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Ageing of rice husk biochar along a freeze-thaw cycles

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Abstract. In order to elucidate the aging possess of biochar, the experiment with treatment biochar with soil were performed. For accelerating aging process, freeing-thawing cycle were conducted to simulate the changing process of the physical and chemical properties of biochar and explore the roles of biochar in the changes of the soil nutrition. Aging treatment has a significant impact on the physical and chemical properties of biochar. The pH values, element composition, oxidation of the surface, absorption capacity of biochar changed in the ageing process. In the simulation test of freeze-thaw cycles, pH of biochar displayed upward trend after the first decline in 25 cycles, and then return to the initial level, indicating that the pH of biochar is not easy to change. Biochar surface oxidation occurs rapidly and significantly in the early, and then stabilized in the latter stage. Surface oxidation degree is higher than the whole. The results showed that surface oxide of biochar protect the internal particles from further oxidation. In the first 25 freeze-thaw cycles, adsorption capacity of biochar to hydroquinone changes from the 5.928 $mg.g-^{1}$ to 11.73 $mg.g^{-1}$, indicating that freeze-thaw cycle treatment increase adsorption capacity of biochar.

1 Introduction

Biochar is admitted as a valuable tool for carbon abatement increasingly, with pyrolysis–biochar systems potentially offering greater carbon-equivalent gain than bioenergy only [1]. biochar may offer additional benefits to soil fertility [2]. Biochar plays a positive role in improving crop yield and promoting low-carbon and sustainable development, due to good physical and chemical properties.

However, these analyses depend on assumptions of the absolute and relative stability of different biochar products in soil. The stable properties of biochar also possess some instability. Nguyen[3] indicated that with the increasing of soil temperature, the loss rate of biological carbon increased, more incubation experiment showed that biochar character changes in its physical and chemical properties under different conditions[4]. The chemical and biological oxidation constantly changing the functional groups and chemical properties when biochar applied into soil[5]. It may also changed adsorption ability of biochar[6]. Different soil environment interact with biochar, leading to the change of biochar properties is different, and then effect on soil. Cultivation experiments study shows that biochar adsorption increased, CEC decreased after aging[7], The physical and chemical properties of biochar are changed inordinately in - 22 ℃ to 70 ℃ cultivation experiments [8]. The pH, adsorption ability CEC, surface functional groups and other important physical and chemical properties will change in the process of biochar aging.

Biochar aging will inevitably affect the content of production function. In a lot of characteristic of biochar, pore structure, element distribution are important, is also the focus in the study of the aging process. Pore structure affected the specific surface area and pore size of biochar, and then affected surface adsorption capacity. Element distribution affects the functional groups and ion exchange capacity, further affects the pH with alkali metals, organic acids, etc.

Aging is a long-term process, conventional methods of field experiment is difficult to meet the needs of the research. So, In this paper, we use freezing and thawing cycle to accelerate the aging process, study on the change rule of physical and chemical properties of biochar, and then analyzes its reason. Explore biochar aging impact on soil nutrients, In order to use biochar reasonable and efficient and provide theoretical basis for a long time.

2 Materials and methods

2.1 Biochar sample

In this study, The rice husk were collected from paddy field in southland of Rice Research Institute, Shenyang Agricultural University, Shenyang, China. The rice husk were air-dried at room temperature then placed in ceramic crucibles each covered with a fitting lid, and pyrolyzed under oxygen-limited conditions in a muffle furnace. The pyrolysis temperature was raised to the values of 400 ℃ at a rate of approximately 20℃ min-

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1and held constant for 30min. After heating for 30min, the biochar samples were allowed to cool to room temperature. The rice husk biochar was used to study the ageing processes of biochar(Figure 1）.

