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Effects of Yak Dung Biomass Black Carbon on the Soil Physicochemical Properties of the Northeastern Qinghai-Tibet Plateau

Xiuyun Min ^{1,2,3}, Jun Wu ^{1,2,3,*} , Jian Lu ^{3,4} and Chunliang Gao ^{1,2}

¹ Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China; minxy@isl.ac.cn (X.M.); chunlianggao@isl.ac.cn (C.G.)

² Qinghai Provincial Key Laboratory of Geology and Environment of Salt Lakes, Xining 810008, China

³ College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China; jlu@yic.ac.cn

⁴ Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China

* Correspondence: junwu@isl.ac.cn or wujunlisa@163.com; Tel.: +86-971-6302-337

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Abstract: The physicochemical properties of soils might be affected by the addition of biomass black carbon, a special black carbon produced by incomplete combustion of biomass. Therefore, this study performed experiments to explore the effects of yak dung biomass black carbon (YBC) on physicochemical properties of soils in the northeastern Qinghai-Tibet Plateau. Three YBCs (pyrolyzed at 300, 500, and 700 °C) were separately added into four typical soils with three addition amounts (1%, 5%, and 10%). Changes of soil texture, pH, electrical conductivity (EC), cation exchange capacity (CEC), CHN contents, morphologies, functional groups, and mineral constituents of soils were comparatively studied. The results showed that addition of YBCs affected physicochemical properties of soils. Soil pH, EC, CEC, and carbon/nitrogen content were positively related with addition amount of YBCs. YBC particles were unevenly distributed among soil particles and positively related with addition amount. Addition of YBCs did not change texture, functional groups, and mineral constituents of soils. These results indicated that addition of YBC would be beneficial to stability of the soil ecosystem and sustainability of the northeastern Qinghai-Tibet Plateau.

Keywords: yak dung biomass black carbon; physicochemical properties; soil; the Qinghai-Tibet Plateau

1. Introduction

Soil ecosystem, a critical component of the Earth, plays an important role in food production, environmental safety, human health, and regional sustainability [1,2]. Black carbon has shown multiple geochemical and environmental behaviors in soil ecosystems, such as contributing to soil organic carbon [3], adsorbing organic pollutants or heavy metals, persisting in the environment [4,5], affecting emissions of greenhouse gas [6], modifying soil fertility and structure [7], and influencing the microbial community [8]. Black carbon (BC) is generally regarded as a soil contaminant because of the strong adsorption capacity for pollutants. The soil physicochemical properties, such as soil texture, pH, EC, cation exchange capacity (CEC), and contents of elements, generally have great impacts on soil ecosystems. The decline of soil organic matter affects soil structure and decreases soil aggregate stability [9,10]. Soil aggregate stability is reported to have a significant influence on crop production and to be significantly positively related with the degree of soil degradation [11]. The soil pH is an important factor affecting the form, availability, and uptake of nutrients [12]. Soil CEC influences water

retention capacity, fertility, and the nutrient retention of soils [13]. The soil physicochemical properties might also be influenced by external matters, such as BC [14].

Yak dung biomass black carbon (YBC) is a special black carbon, which is mainly produced by local herdsman who live on the Qinghai-Tibet Plateau and have the long-term habit of using yak dung as fuel [15]. However, no information on the changes in physicochemical properties, microscopic morphologies, functional groups, and mineral constituents of soils which receive YBCs is available. The northeastern Qinghai-Tibet Plateau is distributed by anthropogenic activities, such as regular heating of local herdsman. Therefore, this study investigated the effects of YBCs on the soil physicochemical properties of the northeastern Qinghai-Tibet Plateau, since it is necessary to investigate the impact of YBCs on the soil ecosystem. The final aim was to explore the potential functions of YBC for soil ecosystems of the study area.

2. Materials and Methods

Soils of the northeastern Qinghai-Tibet Plateau were mainly alkaline, with the predominant types being sandy clay loam and sandy clay. Four typical soil samples (S1–S4) were selected for the following experiments. Soil type S1–S3 was sandy clay loam, while S4 was sandy clay. Yak dung collected from a pasture in Qinghai Province was air-dried at room temperature and smashed to pass through a 0.425 mm sieve. Crucible (100 mL) was densely filled with yak dung, covered by a lid, and put into a muffle furnace (KSL-1200X, Hefei, China). YBCs were produced at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and residence time of 2 h. YBC1, YBC2, and YBC3 referred to YBC produced at 300, 500, and 700 $^{\circ}\text{C}$, respectively. Three YBCs were added into four soils at mass percentages of 1%, 5%, and 10% to investigate the effects of YBCs on the soil properties of the northeastern Qinghai-Tibet Plateau.

