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Research article

Hydrothermal carbonization of biomass from landscape management – Influence of process parameters on soil properties of hydrochars

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ABSTRACT

Besides pyrolysis the technology of hydrothermal carbonization (HTC) is tested to produce hydrochars for soil improvement. The chemical and physical properties of the hydrochars mainly depend on the feedstock and the process parameters reaction time and process temperature. Systematic investigations on the influences of these process parameters on soil properties of hydrochars like water holding capacity (WHC) and cation exchange capacity (CEC) are missing.

In this study, a rush-rich biomass was carbonized within defined HTC process conditions under variation of reaction time and process temperature to produce hydrochars. Analysis of WHC, CEC, the elemental composition and Fourier-transform infrared spectroscopy (FT-IR) were performed to evaluate the influence of HTC process conditions on the pedological hydrochar properties. The results indicated that at increasing reaction severity (reaction time and process temperature) WHC and CEC decreased as well as the elemental O/C ratio. The decrease of WHC and CEC is based on the decrease of the hydrochar surface polarity. However, even the lowest WHC and CEC of investigated hydrochars still exceeded those of pure quartz sand by factors of 5–10. An application of hydrochars produced at severe HTC conditions could improve WHC and CEC of sandy soils. This has to be investigated in further studies.

1. Introduction

In the last decade the use of charcoal for improving soils has grown rapidly. The knowledge about the high potential for soil improvements is based on the fertile, anthropogenic "Terra preta de indio" soils in the Amazon basin, which contain e.g. charcoal, household waste, ashes. Affected by the charcoal, these soils have high contents of plant available nutrients (Glaser et al., 2001; Glaser and Birk, 2012) as indicated by high cation exchange capacities (CEC). Furthermore the water holding capacity (WHC) is improved as well (Steiner et al., 2007).

Technologies for the production of charcoal-like products are pyrolysis and hydrothermal carbonization (HTC) (Libra et al., 2011). Pyrolysis can be seen as the conversion of dry biomass to biochar at temperatures above 300 °C. The conversion of water bathed biomass between 180 °C and 250 °C is classified as HTC with its solid product hydrochar. In addition the feedstock, reaction time and temperature determine the chemical and physical properties of the product suspension of HTC (as well as for pyrolysis) (Libra et al., 2011). This means, the elemental ratios of hydrochars lie in a wide range between soft lignite and bituminous coal (H/C ratios between 1.5 and 0.5 and O/C ratio between 0.5 and 0.2) (Libra et al., 2011). Additionally, hydrochar has been reported to store the carbon in a solid and stable form for long time (Titirici et al., 2007; Huff et al., 2014).

In contrast to many studies with biochar, only a few studies considered the impact of hydrochars in different soils to improve the fertility (Funke and Ziegler, 2010; Dinjus et al., 2011; Reza et al., 2013). It was shown that soil application of "fresh" hydrochars without pretreatment inhibit the seed germination and plant growth (Busch et al., 2012; Gajic and Koch, 2012; Bargmann et al., 2013, 2014). Further studies showed that these effects can be reduced by, e.g., microbial decomposition (Busch et al., 2013; Bargmann et al., 2014).

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A study showed that a hydrochar content of 10% within sandy soils doubles the WHC (Ramke and Hendricks, 2011). Especially low HTC reaction severity (low temperature, short reaction time) resulted in higher WHC. Sevilla et al. (2011) described the more hydrophilic behavior of hydrochars compared to biochars, based on oxygen rich chemical compounds on the surface of the hydrochars. On the other hand, hydrochars are more hydrophobic than the initial biomasses (Acharjee et al., 2011; Coronella et al., 2014).

The knowledge on the CEC of hydrochars is extremely limited (Libra et al., 2011; Kang et al., 2012; Huff et al., 2014). Oxygen rich compounds on the hydrochar surface improve the CEC (Libra et al., 2011; Kang et al., 2012). More serve carbonization conditions (high reaction temperature, long reaction time) remove more oxygen, resulting in lower O/C ratios. Respectively, the CEC and WHC were reduced. On the other hand, stronger carbonization conditions lead to more aromatic structures (Wiedner et al., 2013), which are more recalcitrant and can be advantageous for organic carbon storage in soils (Bamminger et al., 2014; Naisse et al., 2014). In comparison biochars from pyrolysis have in general a lower CEC, caused by a lower O/C ratio (Huff et al., 2014).

Although several studies considered the soil improvement by hydrochars, the influence of process engineering on WHC and CEC are not discussed in detail (Libra et al., 2011). Systematic investigations on the WHC and the CEC of hydrochars are missing. Especially for a production of hydrochars for improving soils more research is needed (Reza et al., 2014a).

Therefore in this study the effects of the two main process parameters (temperature and reaction time) were considered regarding the water holding capacity (WHC), cation exchange capacity (CEC) and the chemical structure (FT-IR) of 16 hydrochars produced from a feedstock, i.e. a rush-rich biomass from landscape management.

