

**Thermal carbonization
(Biochar) of organic
material**

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**Does thermal carbonization (Biochar) of
organic material increase more merits for
their amendments of sandy soil?**

Y. Wu^{1,3}, G. Xu¹, J. N. Sun^{1,3}, and H. B. Shao^{1,2}

¹Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences(CAS), Yantai 264003, China

²Institute of Life Sciences, Qingdao University of Science and Technology, Qingdao 266042, China

³University of Chinese Academy of Sciences, Beijing 100049, China

Received: 13 January 2014 – Accepted: 15 January 2014 – Published: 14 February 2014

Correspondence to: H. B. Shao (shaohongbochu@126.com) and G. Xu (gxu@yic.ac.cn)

Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Organic materials (e.g. furfural residue) are generally believed to improve the physical and chemical properties of the soils with low fertility. Recently, biochar have been received more attention as a possible measure to improve the carbon balance and improve soil quality in some degraded soils. However, little is known about their different amelioration of a sandy saline soil. In this study, 56d incubation experiment was conducted to evaluate the influence of furfural and its biochar on the properties of saline soil. The results showed that both furfural and biochar greatly reduced pH, increased soil organic carbon (SOC) content and cation exchange capacity (CEC), and enhanced the available phosphorus (P) in the soil. Furfural is more efficient than biochar in reducing pH: 5% furfural lowered the soil pH by 0.5–0.8 (soil pH: 8.3–8.6), while 5% biochar decreased by 0.25–0.4 due to the loss of acidity in pyrolysis process. With respect to available P, 5% of the furfural addition increased available P content by 4–6 times in comparison to 2–5 times with biochar application. In reducing soil exchangeable sodium percentage (ESP), biochar is slightly superior to furfural because soil ESP reduced by 51% and 43% with 5% furfural and 5% biochar addition at the end of incubation. In addition, no significant differences were observed between furfural and biochar about their capacity to retain N, P in leaching solution and to increase CEC in soil. These facts may be caused by the relatively short incubation time. In general, furfural and biochar have different amendments depending on soil properties: furfural was more effectively to decrease pH and to increase available P, whereas biochar played a more important role in increasing SOC and reducing ESP of saline soil.

1 Introduction

A large saline soil reserve has been explored in the Yellow River Delta. Seasonal accumulation of salt in the surface soil caused by high soil salinity and water shortage restricts the germination of plants, while poor physical and chemical properties of soil are

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the major obstacles of plant growth. Few categories and small amount of active substances like soil enzyme and microorganisms are important influencing factors of circulation of materials and plants' sustainable utilization of soil resources (Angst, 2012). The low productivity of soil and soil environment deterioration in the Yellow River Delta further aggravate the soil salinity (Bai, 2005; Wang, 2010), thus restricting the growth of crops. The fertilization of organic materials can improve the soil salinity and increase crop yield significantly (Luo, 2008). As a kind of cheap acid organic substance with rich resources, furfural is effective in improving the saline soil (Yang, 2008; Li, 2008). Cai Axing et al. (1997), reported after research that furfural can lower the soil pH and ESP and increase crop yield, which is corresponding with the research results of Li (2008).

Biochar produced by furfural through pyrolysis under anoxia or hypoxia has high organic content and large specific surface area (Demirbas, 2004; Kimetu, 2010; Van, 2010), which plays an important role in water-fertilizer maintenance (Steiner, 2007; Wardle, 2008) and microbial activity improvement (Warnock et al., 2007; Steinbeiss, 2009). It is used as soil amendment (Lehmann and Joseph, 2009; Laird, 2010; Masullili, 2010; Niandou and Ahrnedna, 2010). However, no comparative research on the impact of furfural on the physicochemical properties of saline soil before and after its carbonization has been reported yet. Therefore, based on the indoor constant temperature incubation and leaching test, this paper evaluated the effect of furfural in improving saline soil according to the variation trend of acid-base property, water soluble salt, basic nutrients in soil and cation exchange performance, aiming to provide theoretical basis for the application of furfural and biochar in saline soil improvement.

2 Materials and method

2.1 Materials

The testing soils were collected from the saline soil in the Yellow River Delta (37°45'50" N, 118°59'24" E) with stones and plants eliminated. The collected soil sam-

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ples were natural withered under room temperature and then screened with a 2 mm screen. The physicochemical properties of testing soils were shown in Table 1. The soil showed a pH of 8.3 and an ESP as high as 27 %, known as strong alkaline soil (Lu, 1999).