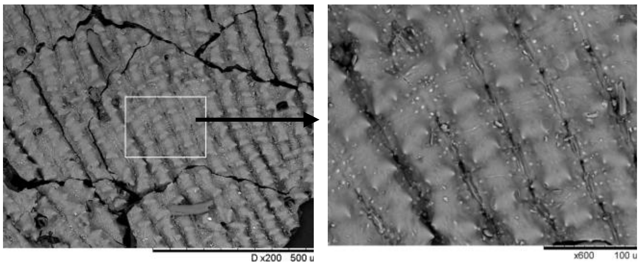

Figure 1. SEM of inside surface of husk biochar

2.2 Ageing experiment

Ageing of biochar was conducted in an aerobic incubation experiment along a freeze-thaw cycles at 30℃/10d,-20℃/10d,25 cycles total. Ten grams of biochar were placed in a PVC Pipe Scrap , which the hight is 60cm, diameter is 4.4cm and 4 mL of water were added to attain a moist environment, and then incubated in the dark.

2.3 Elemental and chemical analyses

Elemental analysis (C, S, N,) of the biochar samples was conducted using a Germany Elemental, The composition of C, N, S, and O of biochar samples were presented on a dry ash-free basis Energy Dispersive X-ray spectrometers (Bruker Nano GmbH).Morphological and surface elemental analyses were carried out by scanning electron microscopy (SEM) and Energy dispersive Spectroscopy (EDS) (Jeol JSM-6400).

The pH value of biochar was measured in 1:20 w/v ratio in either H_2O or 1 M KCl solution. The pH value in 1 M KCl presents the potential pH, since high ionic KCl solution could release exchangeable protons of biochar into solution. Each experiment was conducted in 3 duplicate

In the acid－base titrations, 0.500 g of the biochar samples (0.3-mm sieve) was placed in 50-mL Erlenmeyer flask. Then, 20 mL of deionized water was added to each bottle, and each of the bottles was stirred on a magnetic stirrer for 2 h at 25℃ The samples were then titrated with 0.1 M HCl at 25℃ to the end point at pH 2.0.

The amount of carbonates was determined by volumetric analysis of the CO_2 liberated through adding 4 M HCl solution to the biochar samples (Pansu and Gautheyrou, 2006). About 5 g of CaCO3 was dried at 104℃ and then 0.0000, 0.1000, 0.2000 and 0.3000 g of the dried CaCO3were each weighed as standard substances. Of the prepared biochar samples (0.15-mm sieve), 1.00 g was weighed to determine the carbonate content.

2.4 Statistical analysis

The experiment was set up in a randomized design with three replications. The data were analysed for significance of difference by analysis of variance using Data Processing System (DPS) (Tang and Feng 2006). Means with the same letters are not significantly different .

3 Results and discussion

3.1 Elemental and chemical analyses

The fresh biochar(0) showed a relatively high C concentration(47.985%). After 13 cycles, the C content of the biochar was very significantly lower than other cycles. With the ageing of biochar a decrease in N concentration was observed and the magnitude of these changes increased with the aging cycles, significantly for the last 2cycles In contrast, the concentrations of H did not display differences among biochar samples except the last cycles the H content significantly lower than 3 cycles.

With the ageing of biochar, An decrease in C/N ratio from 1-15 cycles and the last 2 cycles increased very significantly (Table 1).

Table 1Elemental composition of biochar along 25 freeze-thaw cycles (30℃/10d,-20℃/10d)

	C/%	N/%	H/%	C/N	C/H
0	47.985aA	1.278ABC	34.401abA	37.547cdBCD	1.395aA
1	46.627aAB	0.908bcBCD	37.542abA	51.435bB	1.246aA
2	44.642abAB	0.975abcABC	37.976aA	46.763bcBC	1.178aA
3	45.817abAB	1.157abABC	34.882abA	39.752cdBCD	1.332aA
5	45.235abAB	1.21aA	35.650abA	37.291cdBCD	1.278aA
7	47.281aAB	1.420aAB	34.315abA	33.580dCD	1.379aA
9	47.391aA	1.383abcABC	33.159abA	34.290dCD	1.436aA
11	46.287aAB	1.123aABC	33.095abA	41.185cdBCD	1.446aA
13	42.544bB	1.310aA	36.522abA	34.174dCD	1.169aA
15	44.673abAB	1.458dDE	33.10abA	30.652dD	1.355aA
20	46.438aAB	0.613dE	36.579abA	76.331aA	1.270aA
25	47.026aAB	0.554dE	31.667bA	85.408aA	1.494aA

The data indicate mean±SD Means followed by the same letter within a line are not significantly different at the 5% level

The O/C ratios of biochar surface increased rapidly in the first 9 cycles, then deposition till the 15 cycles. There were no significantly change in15-25 cycles. The O/C ratios of entire biochar were wavelike rises with cycle. In the first 9 cycles increases more slowly than surface biochar(Figure 2).