This kind of biomass accrues in large quantities (hundred thousands of tons annually only in Lower Saxony, Germany) when grasslands are cut with respect to especial requirement of nature and landscape conversation (e.g. Flora-Fauna-Habitat). Largely it is without economic utilization so it has to be disposed. The use of this biomass as feedstock for hydrochar production offers a possibility for utilization of biomass from landscape management.

2. Material and methods

2.1. Production of hydrochars and used reference samples

Biomass from landscape management area (moorland meadow area in Lower Saxony, Germany; coordinates N:53.1878 E:8.2997) was used as feedstock. The biomass consisted of sweet grasses (15 vol%) (*Holcus lanatus*, *Deschampsia cespitosa*, *Poa trivialis*, *Anthoxanthum odoratum*) and sedges (10–15 vol%) (*Carex acuta*), herbs (<5 vol%) (e.g. *Rumex acetosa*, *Ranunculus repens*, *Plantago lanceolata*) and rushes (70 vol%) (*Juncus effusus*). In order to obtain reproducible feedstock fractions and reproducible experimental setups, the biomass was air-dried and crushed down to a size of around 0.2 mm diameter. Subsequently 17 used feedstock fractions were analyzed for its elemental composition. Results showed a very good reproducibility and the homogeneity of the feedstock (elemental composition: C: 47.6% + −0.4%; N: 1.8% + −0.0%; H: 6.5 + −0.2%; O: 40.5 + −0.3%). For each of the 16 carbonization experiments, 60 g of the feedstock were homogenized with 400 g deionized water in a metal liner. The pH value of the suspensions was about 5.4. The liner was placed in a 1000 ml autoclave batch reactor (Parr 4523) and the feedstock suspension was stirred at a constant rate of 155 rpm. The suspension was heated up to the desired temperatures (180, 200, 220 or 240 °C) within 90 min and was held for 15; 60; 300; and 720 min–for each of the four temperatures. Subsequently, the reaction mixture was cooled down to room temperature by an integrated single-loop cooling coil. The hydrochar suspension was separated by vacuum filtration (filter paper MN 617), rinsed with 100 ml of deionized water and dried in accordance with DIN EN 14774–3:2010-02 at 105 °C about 24 h to constant weight. The dry char was homogenized and stored for further analysis in amber glass bottles.

As reference samples, quartz sand from a commercial store (washed with deionized water to remove potential contaminants) and the feedstock (raw crushed biomass) were used. Caused by glacial periods many soils in Northern Germany contain high amounts of quartz sand. The quartz sand represents a substrate with low WHC and CEC, similar to Ramke and Hendricks (2011). Both reference samples were dried at 105 °C.

2.2. Analysis of samples

All analysis of dried samples (105 °C) were performed in duplicates (n = 2) and then the arithmetical mean was calculated. The variations of the respective two samples were under 5% and are not considered further. Our results cannot show significant differences but tendencies.

2.2.1. Elemental analysis

The elemental compositions of the dried biomass and the hydrochars were determined with a Vario EL (Elementar) elemental analyzer. The relative weights (in %) of C, H and N were analyzed. The ash content of the biomass was determined by glowing 2 g dry matter for 2 h at 550 °C according to DIN EN 14775:2010–04. The glowing residue was specified as weight percent ash per dry mass. Furthermore, the contents of C, H, N and ash were used for the calculation of oxygen according to the following equation:

$$O[\%] = 100 - C[\%] - H[\%] - N[\%] - \text{ash}[\%] \quad (1)$$

2.2.2. Fourier-transform infrared spectroscopy (FT-IR)

A Bruker Tensor 27 ATR-FT-IR spectrometer was used to analyze the primary components and the chemical structure of the feedstock and the hydrochars. Spectra were collected over 16 scans, at a resolution of 4 cm^{-1}, and over a range of 550–4000 cm^{-1}.

2.2.3. Water holding capacity (WHC)

The WHC was analyzed according to a modified method of Alef (1991). For each sample, 1 g dry matter was homogenized with 14 g of deionized water in snap-cap vials on a shaker for 30 min. Subsequently, the suspension was filtered (filter paper MN 619 G ¼ Ø125 mm) for 30 min and rinsed with 30 ml of deionized water, whereas the filtrate was discarded. Once, no further filtrate building was observed, the filter papers were dried with the sample at 105 °C. The bound mass of water in the filter paper was determined as a duplicate blank, which was subtracted in all measurements. The WHC was calculated according the following equation:

$$WHC\,[g/g] = (m_{wet} - m_{dry} - m_{filter})/m_{dry} \quad (2)$$

with m_{wet} [g]: mass of the wet char sample; m_{dry} [g]: mass of the dry char sample; m_{filter} [g]: mass of the blank filter.

2.2.4. Cation exchange capacity (CEC)

The CEC was determined according to Blume et al. (2011). The procedure is the following: To displace all cations on the surface of the samples, strontium ions (Sr^{2+}) were used in high concentration.