The involved furfural is the cob after industrial distillation. It is in dark brown. The furfural biochar (hereinafter referred as biochar) is made from furfural through 4 h carbonization under 300°. The physicochemical properties of furfural and its biochar were listed in Table 1. Compared with the furfural, the biochar has higher C/N with 83.6 % total carbon (TC) contributed by organic carbon and lower inorganic nitrogen content. It has a CEC of 41.8 cmol kg⁻¹, 12 % higher than the furfural.

2.2 Incubation Method

A soil incubation test was conducted to investigate the similarities and differences of furfural and biochar in influencing the physicochemical properties of saline soil. The test involved five test treatments: (1) CK, Soil without furfural and biochar (2) T_1 , added with 2.5 % furfural; (3) C_1 , added with 2.5 % biochar; (4) T_2 , added with 5 % furfural; (5) C_2 , added with 5 % biochar. Each group was repeated for four times. In the test, each soil incubation container was filled with 500 g saline soil from the Yellow River Delta with a maximum water content of 30 % (evaporated water was replenished every day by weighing method). Soil samples were incubated under constant 25 °C. Take soil samples at 1d, 3d, 7d, 14d, 21d, 28d, 42d and 56d of the incubation, respectively for measuring pH, conductivity, available P, TC, NO₃⁻-N and NH₄⁺-N content. Artificial rainfall was given to the incubated soil at 4d and 38d by using distilled water. Collect the leachate for measuring the P, NO₃⁻-N and NH₄⁺-N content.

2.3 Measuring method

The physicochemical properties of the testing materials were measured by soil agricultural chemical analysis method (Lu, 1999) pH (soil/water = 1 : 2.5), EC (water/soil =

et al. (2011), and Uzoma et al. (2012), also reported a significance increase of TOC in soil by adding biochar, which is important to soil quality improvement and crop yield growth.

3.1.4 Variation of CEC and ESP

In Fig. 4, biochar (compared with furfural) failed to increase the soil CEC significantly as the incubation time went on, which may be related with the short incubation period (Liang, 2006). As the incubation time went on, surface groups of biochar were oxidized, which increased the surface charge density and thereby increased the CEC significantly (Cheng, 2008). Both furfural and biochar can increase the soil CEC ($P < 0.05$) and 5% biochar increased the soil CEC by 15%, indicating the involvement of furfural and biochar can increase the buffer performance of soil (Liang, 2006). This is because the large specific surface area of organic matters and negatively charged functional groups increased the exchange point of soil colloids, thus increasing the CEC (Lehmann, 2009).

In Fig. 5, ESP decreased more significantly when adding biochar compared with the furfural as the incubation time went on. But at the beginning of the experiment, ESP is increased. At the end of the test, ESP of T_2 and C_2 decreased to 51% and 43% of their initial ESP, respectively. On one hand, biochar has a high concentration of exchange. $\text{Ca}^{2+}/\text{Mg}^{2+}$ to replace Na^+ for soil colloidal absorption (Hu and Wang, 1987), thus decreasing the exchange. Na^+ in the soil. Table 1 represented that biochar contains 3 times higher exchange. Ca^{2+} than soil. On the other hand, biochar with loose and porous texture can increase the total porosity of soil (Lehmann and Joseph, 2009), thus losing more exchange. Na^+ during rainfall and reducing the ESP.

3.1.5 Variation of AP

A significant increase of AP content in soil was observed by adding furfural and biochar (Fig. 6). On one hand, both furfural and biochar can lower the soil acidity due to their

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lower pH value, which is accompanied with a significant increase of AP (Devau, 2011). On the other hand, furfural and biochar have higher AP content. The AP content in furfural is about 40 times that in soil (Table 1). Therefore, the application of furfural can increase the AP content in soil directly. The AP content was increased by 2–5 times by adding 5 % biochar and 4–6 times by adding 5 % furfural. This indicated the better performance of biochar compared with furfural in AP growth. According to Table 1, during the carbonization of furfural, the AP content decreased although TP content increased, indicating the occurrence of phosphorus immobilization during the carbonization of furfural. This corresponds with the significance increase of exchang.Ca^{2+} during the carbonization. Therefore, the significant increase of exchang.Ca^{2+} during the carbonization leads to the reduction of AP content (Tunesi, 1999).

