The effect of extraction of labile organic fractions on surface properties of pyrochars

E V Smirnova, K G Giniyatullin, R V Okunev, I A Guseva and K A Gordeeva

Institute of Environmental Sciences, Kazan Federal University, Kremlevskaya str., 18, 420008, Russia

E-mail: tutinkaz@yandex.ru

Abstract. The changes in the properties of pyrochars and the possibility of their use as soil meliorants were evaluated. Pyrochars obtained from linden residues at fixed pyrolysis temperatures of 250°C, 450°C and 650°C and under isothermal conditions in the temperature range from 450°C to 650°C have been studied. Their labile fractions of organic matter extracted with Na₄P₂O₇-NaOH solution and hot water was investigated by UV-VIS spectrometry and after extraction cation exchange capacity of pyrochars was characterized. For the qualitative characteristics of the selected fractions, ratio of the absorption of a colored solution of organic matter at λ = 254 nm to the content of organic carbon was calculated. It was concluded, that the pool of water-soluble and alkaline-soluble organic matter of pyrochars is a mixture of organic compounds of uncertain qualitative composition, whose properties are determined by the pyrolysis temperature. Extraction of this water-soluble and alkaline-soluble organic matter leads to a change in cation exchange capacity of pyrochars.

1. Introduction

Pyrochars are promising meliorants. Their application to soils can be considered as a way to climate change mitigation and increase of fertility, especially in regions with poor soils [1]. The impact of pyrochars on soils can change their physical properties – increase aeration and water retention [2-5]. Properties of pyrochars depending on the technology of production. For example, the cation exchange capacity (CEC) increases during slow pyrolysis, but an increase in the pyrolysis temperature, as well as decrease, affects on this soil property multidirectional. As a product obtained from organic materials, pyrolyzed carbon is a source of labile and stable soil organic carbon pools. According to some authors, pyrolyzed carbon formed at relatively high (above 600°C) temperatures leads to a higher content of aromatic carbon fractions and a lower content of functional groups H and O, and, consequently, to a lower CEC value. A low pyrolysis temperature (> 400°C) can promote to an increase in the functional groups of CO and CH in the organic matter (OM) of pyrochars, which may cause a higher cation-exchange ability [4]. It was considered that the pyrochar just applied to soil does not have a high CEC compared to the soils themselves, but over time, its cation-exchange ability will gradually increase due to oxidation of the surface because of reactions with water, oxygen and organic matter. Pyrochars obtained from woody biomass usually has a higher surface area than other types, which causes its higher adsorption capacity. The qualitative composition of organic compounds also varies widely depending on the type of raw material and the conditions of obtaining the product [6]. In general, individual
characteristics of pyrochars vary greatly depending on the source and method of production, and can have a multi-directional effect on the same soils.

The aim of the work was to estimate the capacity of cationic exchange of linden pyrochars obtained by fixed and uncontrolled pyrolysis temperatures after separation of labile OM fractions by various extractants.

2. Materials and methods

Pyrochars obtained from linden stem residues at fixed pyrolysis temperatures of 250°C (PC250), 450°C (PC450) and 650°C (PC650) and under isothermal conditions in the temperature range from 450°C to 650°C (PC450-650) were studied. During the obtaining of the pyrochars, in uncontrolled temperature conditions, the technology of their processing during pyrolysis with hot water was used.

Extraction of labile fractions from pyrochars was performed in three ways: (1) by extraction with cold distilled water; (2) boiling samples in distilled water for 1 hour [7] and (3) extraction with a mixture of Na$_4$P$_2$O$_7$-NaOH [8]. After isolating the labile organic matter with a mixture of Na$_4$P$_2$O$_7$-NaOH, the pyrochar samples were thoroughly washed with distilled water until the alkaline pH was neutralized.

In the native and modified after removal of the labile OM fractions dried samples, the CEC was determined by the Bobko–Askinazi–Aleshin method in the TSINAO modification [9]. The content of organic carbon in the extracts was determined by wet combustion according to the Tyurin method. All experiments were carried out in triplicate. The absorption spectra of the water-soluble and alkaline-soluble fractions were measured on the Lambda 35 spectrophotometer (PerkinElmer, USA) in the wavelength range of 320-220 nm, after the required dilution of the original extracts.

3. Results and discussion

The results of the determination of CEC in native pyrochars and modified pyrochars after removal of the labile OM fractions are presented in Table 1, and the content of organic carbon extracted from modified pyrochars are presented in Table 2.

Table 1. CEC of native and modified pyrochars, meq 100g$^{-1}$ (mean±standard error, n=3).

| Pyrochar type | Modification       | Native     | Cold water | Hot water | Alkaline solution |
|--------------|--------------------|------------|------------|-----------|------------------|
| PC250        |                    | 28.5±2.99  | 21.3±1.25  | 14.9±1.52 | 96.3±6.88        |
| PC450        |                    | 31.0±1.91  | 48.8±4.27  | 13.8±1.50 | 100.0±11.2       |
| PC650        |                    | 24.5±3.40  | 50.0±2.04  | 26.9±2.77 | 115.0±11.23      |
| PC450-650    |                    | 21.0±0.58  | 23.8±1.25  | 21.3±2.39 | 83.8±2.25        |

Table 2. Labile organic matter carbon extracted from pyrochars mg g$^{-1}$ (mean±standard error, n=3).

| Pyrochar type | Modification       | Cold water | Hot water | Alkaline solution |
|--------------|--------------------|------------|-----------|------------------|
| PC250        |                    | 0.66±0.018 | 1.09±0.004 | 11.36±0.238      |
| PC450        |                    | 0.40±0.006 | 1.27±0.026 | 9.01±0.149       |
| PC650        |                    | 0.29±0.012 | 0.48±0.004 | 5.03±0.03        |
| PC450-650    |                    | 0.05±0.012 | 0.04±0.007 | 0.52±0.015       |

Data obtained during the study show that in native pyrochars prepared in the mode of low fixed temperatures (PC250 and 450), CEC values are similar. At a temperature of 650°C (PC650) some decrease is observed. What is natural, because the increase in the pyrolysis temperature leads to the combustion (and removal) of organic matter.