The soil texture was measured by Bouyocou hydrometer method [16]. Soil types were determined according to taxonomy of the United States Department of Agriculture (USDA) [17]. The electrical conductivity (EC) and pH of soil were determined by measuring corresponding parameters of the supernatants of suspension with a solid-water ratio of 1:2.5 by a Myron L 6PII (Myron L Company, Carlsbad, USA). The CEC of soil samples was measured by using the exchange method [18].

A CHN analyzer (Elementar VARIO EL cube, Langensfeld, Germany) was used to determine the contents of C, H, and N of all samples. A scanning electron microscope (SEM JSM-5610LV, JEOL, Japan) was used to investigate the surface morphology of all samples. Fourier transform infrared (FTIR) spectra of all samples were obtained by Nexus (Thermo Nicolet Corporation, USA). Raman spectrum spectra of all samples were obtained by a Microscope Raman Spectrometer (DXR, Thermo Fisher Scientific, USA). The mineral constituents of all samples were determined by X-ray diffraction (XRD) spectrometry (Axios, PANalytical, The Netherlands).

All data were processed using Origin 9.0 (OriginLab Corporation, Northampton, MA, USA).

3. Results and Discussion

3.1. Change in pH, EC, CEC, and Texture of Soils Affected by Addition of YBCs

The types of target soils added by YBCs with different percentages did not change, except S4 with 10% of YBC3 added (Figure 1a), although the proportions of sand, clay, and silt in soils with added YBC varied to some extent (Figure 1b). The sand proportions of all soil samples increased with the addition of YBC1, while those decreased with the addition of YBC3 (Figure 1a). The addition of YBC2 did not remarkably change the sand proportions of soil samples, except for S2. The clay proportions of soil samples increased with the addition of YBCs. No obvious variety existed in the silt proportions of soil samples when adding YBCs. Moreover, the addition of YBC1 had the strongest impact on sand proportions, while the addition of YBC3 had the greatest impact on clay proportions. The soil texture was the most significantly affected by adding 10% YBC (Figure 1a). The addition of special BC, such as biochar, might have different influences on coarse textured and fine-textured soil [19,20].

Soil bulk density can be reduced because biochar is generally composed of low density particles [21]. Moreover, the changes in soil texture will subsequently cause the change of soil pore sizes [22].

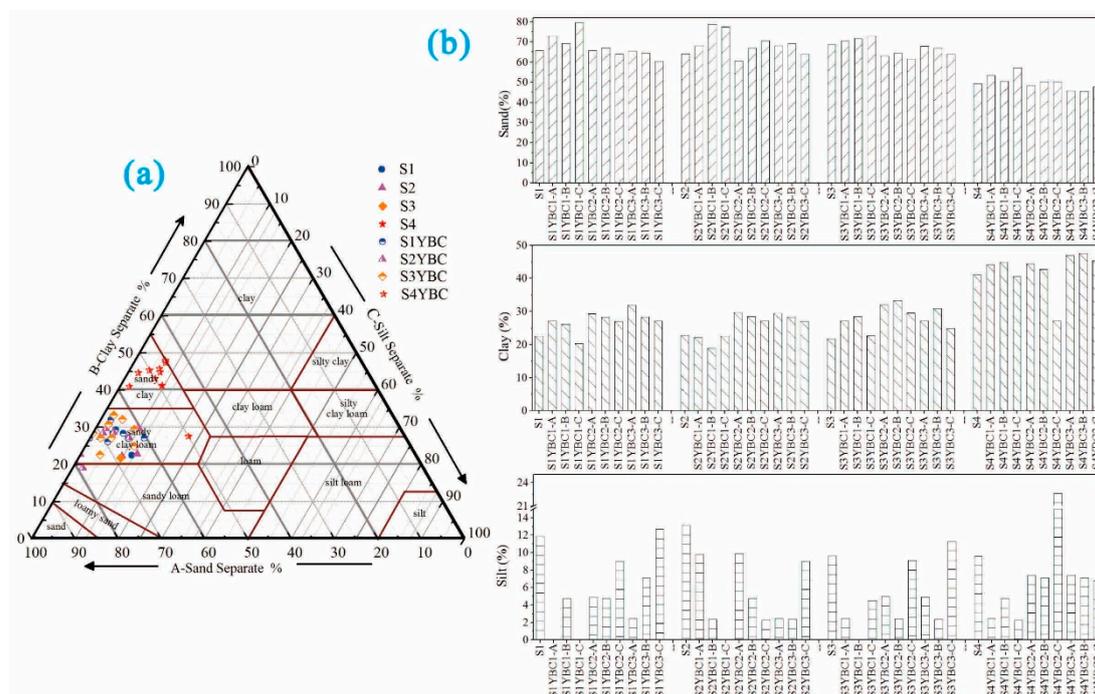


Figure 1. Changes in texture (a) and contents of silt, sand, and clay (b) of soils with added yak dung biomass black carbon (YBC). Symbols -A, -B, and -C represent YBC addition percentages of 1%, 5%, and 10%, respectively.