3.1.6 Variation of NO_3^- -N and NH_4^+ -N

In Fig. 7, NH_4^+ -N in all five treatments increased firstly and then decreased. It reached the peak at 14 d and then decreased gradually. At the end of the test, NH_4^+ -N decreased to less than 2 mg kg^{-1} . This may be caused by the gradual decrease of organic nitrogen that is easy to be mineralized (Stanford and Epstein, 1974; Powers, 1990; Wennman and Kätterer, 2006), increased ammonia volatilization in soil due to the increased soil pH value (Dancer, 1973) and NH_4^+ -N losses caused by leaching. Significant decrease of NO_3^- -N concentration was observed after two artificial rainfalls (Fig. 8). Particularly, NO_3^- -N concentration of five groups decreased by more than 95 %, indicating the easy leaching losses of NO_3^- -N (Delgado, 2002).

It can be seen from Fig. 7 and Fig. 8 that furfural and biochar did not increase the inorganic nitrogen in soil ($P > 0.05$) (Bhupinder, 2010). This may be caused by their lower inorganic nitrogen content.

3.2 Impact of furfural and biochar on soil leachate

It can be known from Table 2 that during the first leaching process, leachate from groups with biochar and furfural showed an obvious increase of NH_4^+ -N concentration. The NH_4^+ -N concentration in the leachate increased with the increasing of furfural and biochar dosages. During the second leaching process, no significant difference of NH_4^+ -N concentration in all five treatments was observed. With the increasing of leaching processes, the NH_4^+ -N and NO_3^- -N concentrations in leachate from all treatments decreased significantly. The NO_3^- -N concentrations in leachate from C_1 decreased from 14.85 mg L^{-1} of the first leaching process to 0.6 mg L^{-1} . The involvement of furfural and biochar did not reduce the leaching losses of inorganic nitrogen. Soluble salts, such as NO_3^- -N and NH_4^+ -N, will be dissolved out and lost during rainfall or irrigation.

During the two leaching processes in this test, AP concentration in leachate from C_1 and C_2 increased, which increased continuously with the increasing of biochar dosage. This may be caused by the poor AP retaining capacity of biochar, thus making AP easy to lose through leaching. However, the AP concentration in leachate from T_1 and T_2 decreased with the increasing of furfural dosage, indicating its better retaining capacity of AP compare with biochar.

4 Conclusions

(1) Compared with biochar, furfural lowers soil pH and improves phosphorus activity as well as utilization rate more significantly. 5 % biochar can increase the AP content by 2–5 times, while 5 % furfural can increase the AP content by 4–6 times. This is closely related with the lower pH value of furfural.

(2) Compared with furfural, biochar increases the TOC significantly, up to 62%. At the end of the test, the ESP of C_2 decreased to 43% ESP of CK, lower than the ESP of groups with furfural. This is related with the porous structure of biochar and its higher exchangeable Ca^{2+} content. Although both furfural and biochar increase the soil EC,

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furfural presents greater increase of soil EC, indicating the less impact of carbonization of furfural on soil salinity increase during the improvement. This is beneficial for the improvement of saline soil.

(3) Both furfural and biochar fail to increase the inorganic nitrogen in soil, which may be related with ammonia nitrogen volatilization and lower nitrate content. The inorganic nitrogen and AP content in leachate from groups with biochar did not reduced. Furthermore, biochar fail to achieve higher increase of CEC compared with furfural. However, long-term impact of biochar caused by the oxidization of its surface groups deserves more attentions.

Acknowledgements. This research was partially supported by the National Natural Science Foundation of China (No.41001137; 41171216), One Hundred-Talent Plan of CAS, the CAS/SAFEA International Partnership Program for Creative Research Teams, the Important Direction Project of CAS (KZCX2-YW-JC203), Yantai Science & Technology Development Project (No.2011016; 2010245), Yantai Double-hundred Talent Plan (XY-003-02), 135 Development Plan of YIC-CAS and the Science & Technology Development Plan of Shandong Province (010GSF10208).