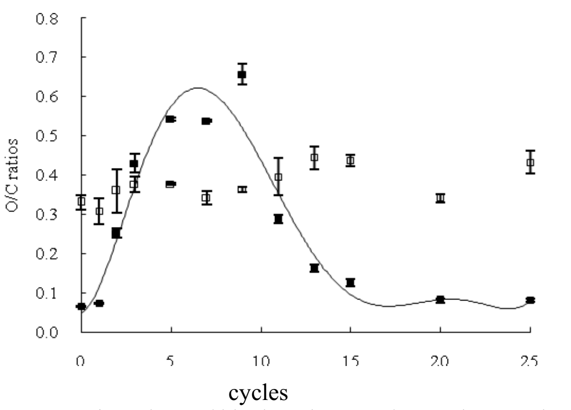

Figure 2. O/C rations of biochar along 25 freeze-thaw cycles
Note：Solid black squares were the observations of biochar surfaces(determined by EDS) and open squares those of entire biochar particle

The pH values of the biochar keep decreased in the first 11 cycles, particularly at 7, 9 and 11 cycles decreased significantly, then increased substantially from 13-20 cycles. No significantly change among 20,25and 0-3cycles.The lower pH values in 1M KCl solution compared to in H_2O were due to the release of exchangeable acidity in the KCl solution.

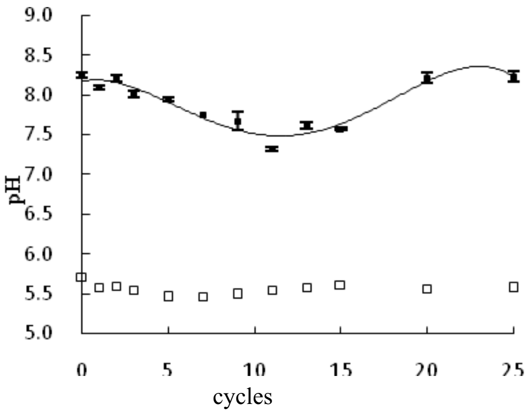

Figure 3. pH of husk biochar in 25cycles,
Note：Solid black squares were the normal pH with deionized water of biochar and open squares were the potential pH with 1M KCLof biochar

Biochar is alkaline, with high pH, Figure 3 show the pH changes of biochar in different Freeze-thaw cycles. In 25 cycle, the pH of biochar always higher than 7, the minimum is 7.33 (11 cycle), the highest is 8.25(0 cycle). The pH dropped significantly from the second cycle and then increased after the 13th cycle, appear frist falling and then rising. At the last 20, 25 period keep steady and there was no significant difference with original biochar pH. Although the pH value decline in the early treatment , the pH is above 7.33 in all the cycle and back to the original pH value at last. Indicated that biochar alkaline is relatively stable.

From Fig.3 we can see that the pH value between 5.45 - 5.71,PH value does not change significantly in 25 freeze-thaw cycle in1N KCL. There was a slight decline in early-stage,then rebound and maintain stability.

