Journal of Analytical and Applied Pyrolysis 121 (2016) 165–172

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Characterization of nanoparticles of biochars from different biomass

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ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form 19 July 2016
Accepted 20 July 2016
Available online 21 July 2016

Keywords:
Biochar
Nanoparticle
Nanomaterial
Black carbon
Charcoal

ABSTRACT

The research on biochar is focused primarily on the estimation of biochar as a "macro" fraction, and not much attention is devoted to its fractions with finer particles. The aim of the study was to characterize the physicochemical properties of biochar nanoparticles (biochar-NPs). The properties of the biochar-NPs were also compared to the properties of initial biochars. The results of this study indicate that the properties of biochar-NPs differ from the properties of their macro-counterparts. The differences were observed in the pH, cation exchange capacity, content of particular elements, and aromaticity/polarity not only based on the type of biochars, but also the regularities in the differences between their macro- and nano-forms. The nano-biochars had a larger surface area and smaller pore sizes than the corresponding macro-biochars and were characterized by a higher negative zeta potential and greater diversity of crystalline forms than the macro-biochar. Moreover, nano-biochar had significantly lower levels of C, H, and N compared to macro biochars.

1. Introduction

In recent years, a number of studies have been published on the beneficial properties of biochars [1,2] and the risks associated with their uncontrolled use [3–7]. The physicochemical properties of biochars [8] in the relation to pyrolysis temperature and their precursors have been thoroughly investigated. In those studies, biochars are estimated as a whole, and the properties of biochars in the relation to the size of particles are hardly reported. The previous studies [8–10] show that depending on the size of their particles, biochars can differ significantly from one another. However, the studies conducted so far have been concerned mainly with the macro-fraction of biochars, and biochars are also expected to contain natural structures at the nano-scale level.

The same materials at the nano-scale display completely different properties compared to their macro counterparts [11]. The properties of the nano-structures present in biochars have been found to be different than those of their macro-counterparts. The applications of biochars, obtained under artificial conditions, in soils may increase the level of biochar nanoparticles (biochar-NPs) in the environment. Biochar-NPs, similar to the already well-known particles of black carbon [12] can directly or indirectly exert an impact on living organisms, affecting the mobility and the bioavailability of other contaminants.

In recent years, however, it is observed that biochar is produced from a variety of materials. The use of biochar produced, e.g., from sewage sludge [13] or from other waste materials [14] containing anthropogenic contaminants may lead to the emission of those contaminants and anthropogenic nanomaterials (ENMs) [15,16] or ENMs-nano biochar nanohybrids to the environment, which may, in the time perspective, have a significant effect on many processes occurring in the environment. Buha et al. [17] concluded that the combustion of sewage sludge can contain the elevated levels of nano-fraction of heavy metals of anthropogenic origin.

There is a lack of information on the properties of biochar-NPs, and therefore it is hard to predict whether, they will reduce the bioavailability of contaminants similar to that of carbon black [12] or they will play the role of contaminant carriers (example of Trojan horse) similar to carbon nanotubes [18]. Much attention has been devoted to the fascination of biochars; however, the risk related with their use has not been investigated in detail [19]. The studies concerned with the risk of biochars are focused mainly on their contaminants [3–6], whereas the information on mechanism of various particles on organisms and the environment is not known.

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http://dx.doi.org/10.1016/j.jaap.2016.07.017
0165-2370/

Carbon nanostructures, e.g., carbon nanotubes and fullerenes can cause a disturbance in the equilibrium of the environment by modifying the fate of contaminants [20]. The same may happen in the case of biochar-NPs whose amounts can be considerably greater than those of carbon nanotubes, because of their increasing common use for the fertilization and soil remediation. Therefore, the identification of the nanostructures in biochars and the determination of their properties are highly important. Under environmental conditions, the characterization of nanostructures present in biochars can not only expand the current knowledge in this area, but also can help estimating the potential threats related to their migration or interactions with other contaminants or components of the environment.

Therefore, first, it is necessary to identify those nano-structures and determine their properties to investigate their potential effect on the environment in the future. The aim of this study was the extraction of biochar-NPs produced from different biomass (miscanthus, willow, and wheat straw) and their complete physicochemical characterization in the context of the properties of initial biochars and the future threat to the environment from their nanoforms.

2. Materials and methods

2.1. Characteristics of biochars

All the biochars investigated were obtained from commercial manufacturer and were produced by pyrolysis where the feedstock is thermochemically decomposed at a temperature range from 350 °C (start of pyrolysis) to 700 °C (max. pyrolysis temperature) in an oxygen-poor atmosphere (<1% O_2). Biochars BC-m and BC-w were produced of elephant grass (miscanthus) and wicker, respectively and were provided by commercial manufacturer Fluid S.A. (Sędziszów, Poland). Biochar BC-s was produced of wheat straw and was provided by Mostostal Sp. zo.o. (Wrocław, Poland).