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Table 1. The physical and chemical properties of materials in this study.

	pH	EC (mscm^{-1})	TC (gkg^{-1})	TN (gkg^{-1})	CEC (cmolg^{-1})	ESP (%)	TP	AP	NO_3^- -N (mgkg^{-1})	NH_4^+ -N	exchang. Cations (mgkg^{-1})			
											K^+	Na^+	Mg^{2+}	Ca^{2+}
soil	8.3	0.5	16.9	1.0	7.2	26.9	550	5	52.2	15.4	120	446	557	3007
furfural	2.9	3.9	394.9	9.8	37.4	13.8	903	196	1.4	44.4	1132	759.5	1252	4373
biochar	4.5	2.7	506.4	11.5	41.8	12.4	1222	139	0.8	1.7	11 616	1190	1377	9156

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Table 2. Change of inorganic N and available P in leaching solution.

Treatment	Leaching first-incubation for 3 d			Leaching second-incubation for 38 d		
	NH ₄ ⁺ -N (mgL ⁻¹)	NO ₃ ⁻ -N (mgL ⁻¹)	AP (μgL ⁻¹)	NH ₄ ⁺ -N (mgL ⁻¹)	NO ₃ ⁻ -N (mgL ⁻¹)	AP (μgL ⁻¹)
soil	0.41 ± 0.15 ^a	28.93 ± 5.05 ^a	65.25 ± 6.21 ^a	0.18 ± 0.07 ^a	2.22 ± 1.92 ^a	27.62 ± 10.5 ^a
soil +2.5 % biochar	2.68 ± 0.96 ^{bc}	14.85 ± 3.75 ^b	73.45 ± 3.59 ^a	0.49 ± 0.17 ^b	0.6 ± 0.37 ^a	36.06 ± 11.06 ^a
soil +2.5 %	1.02 ± 0.01 ^a	61.13 ± 3.69 ^c	61.98 ± 5.11 ^a	0.26 ± 0.09 ^a	0.15 ± 0.02 ^a	25.58 ± 7.66 ^a
soil +5 % biochar	2.94 ± 0.28 ^c	40.97 ± 6.88 ^d	88.47 ± 7.51 ^b	0.18 ± 0.003 ^a	0.54 ± 0.57 ^a	64.53 ± 8.66 ^b
soil +5 %	1.97 ± 0.31 ^b	80.34 ± 9.08 ^e	59.24 ± 6.89 ^a	0.2 ± 0.09 ^a	0.47 ± 0.31 ^a	18.66 ± 3.71 ^a

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Table A1. Nomenclature.

EC:	Electrical conductivity
TC:	total carbon
TN:	Total nitrogen
TP:	Total phosphorus
AP:	Available phosphorus
SOC:	Soil organic carbon
CEC:	Cation exchange capacity
ESP:	Exchangeable sodium percentage

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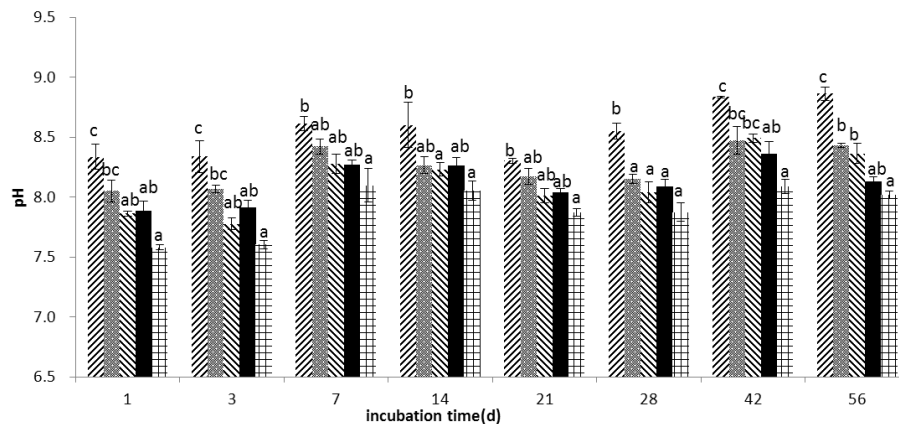


Fig. 1. Effects of the added furfural and biochar on soil pH. CK; C1: soil added with 2.5% biochar; T1: soil added with 2.5% furfural; C2: soil added with 5% biochar; T2: soil added with 5% furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

