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Characteristics of the surface chemistry of linden pyrochar after removal of labile organic matter

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Abstract. The changes of chemical properties of the pyrochar surface were studied in the laboratory experiment that simulated pedogenic transformation of pyrochar under the influence of soil biota. The native pyrochar samples were obtained by pyrolysis of linden wood residues at the temperature of 250°C, 450°C and 650°C. Their modified samples were obtained by removing an easily degradable pool of organic substances that can be used by microorganisms during the first months after application to the soil. In low-temperature linden pyrochar (250°C and 450°C) dominated carboxylic and phenolic surface groups, in high-temperature (650°C) - lactonic groups. After removal of readily decomposable organic substances the acidity of the phenolic and lactonic groups in pyrochar of low-temperature pyrolysis sharply decreased. Characteristic feature of all studied samples is the presence in IR spectra of absorption bands of gyroxyl, carbonyl, methylene groups and organosilicon polymers. The feature of IR spectra of linden pyrochar (250°C and 450°C) is the presence of absorption bands of the stretching vibrations of the tertiary alcohols and phenols C-O group.

1. Introduction

Eco-pyrochar is derived from available agricultural and forestry wastes that do not pose a threat to the environment and human health [1]. They are mainly used to increase the soil fertility and reduce the greenhouse gas emissions [2-4]. The main factors that determine the physical and chemical properties of pyrochar (PC), as well as the surface chemistry are plant residues and the technology of their production [5-7], produce and use PCs as sorbents of heavy metals, pesticides, various ions, organic pollutants, as well as to reduce the leaching of nutrients from the soil [8-13]. Their practical application is based on the ability to interact with atoms, ions and molecules of other substances through of chemical groups on the particles surface [14]. The scientific literature describes research works of the study of pyrogenic organic matter (OM) surface chemistry [15-18] and there are practically no publications about the study of PC chemical properties changes in soil conditions. The main difficulty of studying the change of PC chemical properties in soils is the physical separation of pyrogenic particles from the soil matrix. The purpose of this work is to study in the model experiment of the pedogenic transformation of PC chemical properties.

2. Material and methods
To study the changes of properties and surface chemistry of the pyrogenic OM the native and modified PCs samples were studied in the model experiment. Native samples were obtained from the stem wood linden of Laishevsky region of RT. The pre-cut samples were initially crushed to a chip size by a knife crusher and then subjected to pyrolysis in a laboratory retort d = 32 mm in a muffle furnace with a vapor-gas mixture withdrawn through a condenser under various temperature conditions of 250°C (PC<sub>250</sub>), 450°C (PC<sub>450</sub>) and 650°C (PC<sub>650</sub>). The weight of the sample was 50g, and the rate of heating with pyrolysis to the regime temperature was 10°C/min. After heating to the regime temperature, the retort was held in the isothermal regime until the gas formation ceased, followed by cooling. The temperature fixation was carried out by chromel alumel thermocouples inside and outside of the retort. The cooled and stabilized PC was re-ground and subjected to separation on sieves. The modified PC were obtained by boiling native samples in distilled water in the flasks under reflux for 1 hour. After removal of OM extracted by hot water the PC was dried to constant weight. Boiling was carried out for the decomposition of the readily decomposable fractions of the PC organic substance which can be used by microorganisms for several months after their introduction into the soil. Carbon extracted by hot water is the indicator of readily decomposable carbon of organic compounds in the soil, i.e. active pool of soil OM [19].

The study of the PC samples morphology has been performed with field emission scanning electron microscope (SEM) Merlin (Carl Zeiss). Surface morphology was surveyed with an accelerating voltage of primary electrons of 5 kV and probe current of 300 pA for the minimal impact on the object of investigation. Elemental microanalysis was carried out using energy dispersive spectroscopy using an X-Max (Oxford Instruments) detector mounted on an SEM at an accelerating voltage of 20 kV and probe current of 600 pA. The determination of the functional groups of native and modified PC samples was carried out using the Boehm method [20], taking into account recommendations for standardizing of the experimental conditions [21-23]. The titration was carried out on an automatic ATP titrator with a drop volume of 0.07 ml / 2 minutes to pH = 7. The IR spectra of the samples was obtained by the method of disturbed total internal reflection on a Perkin-Elmer spectrometer with a PIKE MIRacleTM attachment in the range 4000-660 cm<sup>-1</sup>. Interpretation of IR spectra was carried out on the basis of work [24].

3. Results and discussion

Figure 1 shows the SEM images of microstructure of linden PC samples. These images show that the PC is a highly porous carbon material with micropores which repeats the picture of natural "nutrient" channels of the original wood.