The pH, EC, and CEC values of YBC1/YBC2/YBC3s were 7.55/9.72/10.49, 722.25/168.50/1346 $\mu\text{S}/\text{cm}$, and 73.52/108.29/44.41 cmol kg^{-1} , respectively (Figure 2). The properties of YBCs were similar to the previous studies [23,24] and were significantly affected by pyrolysis temperature [25,26]. The pH, EC, and CEC values of S1/S2/S3/S4 were 8.90/8.46/8.38/8.55, 356.80/505.50/111.25/41300.00 $\mu\text{S}/\text{cm}$, and 10.99/6.02/4.14/10.92 cmol kg^{-1} , respectively (Figure 2). Interestingly, pH values of soil samples S1 and S2 added by YBC1 reduced, while those of soil samples S3 and S4 added by YBC1 did not change (Figure 2). When YBC2 and YBC3 were added into four soils, the pH values of soil samples positively increased with the addition amounts of YBC2 and YBC3 (Figure 2a). The EC values of soil samples S1, S2, and S3 increased with additional amounts of YBCs, while those of S4 with the addition of YBCs decreased due to the higher EC of S4 (Figure 2b). The CEC values of all soil samples added by YBCs were also positively related with addition amounts of YBCs because CEC values of YBCs were greater than those of soil samples (Figure 2c). The additional amount of YBC was positively related with EC, CEC, and CHN contents of four typical soil samples (S1–S4) at $p < 0.01$ (Table 1).

The results regarding the effects of adding YBC on pH, EC, and CEC of soils were consistent with previously published studies [27–29]. A significant increase in soil pH after addition of special BC, such as biochar, was observed in these research studies [27–29]. A change of soil pH might affect the soil CEC [30], change the nutrient availability of soils [12], and facilitate adsorption of some elements on the plant root [14]. Therefore, the nutrient availability and uptake, plant growth, and crop production in the northeastern Qinghai-Tibet Plateau might be increased owing to the introduction of YBCs.

3.2. Effects of Adding YBCs on the Morphologies of Soils

The morphologies of soils added by YBCs at different addition amounts were illustrated in Figure 3. SEM images clearly showed that YBC particles were unevenly distributed among soil particles. The micro-morphology of soils changed dramatically owing to the addition of YBCs (Figure 3).

YBCs exhibited a porous structure, therefore the addition of YBCs could increase soil porosity, water holding capacity, available water content, water retention, and adsorption ability [31–33]. The increase in soil water holding capacity is important for yield improvement [34]. Increase in soil porosity also plays a crucial role in immobilization of pollutants in soil [35]. Therefore, it is reasonable to hypothesize that porosity, pollutant adsorption capacity, water storage capacity and infiltration rates, and aggregate stability of soils in the northeastern Qinghai-Tibet Plateau will be improved after direct or indirect addition of YBCs.