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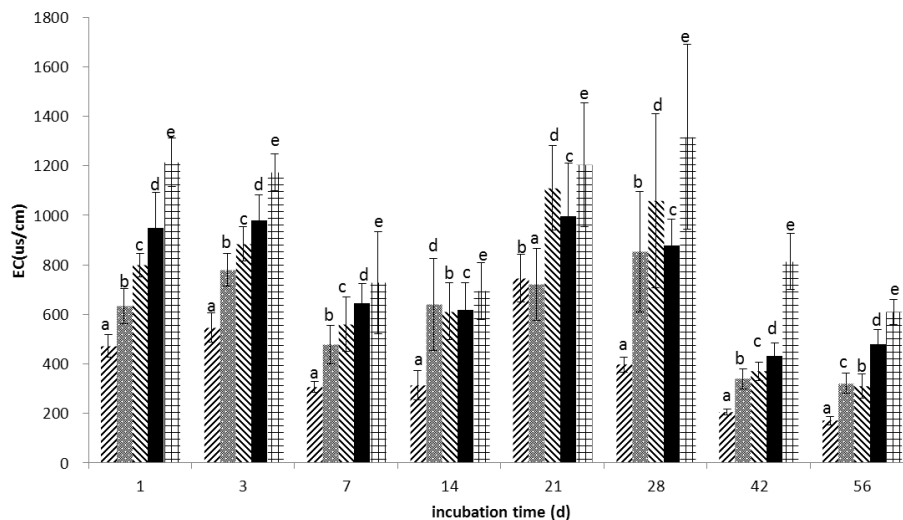


Fig. 2. Effects of the added furfural and biochar on soil EC. CK; C1: soil added with 2.5% biochar; T1: soil added with 2.5% furfural; C2: soil added with 5% biochar; T2: soil added with 5% furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

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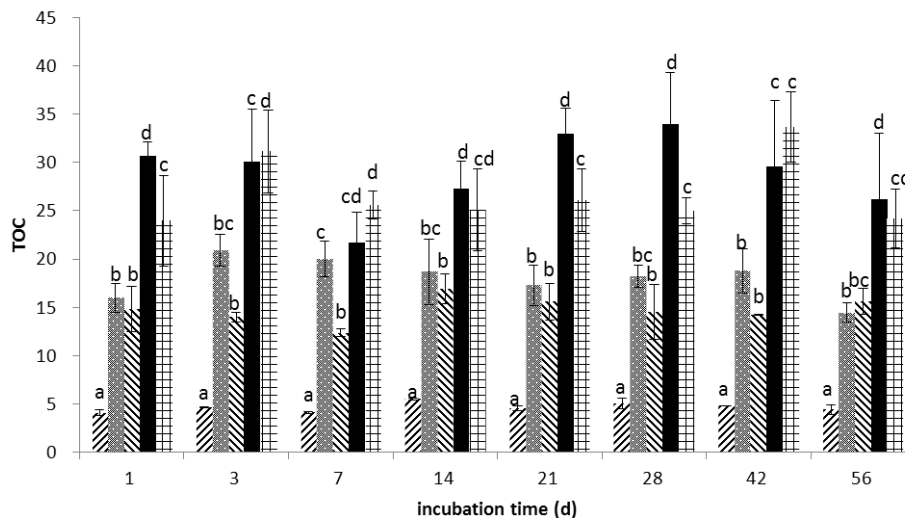


Fig. 3. Effects of the added furfural and biochar on soil organic matter contents. CK; C1: soil added with 2.5% biochar; T1: soil added with 2.5% furfural; C2: soil added with 5% biochar; T2: soil added with 5% furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

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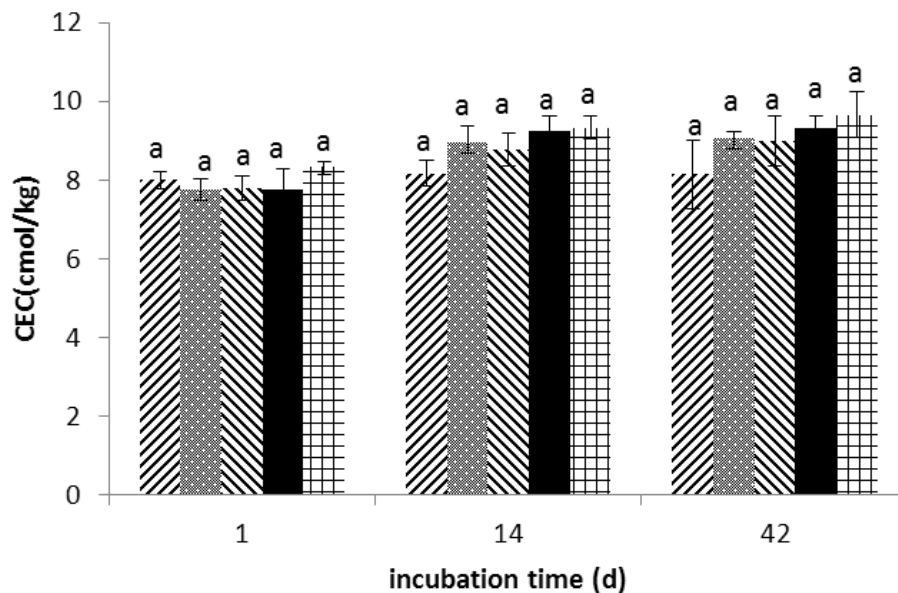


