSBC, and La-SSBC-P could have better control over the contact time of P with the clay oxides and also represent a barrier (higher CEC) for the cations which ultimately enhanced the P bioavailability (Pogorzelski et al., 2020). Moreover, results indicated that EC of the soil treated with SSBC, SSBC-P, La-SSBC, and La-SSBC-P was enhanced after ryegrass plantation, which justified the biochar-mediated increase of nutrients in the soil (Shen et al., 2017).

The modified biochars have the ability to influence the growth and yield of ryegrass which was indicated in the current study (Table 2). To the fact, that the growth of ryegrass in the control treatment was insignificant which might be due to the risk of the blockage of trace elements as well as the phosphate in the $CaCO_3$ rich alkaline soil (Table 2). While, the incorporation of SSBC-P in the soil increased the phosphate concentration in the leaves than un-amended SSBC because the SSBC-P has a greater capacity of adsorption of phosphate than the SSBC. However, the La-SSBC can be inconsiderate to the coexisting citrate, chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) (Li et al., 2020). Therefore, La is immobilized with $CaCO_3$ that led to increase the release of P in amended soil which could be readily available to crop plants. Additionally, the significant improvement in C contents in the alkaline soils may facilitate the release of organic nutrients, N, P, and S which might contribute in the enhancement of soil fertility and finally promote the plant growth (Banwart et al., 2019). On the contrary, total K decreased under P-La modified biochar application compared to the SSBC alone (Table 2) which might be due to the removal of water from the plants as K^+ is involved in many physiological processes, including protein synthesis and maintaining the water balance in the plant. Therefore, the evidence regarding the significant increase in K under biochars amended soils could promote crop productivity in alkaline soils (Wu et al., 2019). Meanwhile, a decline in the EC value under cultivated control treatment might indicate that the plants have absorbed most of the nutrients from the studied soil (Zheng et al., 2018; Kamran et al., 2020b). Moreover, it has been previously reported that the sewage sludge induced biochar contains higher mineral contents of P in the soil which was readily available to plants rather than crop residues, manures, or woody biochars (Hossain et al., 2020).

The La-SSBC-P treatment could prolong and maintain a higher level of P for plants, source of slow-release pattern, and homogenous sources of P in soil. Li et al. (2020) reported that the P-laden biochar might increase the P use efficiency in soil. This tool leads to the highest germination rate in the La-SSBC-P application in alkaline soil. In addition, plant height and phosphate concentration were also significantly increased among all the amendments relative to control. It has been reported that the co-existence of La^- anions in La-modified biochar has insignificant effects on phosphate availability (Liao et al., 2018). The crop performance was improved with the application of P-La modified biochars (Tables 2–3) which might be due to their involvement in the fixation and solubilization of nutrients (C, K, P) in rhizosphere. However, the risk of P loss could be existed because of the surface flow and subsurface flow (Huang et al., 2020). La involvement in the pyrolysis can reduce the OM and free-radicals in the La modified biochar (Li et al., 2017) and La may immobilize with $CaCO_3$.

In current study, FITR findings endorsed that the appearance of new peaks of O-P-O and P-O along with hydro-carbide bonding showed the functional groups (O-H, N-H) (Fig. 2) and the existence of La-O which confirmed the significant difference before and after the adsorption of P. These bonds were present in the sewage sludge biochar in the form of mineral $Ca_3(PO_4)_2$ (Li et al., 2018). Moreover, the higher N content in La-SSBC was related to the utilization of lanthanum nitrate (Wang et al., 2016). Meanwhile, the La involvement significantly decreased the influence during biomass pyrolysis (Wang et al., 2015). Moreover, the functional groups were absent in the simple biochar and phosphate modified-biochar, which could easily improve the P adsorption capacity with electrostatic repulsion between positively charged functional groups and negatively charged P on biochar surface (Wu et al., 2019). Thereby, the grafting of functional groups in La-SSBC can enhance the functionality of biochar which ultimately act as an effective P fertilizer which improved the ryegrass growth under alkaline soil conditions (Fig. 2).

The changes in the soil pH and $CaCO_3$ were more apparent under La-SSBC, SSBC-P, and La-SSBC-P treatments and showed negative loading scores with both PC1 and PC2 (Fig. 4). The PCA results demonstrated the positive effects of the different decorated biochar treatments on the alkaline soil and plant properties. In particular, the La-SSBC-P biochar showed significant potential to promote alkaline soil health which in turn enhanced P contents in alkaline soil and ryegrass leaves. The plant dry biomass and K contents were more influenced by the change in soil total organic C, CEC, and EC as indicated by the positive loading scores of PC1 and the negative loading scores of PC2.

5. Conclusion

It was found that the La modification of biochar showed no influence in the soil due to its precipitation and/or immobilization with limestone while the soil available P was increased. Moreover, La-SSBC-P showed the highest germination percentage, concentration of P, and K uptake in the leaves of ryegrass, and better plant height among all other tested biochars which clearly suggested that La-SSBC-P can be used as P fertilizer under alkaline soil conditions. The application of La-SSBC-P significantly enhanced the ryegrass growth and soil quality under alkaline soil conditions. Therefore, La-SSBC-P is recommended for field trials as it could be a promising development as a P fertilizer in alkaline soils for agronomic purposes.

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CRediT authorship contribution statement

Zouhair Elkhlifi: Data curation, Formal analysis, Investigation, Writing - original draft. **Muhammad Kamran:** Resources, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Ahsan Maqbool:** Writing - original draft, Writing - review & editing. **Ali El-Naggar:** Writing - original draft, Writing - review & editing. **Jerosha Ifthikar:** Formal analysis, Writing - original draft. **Aasma Parveen:** Writing - original draft, Writing - review & editing. **Saqib Bashir:** Writing - original draft, Writing - review & editing. **Muhammad Rizwan:** Writing - original draft, Writing - review & editing. **Adnan Mustafa:** Writing - original draft, Writing - review & editing. **Sana Irshad:** Writing - original draft, Writing - review & editing. **Shafaqat Ali:** Data curation, Investigation, Writing - original draft, Writing - review & editing. **Zhuqi Chen:** Resources, Supervision, Formal analysis, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2021.112173.

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