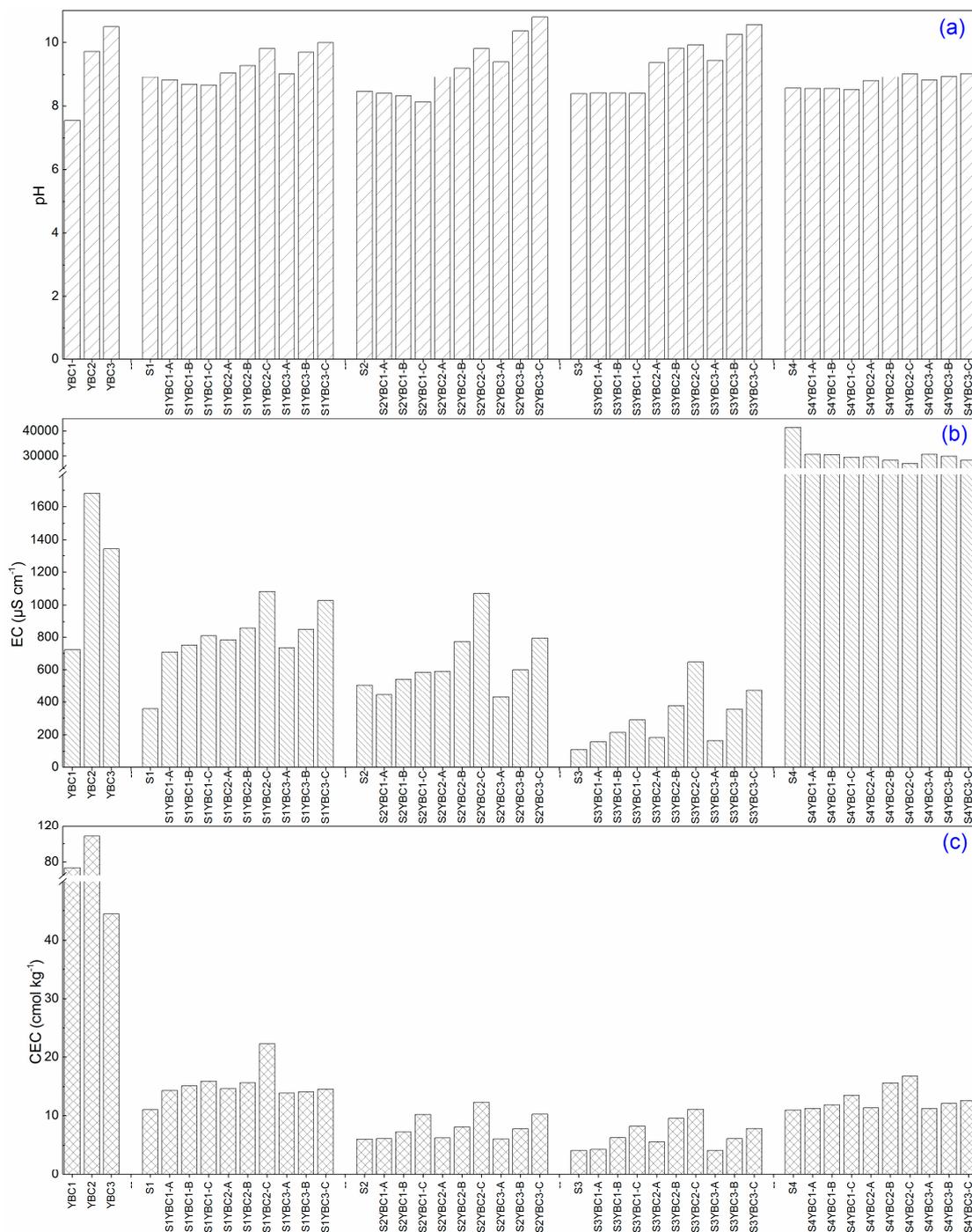


Figure 2. Changes in pH (a), electrical conductivity (EC) (b), and cation exchange capacity (CEC) (c) of soils with addition of YBC. Symbols -A, -B, and -C represent YBC addition percentages of 1%, 5%, and 10%, respectively.