Fig. 4. Effects of the added furfural and biochar on soil CEC. ▧ CK; ▩ C1: soil added with 2.5 % biochar; ▨ T1: soil added with 2.5 % furfural; ■ C2: soil added with 5 % biochar; + T2: soil added with 5 % furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

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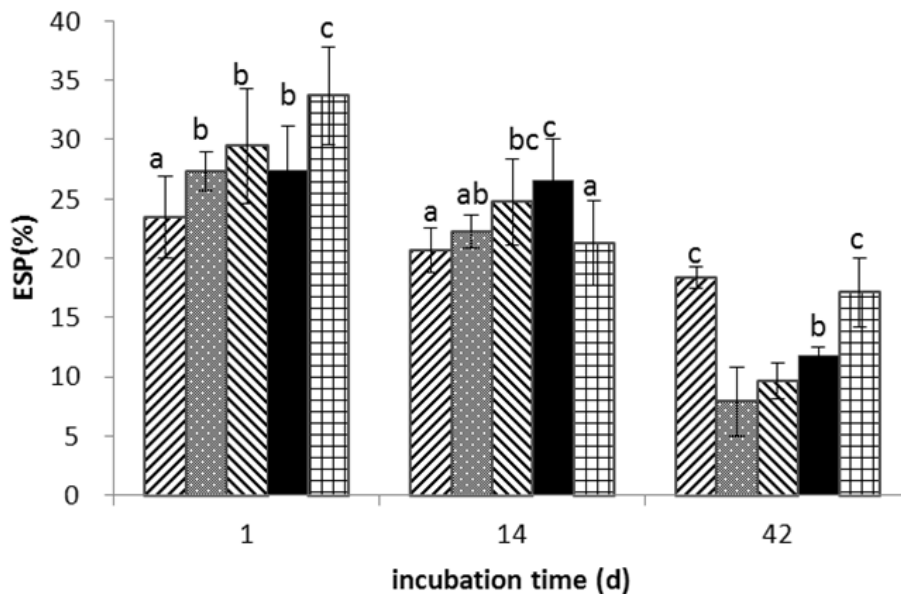


Fig. 5. Effects of the added furfural and biochar on soil exchange ESP. \diagup CK; \boxtimes C1: soil added with 2.5% biochar; \diagdown T1: soil added with 2.5% furfural; \blacksquare C2: soil added with 5% biochar; \boxplus T2: soil added with 5% furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

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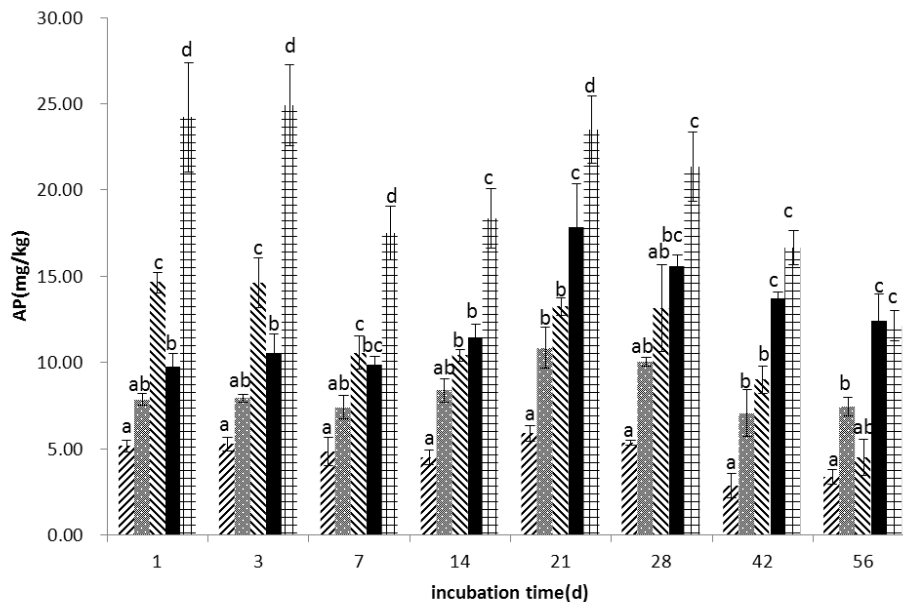