![Figure 1](image1.png)

**Figure 1.** SEM images of native linden PC (a) and modified linden PC after boiling of water (b).
Most of the internal space of the sample is pores with a diameter of 10 - 30 μm. These pores are large for the penetration of root hairs of plants which mainly are in the macroporous space filled with water [25]. However, they are most suitable for growth and development of microorganisms.

Figure 2 shows the areas within the elemental composition of native and modified PC samples surface was quantified.

![Figure 2. SEM images and elemental composition of native linden PC.](image)

The main part of the elemental composition of the internal space of the PC sample is carbon and oxygen. Among these mineral elements were found macro and microelements of plant nutrition (figure 2, 3). Within the pores with the diameter of about 30 μm were discovered mineral crystals of about 5 μm in size (figure 2; spectrum 1). The increased oxygen content in spectra 1 and 3 indicates that oxygen is not only adsorbed on the surface of the pyrogenic OM, but is also chemically bonded to the mineral elements.

In the modified samples the mineral crystals were scattered over the surface of the PC slice (figure 3; spectrum 4 and 5). In the chemical composition iron and silicon absent in native samples were also found there.
Figure 3. SEM images and elemental composition modified linden PC.

The total acidity of functional groups in native samples was from 297 to 1560 μmol/g, in modified from 367 to 1451 μmol/g (table 1). Carbonyl groups predominate in native samples PC250 and their amount increases after removal of organic substances extracted by hot water. The acidity of the lactonic group in the modified samples is on the contrary reduced. Thus after application of linden PC250 into the soil the acidity of the phenolic and carboxyl groups will increase.

Table 1. Acidity of PC surface functional groups.

| Functional groups | PC250  | Acidity, μmol/g | PC450  | Acidity, μmol/g | PC650  | Acidity, μmol/g |
|-------------------|--------|-----------------|--------|-----------------|--------|-----------------|
|                   | Native | Modified       | Native | Modified       | Native | Modified       |
| Phenolic          | 397    | 464            | 1167   | 492            | 63     | 85             |
| Lactonic          | 265    | 71             | 322    | 340            | 227    | 224            |
| Carboxylic        | 852    | 916            | 71     | 33             | 7      | 58             |
| Total             | 1514   | 1451           | 1560   | 865            | 297    | 367            |

The acidity of the PC450 functional groups is mainly due to the presence of phenolic and lactonic groups which after the removal of readily decomposable organic substances are sharply reduced. The acidity caused by carboxylic groups is insignificant and after the removal of easily decomposable fractions of OM the acidity carboxylic groups decreases 2 times. The acidity of the PC650 functional groups is determined by the presence of lactonic groups. After the removal of the readily decomposable OM pool the slight increase in the acidity of phenolic and carboxylic groups is observed.

Thus, with the increase in the pyrolysis temperature the acidity of the functional groups in PCs decreases. In PC250 and PC450 predominate carboxylic and phenolic functional groups, in PC650 - the basic acidity of the functional groups is formed by lactonic groups.
The PC absorption bands are presented in table 2. A broad absorption band is observed in all samples in the region of stretching vibrations of hydroxy groups (~3400 cm\(^{-1}\)), but in PC\(^{650}\) its intensity is lower and indicates a decrease in the number of hydroxy groups. In native and modified samples the frequencies are characteristic of symmetric and asymmetric valence and deformation vibrations of methylene groups. Also all considered spectra have strong absorption in the 1700-1742 cm\(^{-1}\) region which corresponds to the carbonyl group of organic compounds.

In PC samples of high-temperature pyrolysis the absorption band is shifted toward the lower boundary of the usual interval which is probably related with the conjugation of aromatic rings. Characteristic feature of IR spectra is the presence of bands group between 1650 and 1450 cm\(^{-1}\) which is typical for stretching vibrations of the aromatic ring.