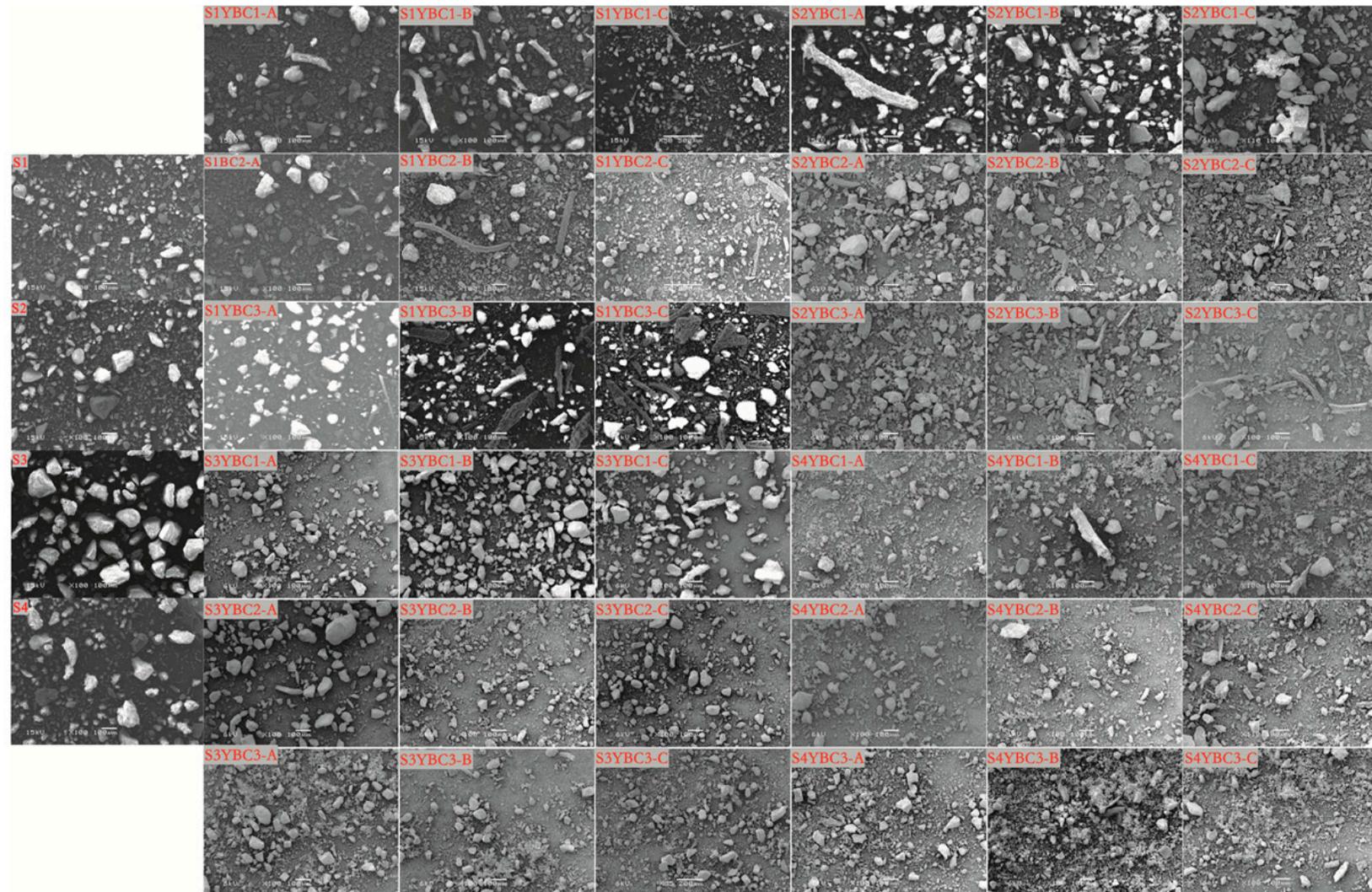


Figure 3. The morphologies of soils with addition of YBCs. Symbols -A, -B, and -C represent YBC addition percentages of 1%, 5%, and 10%, respectively.

Table 1. Pearson correlation coefficient matrix for the addition amount of YBCs, pH, electrical conductivity (EC), cation exchange capacity (CEC), and contents of elements C, H, and N in soil samples.

		Addition Amount	pH	EC	CEC	C	N	H
S1	Addition amount	1						
	pH	0.062	1					
	EC	0.637 *	0.631 *	1				
	CEC	0.895 **	−0.021	0.678 *	1			
	C	0.994 **	0.000	0.590 *	0.896 **	1		
	N	0.911 **	−0.190	0.539	0.896 **	0.937 **	1	
	H	0.254	−0.740 **	−0.312	0.172	0.315	0.484	1
S2	Addition amount	1						
	pH	0.061	1					
	EC	0.744 **	0.478	1				
	CEC	0.915 **	0.000	0.763 **	1			
	C	0.994 **	0.024	0.700 **	0.913 **	1		
	N	0.921 **	−0.117	0.594 *	0.907 **	0.953 **	1	
	H	0.333	−0.527	−0.145	0.260	0.418	0.586 *	1
S3	Addition amount	1						
	pH	0.007	1					
	EC	0.879 **	0.361	1				
	CEC	0.917 **	−0.047	0.869 **	1			
	C	0.996 **	−0.056	0.844 **	0.917 **	1		
	N	0.917 **	−0.163	0.736 **	0.906 **	0.942 **	1	
	H	0.233	−0.635 *	−0.090	0.168	0.299	0.447	1
S4	Addition amount	1						
	pH	0.323	1					
	EC	−0.975 **	−0.331	1				
	CEC	0.902 **	0.213	−0.877 **	1			
	C	0.995 **	0.243	−0.975 **	0.903 **	1		
	N	0.917 **	0.016	−0.941 **	0.899 **	0.945 **	1	
	H	−0.045	−0.660 *	−0.034	−0.076	0.014	0.216	1

Note: Symbols ** and * indicate $p < 0.01$ and $p < 0.05$, respectively.

3.3. Changes in CNH Contents of Soil with Addition of YBCs

Biomass carbon, including biochar, mainly contains C, H, O, N, and S to provide nutrients to the plant [36]. Carbon contents of YBC1, YBC2, and YBC3 were 473.55, 416.45, and 404.25 mg g^{−1}, respectively, while C/N contents were 36.24/24.90, 18.81/19.75, and 7.95/13.75 mg g^{−1}, respectively (Figure 4). The C/H/N contents of S1, S2, S3, and S4 were 53.90/5.46/0.70, 21.15/2.91/0.35, 21.00/2.36/0.70, and 47.20/14.37/0.90 mg g^{−1}, respectively (Figure 4). Therefore, CN contents of soils increased with addition amount of YBCs (Figure 4). The hydrogen contents of most soil samples increased with the addition of YBCs, while those of soil S4 with added YBC2 and YBC3 slightly varied due to the high H content of S4 itself. The addition of YBCs could increase the organic matter, the aggregate stability, fertility, and nutrient availability of the soil [37,38]. Therefore, YBCs could provide fertilizer-like function to some extent and be assimilated by plants and microorganisms. Moreover, YBCs have great potential as a soil amendment and carbon immobilization when entering the soil ecosystem, which is beneficial to the regional sustainability of the northeastern Qinghai-Tibet Plateau.