Hot water treatment has a significant effect on PC250 and PC450. For this pyrochars CEC is more than 2 times lower. Possibly due to the removal of chemical agents contained in large quantities in
pyrochars produced at low temperatures. In the PC650 this effect under hot water treatment is not observed. probably due to the low content of organic matter.

After removing with cold water the labile organic matter of pyrochar. CEC increases by about 2 times in PC450 and PC650. A small amount of OM is extracted with cold water and the sorption capacity is increased. possibly due to the removal of water-soluble mineral substances from the pyrochar surface. which overlaps the sorption centers.

As well as using water treatment with alkaline solution leads to changes in the pyrochars surface chemistry. There is an increase of 3-4 times the sorption capacity in all studied samples. The mechanism of such exposure may be heterogeneous: the release from pyrochars sorption centers of organic and mineral compounds that encapsulate them. increasing of surface charge due to the possible effect of the extractant or appearance of new sorption centers on the surface.

The same CEC values in PC450-650 in native samples and pyrochars after extraction with cold and hot water. are most likely related to the technology of their preparation. when the water-soluble OM fractions are removed during the pyrolysis process. Application to pyrochar a mixture of Na2P2O7-NaOH leads to increasing CEC. Organic carbon from these samples is extracted by alkaline solution in a small amount (0.52 mg g⁻¹). but CEC increases by more than 4 times. which indicates a change in the surfaces of the pyrochars.

Scanning electron microscope (SEM) images of the native and modified pyrochar (after removal of the labile organic matter by boiling in water) given earlier in the work [10] showed the presence of cationic and anionic sorption centers. OM and accumulation of mineral compounds. These components is probably leads to the heterogeneous effect of various solvents on the studied pyrochar properties.

From the obtained CEC dates for pyrochars after the removal of a labile chemical agent by various extractants. it can be concluded that directional modifications can be made to increase product sorption capacity with simple treatments (for example. using hot water or alkaline solution).

According to the data given in table 2 the amount of released organic matter depends on the pyrolysis temperature. With increasing of temperature organic carbon can be extracted: with cold water – from 0.66 mg g⁻¹ in PC250 to 0.29 mg g⁻¹ in PC650. with hot water - from 1.09 to 0.48 mg g⁻¹. with alkaline solution - from 11.36 to 5.03 mg g⁻¹. respectively. Extremely small amounts of organic carbon were extracted from PC450-650. This is probably related to the technology of treatment with hot water when they are produced.

The removal of labile chemical agents from the surface can lead to various effects on the sorption properties of pyrochars. The organics extracted by different extractants are heterogeneous in nature. Water-soluble fractions may contain a large number of functional groups. and their removal leads to a decrease in CEC. if the organics are hydrophobic. its removal. on the contrary. may lead to an increase of this property.

To qualitatively description of the OM fractions of pyrochars extracted by hot water and alkaline solution. absorption spectra were measured in the range of 320–220 nm (Figure 1). The form of the spectra is generally typical for organic compounds of uncertain composition and they are characterized by a gradual increase in the absorption intensity with decreasing wavelength. At the same time. almost all spectra have diffuse absorption peaks with a maximum of 270-280 nm. which most likely can be attributed to ketodien - products of deep oxidation of lipids [11] that present in labile fractions of pyrochars [6].

For the qualitative characteristics of the selected fractions. the SUVA254 criterion. which represents the ratio of the absorption of a colored solution of organic matter at λ = 254 nm to the content of organic carbon in it. was calculated. The SUVA254 criterion is considered a reliable indicator characterizing the degree of aromaticity of natural colored organic compounds [12].

The SUVA254 value for fractions isolated with hot water from pyrochars obtained at a pyrolysis temperature of 250°C is 2.1. 450°C - 4.8. 450°C - 2.8 L mg⁻¹m⁻¹. The value of SUVA254 for the fractions isolated by alkaline solution is significantly higher. For alkaline-soluble OM from pyrochars. obtained at a pyrolysis temperature of 250°C - 10.4. 450°C - 24.2. 450°C - 2.8 L mg⁻¹m⁻¹. With an increase in the
pyrolysis temperature (up to 450°C). the aromaticity of the mobile OM of pyrochars increases. Further increase in the pyrolysis temperature leads to decrease of aromaticity.

![Absorption spectra in the UV range (220-320 nm) of OM fractions isolated from pyrochars with hot water (A) and Na₄P₂O₇-NaOH (B) (pyrolysis temperature: 1 - 250°C. 2 - 450°C. 3 - 650°C).](image)

From the analysis of the spectra, we can conclude that the pool of water-soluble and alkali-soluble OM of pyrochars is a mixture of organic compounds of uncertain qualitative composition, whose properties are determined by the pyrolysis temperature. Influence of this OM on the properties of pyrochars and, in particular, their adsorption properties can be quite heterogeneous.

4. Conclusion
From the study it can be concluded that the pyrolysis temperature affects to the content and qualitative composition of labile OM fractions of linden pyrochars. Water-soluble and alkaline-soluble OM is a mixture of organic compounds of undetermined qualitative composition. Their extraction leads to a change in CEC values of pyrochars. According to observable changes in the sorption properties of pyrochars after the labile OM removing by various extractants (hot water, Na₄P₂O₇-NaOH), it can be concluded that directional modifications can be made to increase their sorption capacity with simple methods.

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