A broad and very intense band in the range from 1100 cm\(^{-1}\) to 1000 cm\(^{-1}\) is probably related to the presence of organosilicon polymers in which silicon and oxygen atoms alternate in the molecule.

| Sample   | Wave numbers, cm\(^{-1}\) (group and \(\pi\) vibration)                                                                 |
|----------|-------------------------------------------------------------------------------------------------------------------------|
|          | Pyrolysis temperature of 250°C                                                                                           |
| Native PC| 3340 (vOH), 2930 (v\(_{5v}\)CH\(_3\)), 2857 (v\(_{1v}\)CH\(_2\)), 1738 (vC=O), 1606 (vC=C), 1515 (vC=C), 1455 (\(\delta\)CH\(_2\), \(\delta\)CH\(_3\)), 1427 (\(\delta\)OH), 1373 (\(\delta\)CH\(_3\)), 1321 (vC-O), 1235 (vC=O-O), 1159 (vO-C-C), 1031 (cycl (R\(_5\)SiO\(_3\))), 892 (\(\delta\)OH) |
| Modified PC| 3355 (vOH), 2927 (v\(_{5v}\)CH\(_3\)), 2856 (v\(_{1v}\)CH\(_2\)), 1727 (vC=O), 1602 (vC=C), 1513 (vC=C), 1453 (\(\delta\)CH\(_2\), \(\delta\)CH\(_3\)), 1423 (\(\delta\)OH), 1373 (\(\delta\)CH\(_3\)), 1320 (vC-O), 1240 (vC=O-O), 1160 (vO-C-C), 1033 (cycl (R\(_5\)SiO\(_3\))), 884 (vO-O) |
|          | Pyrolysis temperature of 450°C                                                                                           |
| Native PC| 3343 (vOH), 2928 (v\(_{5v}\)CH\(_3\)), 2856 (v\(_{1v}\)CH\(_2\)), 1742 (vC=O), 1607 (vC=C), 1515 (vC=C), 1456 (\(\delta\)CH\(_2\), \(\delta\)CH\(_3\)), 1426 (\(\delta\)OH), 1368 (\(\delta\)CH\(_3\)), 1316 (vC-O), 1209 (vC-O), 1159 (vC-O), 1033 (cycl (R\(_5\)SiO\(_3\))) |
| Modified PC| 3338 (vOH), 2928 (v\(_{5v}\)CH\(_3\)), 2857 (v\(_{1v}\)CH\(_2\)), 1740 (vC=O), 1607 (vC=C), 1515 (vC=C), 1460 (\(\delta\)CH\(_2\), \(\delta\)CH\(_3\)), 1428 (\(\delta\)OH), 1368 (\(\delta\)CH\(_3\)), 1316 (vC-O), 1218 (vC-O), 1160 (vC-O), 1033 (cycl (R\(_5\)SiO\(_3\))) |
|          | Pyrolysis temperature of 650°C                                                                                           |
| Native PC| 3341 (vOH), 2926 (v\(_{5v}\)CH\(_3\)), 2853 (v\(_{1v}\)CH\(_2\)), 1700 (vC=O), 1599 (vC=C), 1516 (vC=C), 1451 (\(\delta\)CH\(_2\), \(\delta\)CH\(_3\)), 1428 (\(\delta\)OH), 1377 (\(\delta\)CH\(_3\)), 1037 (cycl (R\(_5\)SiO\(_3\))), 875 (vO-O) |
| Modified PC| 3316 (vOH), 2925 (v\(_{5v}\)CH\(_3\)), 2855 (v\(_{1v}\)CH\(_2\)), 1700 (vC=O), 1598 (vC=C), 1513 (vC=C), 1451 (\(\delta\)CH\(_2\), \(\delta\)CH\(_3\)), 1440 (\(\delta\)OH), 1377(\(\delta\)CH\(_3\)), 1036 (cycl (R\(_5\)SiO\(_3\))), 882 (vO-O) |

A feature of the IR spectra of linden PC of the pyrolysis temperature of 250°C and 450°C is the presence of absorption bands of the valence vibrations of the C-O group of tertiary alcohols and phenols near 1150 cm\(^{-1}\), 1410-1310 cm\(^{-1}\) and 1200 cm\(^{-1}\), 1410-1310 cm\(^{-1}\) respectively.

4. Conclusion

Analysis of the study of results showed that in the linden PC\(^{250}\) and PC\(^{450}\) dominated carboxylic and phenolic functionalities groups, in the linden PC\(^{650}\) dominated lactone groups. After removal of readily decomposable OM the acidity of the phenolic and lanatic groups in the PC of low-temperature pyrolysis considerably decreases. The acidity of functional groups in the PC\(^{650}\) is determined by the presence of lactonic groups. After the removal of the readily decomposable OM fractions there is a slight increase in the acidity of phenolic and carboxyl groups. Characteristic feature of all studied samples is the presence in the IR spectra of absorption bands of glyroxyl, carbonyl, methylene groups
and organosilicon polymers. A feature of the IR spectra of linden PC\textsuperscript{250} and PC\textsuperscript{450} is the presence of absorption bands of the stretching vibrations of the tertiary alcohols and phenols C-O group.

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