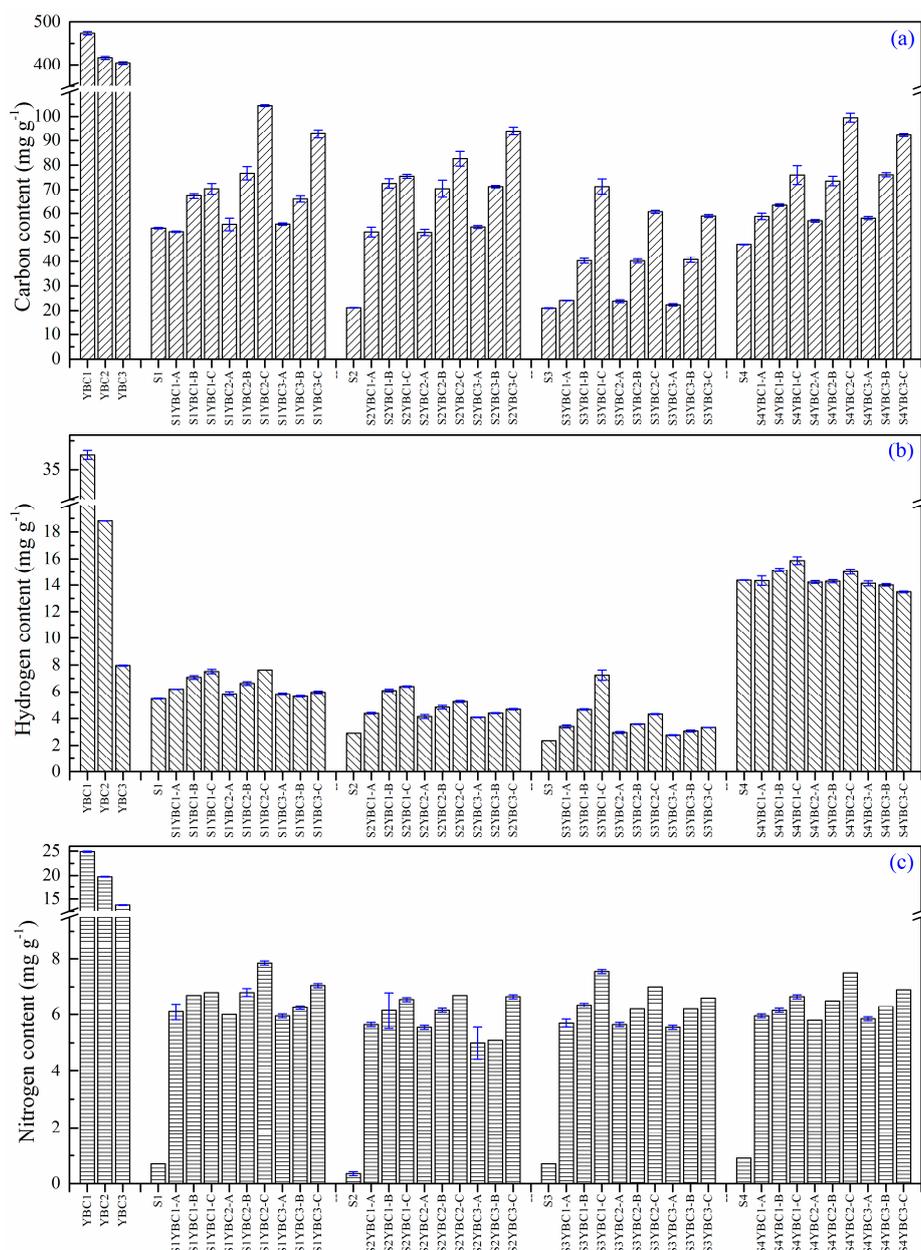


Figure 4. Changes in the contents of carbon (a), nitrogen (b), and hydrogen (c) of soils with added YBCs. Symbols -A, -B, and -C represent YBC addition percentages of 1%, 5%, and 10%, respectively.

3.4. Changes in Spectral Characteristics and Mineral Constituent of Soil with Addition of YBCs

The infrared and Raman spectra of soils with added YBCs were illustrated in Figure 5. Slight differences existed in the FTIR spectra of the soils with added YBCs at different percentages (Figure 5(a1–a4)). The bands in the region $3650\text{--}3350\text{ cm}^{-1}$ were attributed to the stretching vibration of O-H/N-H groups of polymeric compounds, predominantly due to the presence of cellulose, while those at $2850\text{--}3050\text{ cm}^{-1}$ could be regarded as alkyl C-H stretching [39]. The bands of soil samples with peaks around 1650 cm^{-1} were ascribed to the presence of carboxyl groups (C=O), while the bands observed around 1100 cm^{-1} and 900 cm^{-1} were assigned to alcohol group and amine groups [24,40]. The peaks around $800, 700, 550,$ and 460 cm^{-1} explained the presence of Fe-O, Al-O, A-O-Si, and Si-O, respectively [41,42]. The infrared peaks of soils with the addition of YBCs were very similar, indicating that all soil samples had some adducible functional groups and the addition of YBCs did not affect the relative intensity of the groups. The Raman spectrum peak around 3700 cm^{-1} was observed (Figure 5(b3)), which

corresponded with the FTIR spectra of O-H/N-H groups. The bands in the region of 3350–2400 cm^{-1} were consistent with the FTIR spectra of alkyl C-H groups, while those at 2500–1000 cm^{-1} could be consistent with the FTIR spectra of carboxyl groups (C=O) (Figure 5(b2–b4)). Raman spectra of soils with the addition of YBCs also showed slight variance (Figure 5(b1–b4)). In summary, the addition of YBCs slightly affected the soil functional groups of the northeastern Qinghai-Tibet Plateau.