2.2. Sampling and fractionation nano-biochars

The separation of nano-particles of biochars was performed using the protocol described by Li et al. [21] and Tang et al. [22]. All the procedures were conducted in triplicates. A probe-type ultrasonic Vibrator was used to physically disperse the biochars. Biochars dispersion was prepared by vibrating 3 g of biochar in 80 mL water in a 100 mL glass beaker, placed in a cooling bath using a circulating water system to keep the temperature <20 °C. After sonication, the aqueous suspension was passed through a 500 μm sieve, and then the sieved suspension was centrifuged to keep the nanosized particles suspended in the supernatant based on the Stokes Law [22]. The suspension was placed in a 50 mL glass centrifuge tube, centrifuged at 3,500*g* for 24 min, and then repeated again to extract biochar-NPs. The residue after centrifugation was discarded and the supernatant contained biochar-NPs was characterized directly (microscopy, hydrodynamic size and surface charge) or after drying (in water bath) has been directed to other characterization methods.

2.3. Macro- and nano-biochars characterization

The chemical properties of macro- and nano-biochars were determined by the standard methods. The pH was measured in 1 M KCl after 24 h in the liquid/biochar at a ratio of 10. The cation exchange capacity (CEC) was determined according to the procedures reported for soil analysis.

X-ray diffraction (XRD) patterns were recorded at room temperature using a Empyrean (PANalytical, 2012) X-ray diffractometer equipped with Cu Kα (λ = 0.15406 nm) radiation (45 mA, 40 KV). Diffraction peaks were collected by step scanning in the scan range 5–80° at a step width of 0.020°. The average size of nanocrystallites (D_{cr}) was estimated according to the Scherrer equation [23]. Crystalline structure of samples was analyzed using the JCPDS Database (International Center for Diffraction Data, PA, 2001).

To analyze the specific surface area of materials, nitrogen (N_2) adsorption–desorption isotherms were recorded using a micrometrics ASAP 2405 N adsorption analyzer (Micrometrics ASAP 2405 N, USA). Specific surface area was calculated according to the standard BET method [24]. The amounts of carbon (C), hydrogen (H), and nitrogen (N) were determined using a CHN equipment (Perkin–Elmer 2400). Total O was determined by subtraction as follows [25]:

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

Ash content of residues from biogas production and biocharsamples was determined estimated following the ASTM D 3176 standard method by combustion of dry samples at 760 °C for 6 hand measured as the residue remained after heating [26]. The ash content was determined according the following Eq. (2):

$$\textit{Ash content}\ [\%] = \frac{\textit{weight of ash}}{\textit{dry weight of biochar}} \times 100 \quad (2)$$

The X-ray fluorescence (XRF) spectroscopy technique was used for the characterization of the inorganic constituents of biochar and biochar-NP samples. The analysis was used to identify metals in the samples with atomic numbers in the range from uranium to sodium (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Sb, Ba, Pb and Bi) and to measurement these elements content. The Axios mAX (PANalytical, Netherlands, 2012) X-ray fluorescence spectrometer was used, operating on the basis of the measurement of the wavelength dispersion – WDXRF (Wavelength Dispersive X-ray Fluorescence), using SuperQ software (version 5.0). The samples for measurement were prepared in the form of compressed tablets. They were excited ceramic X-ray tube Rh SST-mAX equipped with an ancestral anode with power of 4 kW.

The hydrodynamic size and surface charge (ZP) of the samples were determined by measuring the zeta potential of colloidal biochar according to the procedure by Johnson and Davis [27]. Macro- or biochar-NPs (1 g) were added to 100 mL of water, and the solution was shaken at 250 rpm for 30 min using a mechanical shaker. The shaken solution was then placed in a sonic bath to break the particles into colloids, and the solution was filtered using a 0.45 lm filter paper. The electric mobility of each supernatant solution was determined using a Zetasizer 3000 by Malvern instrument, and the Smoluchowski's formula was used to convert the electric mobility into zeta potential.

Biochar-NPs were characterized by transmission electron microscopy with energy-dispersive X-ray analysis (TEM-EDX) using a Titan G2 60–300 kV FEI Company. Microscopic studies were carried out at an accelerating voltage of the electron beam equal to 300 kV. For TEM measurements, a drop of the colloidal solution of NPs was placed on a 50 Å thick carbon-coated copper grid. The sample was left on the filter paper until ethanol was evaporated. Subsequently, the sample applied to the grid was inserted to holder and moved to electron microscope.

3. Results and discussion

3.1. Physicochemical properties

The particle size distribution of the investigated biochar-NPs is shown in Fig. 1. The contribution of the nanoparticles for nano-BC-s and BC-w was similar in the range representing nano-size. The highest contribution was observed from the particles occurring