Fig. 6. Effects of the added furfural and biochar on soil available P contents. CK; C1: soil added with 2.5% biochar; T1: soil added with 2.5% furfural; C2: soil added with 5% biochar; T2: soil added with 5% furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

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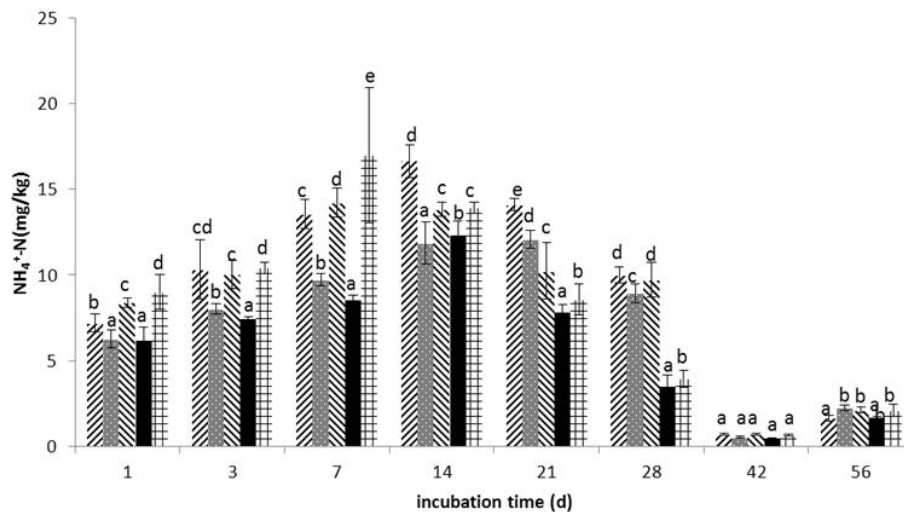


Fig. 7. Effects of the added furfural and biochar on soil NH_4^+ -N contents. CK; C1: soil added with 2.5% biochar; T1: soil added with 2.5% furfural; C2: soil added with 5% biochar; T2: soil added with 5% furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).

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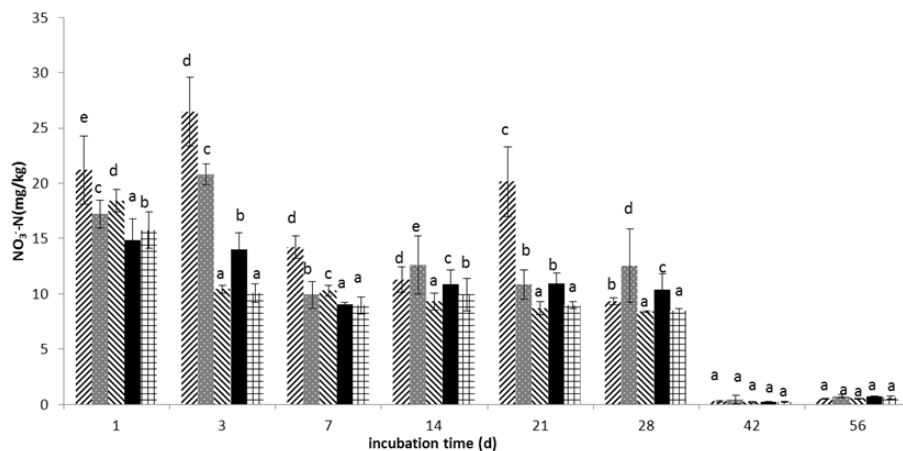


Fig. 8. Effects of the added furfural and biochar on soil NO_3^- -N contents. CK; C1: soil added with 2.5% biochar; T1: soil added with 2.5% furfural; C2: soil added with 5% biochar; T2: soil added with 5% furfural. The vertical lines are means ($n = 3$) \pm standard error, different letters represent significant differences (Tukey post hoc test, $p < 0.05$).