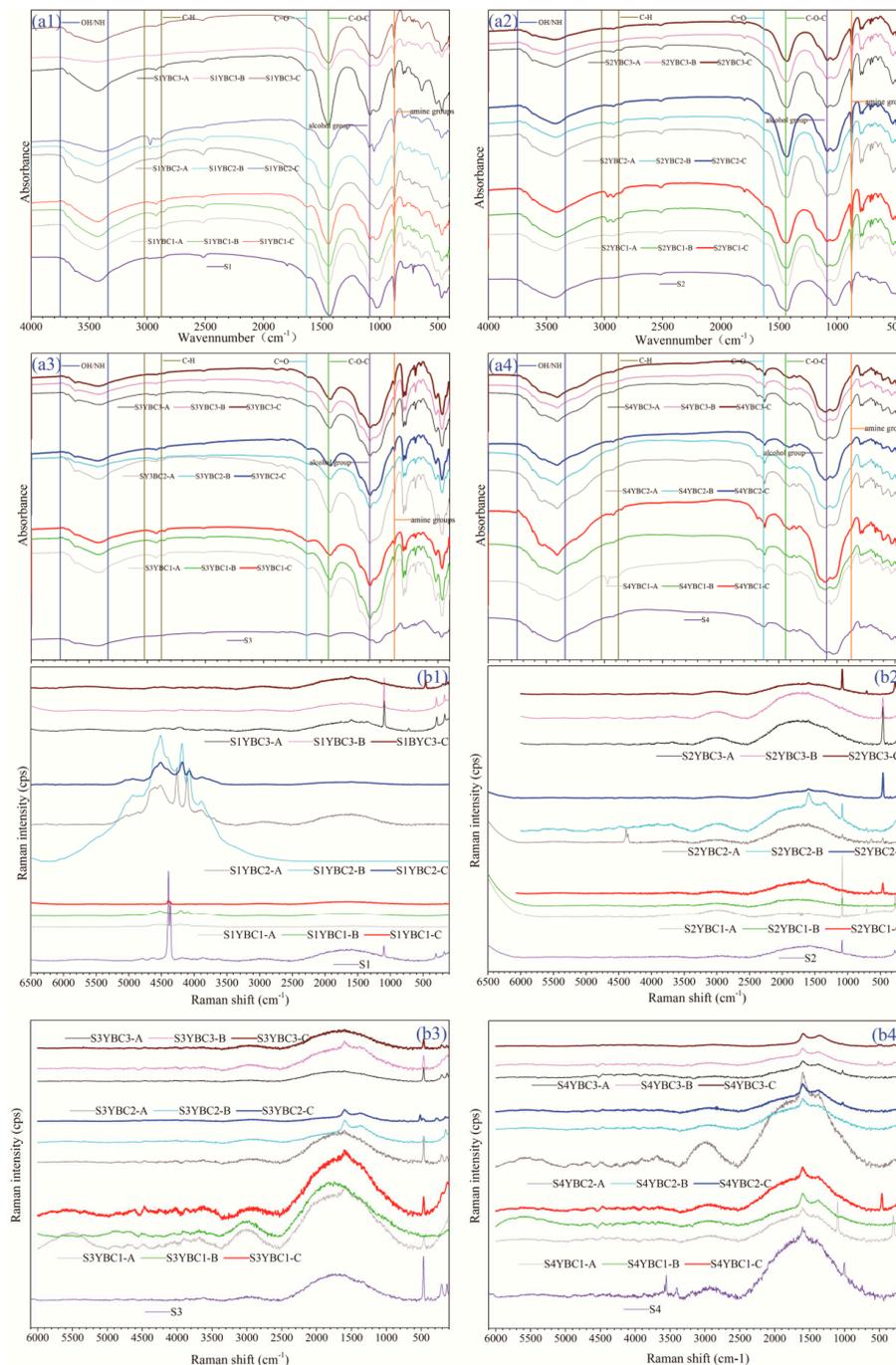


Figure 5. The infrared spectra of S1 with the addition of YBCs (a1), the infrared spectra of S2 with the addition of YBCs (a2), the infrared spectra of S3 with the addition of YBCs (a3), the infrared spectra of S4 with the addition of YBCs (a4), Raman spectra of S1 with the addition of YBCs (b1), Raman spectra of S2 with the addition of YBCs (b2), Raman spectra of S3 with the addition of YBCs (b3), and Raman spectra of S4 with the addition of YBCs (b4). Symbols -A, -B, and -C represent YBC addition percentages of 1%, 5%, and 10%, respectively.