3.2 The influence of the freeze-thaw cycle treatment on carbonate content of biochar

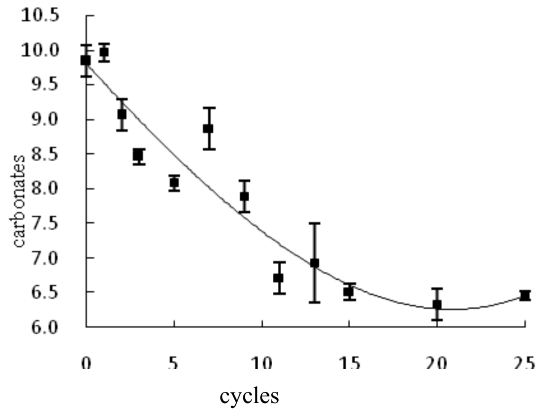

Figure 4. Carbonates content of biochar along 25 freeze-thaw cycles

Figure 4 is the condition of carbonate content changes of biochar. The carbonate content of biochar is low, Original biochar carbonate content is $9.835 cmolkg^{-1}$,and then fall down .After freezing and thawing cycle treatment, carbonate content present down trend and keep stable after 11 cycles.

3.3 The influence of the freeze-thaw cycle treatment on Adsorption capacity of biochar

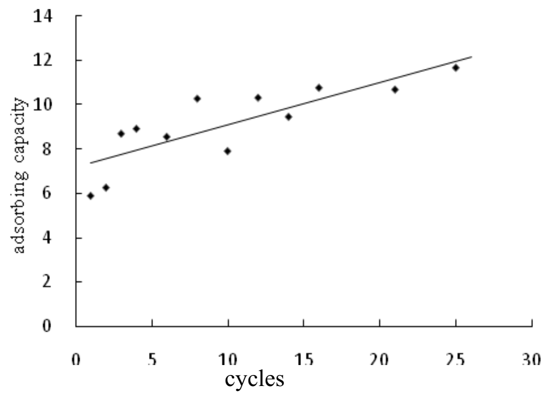

Figure 5. Adsorption capacity of biochar along 25 freeze-thaw cycles

The adsorption hydroquinone of biochar is showed in Figure 5, We can see that during the freeze-thaw cycle biochar adsorption ability slowly rising.This study use hydroquinone as adsorbent, because hydroquinone allelopathy to plant.

Biochar has rich pore structure, The increases of biochar for hydroquinone adsorption may be due to freezing and thawing cycle caused the change of pore structure.

4 Conclusion

Under different environmental conditions, the change of biaochar are different. In the nature soil, four seasons alternately, freeze-thaw cycle[9], Wind and rain erosion[10] can cause the physical and structures change of biochar. For example from larger particles to small particles, from a lower layer soil displacement to the deep soil.

In the aspect of chemical properties, the aromatic structure will increased when biochar stayin soi for a long time[11]. Elements will change and surface charge will also change.

The results show that biochar pH change in the freezing and thawing cycle, but in the end and return to the original. It proved that is not easy to change biochar pH. This study suggests that the pH changes associated with carbonate content and the change of functional groups. The oxidation on the surface of biochar more significant than inner during freezing and thawing cycle. Surface oxidation occurred earlier and bigger, The level of oxidation of overall biochar are less than surface oxidation. The freeze-thaw cycle of biochar effects of surface structure characteristics irregularly, shows that biochar surface structure characteristics affected by various factors. The freeze-thaw cycle can increase biochar adsorption ability of hydroquinonesignificantly.

study shows that biochar alkaline depends on the content of carbonate[12].But in this study the change of pH value during the process of freezing and thawing cycle is not completely consistent with the carbonate content. We speculate that pH value is not only related to the carbonate content and it also correlate with the carbonate content and the functional groups.

Carbonization process of biochar greatly increase its stability in nature,its the basis of the stability of structure. With the development of biochar industry, The character of the artificial preparation biochar is not set in stone, Different materials with different firing temperature and time produced properties of biochar are different. The stability of the under different environmental conditions are different. Studies have confirmed that biochar in the cultivation of the short time (6 months, 12 months) during22 ℃-70 ℃, the properties of the biochar are changed in different degrees [13]. This study have th same conclusion.

This study also concluded that the physical and chemical properties of biochar are changed in the process of freezing and thawing alternation. At the same time the study was done under the condition of indoor simulation With the actual situation may be different in nature. This study will provide theoretical basis for biochar research in the future.

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