XRD patterns showed that the soils with addition of YBCs were mainly composed of quartz, albite, calcite, dolomite, lizardite, chromite, and biotite (Figure 6). Carbon-related components of all soils with the addition of YBCs were rarely detected, owing to the relatively weak fluorescence intensity of carbon. The XRD patterns of all soils with the addition of YBCs were very similar, indicating that the addition of YBCs would not affect the mineral constituency of soils in the study area.

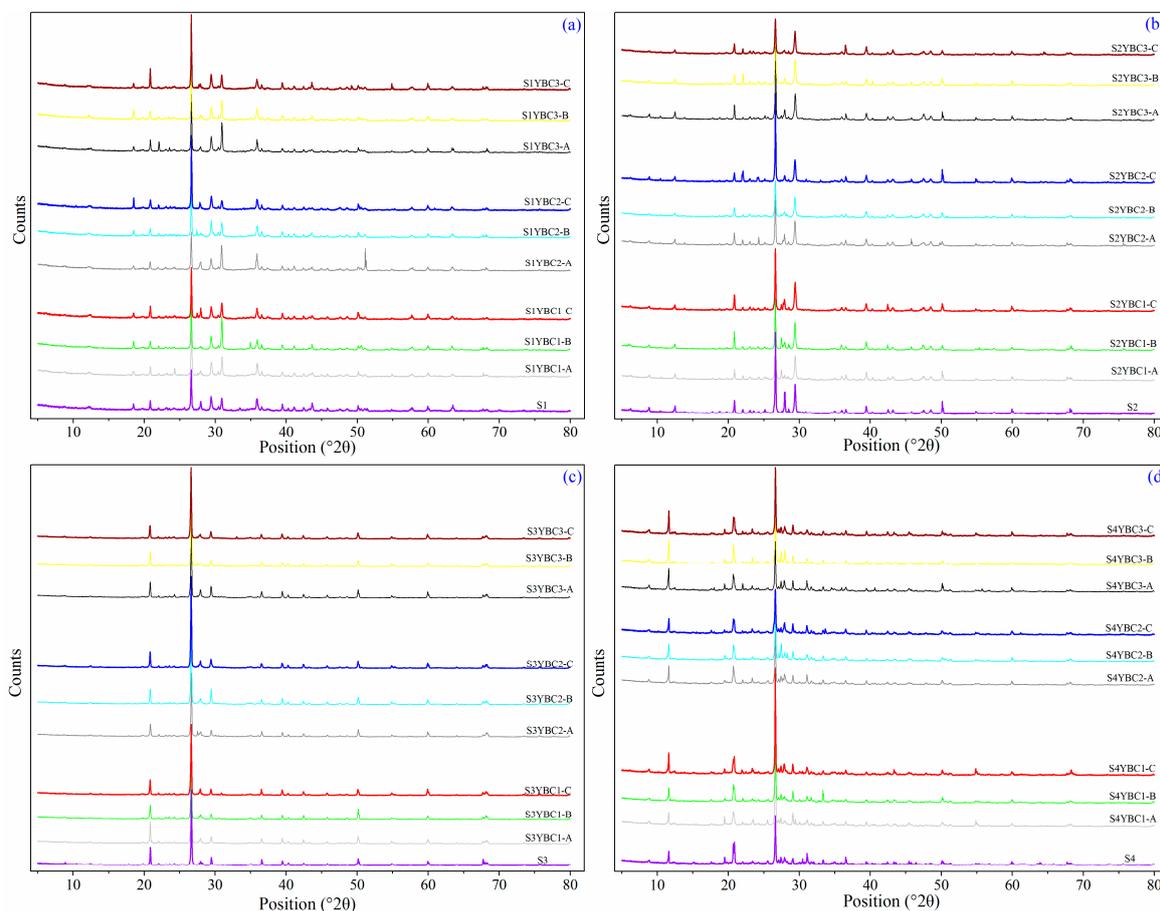


Figure 6. The X-Ray Diffraction spectra of S1 (a), S2 (b), S3 (c), and S4 (d) with the addition of YBCs.

4. Conclusions

Results showed that the addition of YBCs affected the soil physicochemical properties of the northeastern Qinghai-Tibet Plateau. The EC, CEC, pH, and CHN contents of soils changed with the addition of YBCs. YBC particles were unevenly distributed among soil particles. The addition of YBCs did not change the functional groups and mineral constituents of soils in the study area. In summary, YBCs might have a positive impact on soil ecosystems after they enter the soils of northeastern Qinghai-Tibet Plateau, if considering the improvement of soil physicochemical properties by adding YBCs.

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Conflicts of Interest: The authors declare no conflict of interest.

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