

Assessing the Potential of Using Biochar as a Soil Conditioner

D M Glazunova, P A Kuryntseva, S Y Selivanovskaya and P Y Galitskaya

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

E-mail: polinazwerewa@yandex.ru

Abstract. Biochar is a product of pyrolysis of biomass such as plant tissues, manures, sewage sludge, organic fraction of municipal solid wastes etc. Nowadays, biochar is being discussed as an alternative fertilizer that improves the air and water balance of the soil and provides soil microbiota with slow releasing biogenic elements. Many factors such as initial substrate properties, pyrolysis temperature and regime may influence biochar characteristics. In this study, characteristics of the two biochars prepared from chicken manure (ChM) and sewage sludge (SS) at 550 °C were analyzed in order to reveal their agricultural potential. It was found, that the ChM biochar had a pH value of 5.80 ± 0.21 , which was 1.6 lower than the pH of the SS sample. The electrical conductivity of the ChM sample was 6 times higher than that of the SS sample, being 6.42 ± 0.30 mS cm⁻¹ and 1.02 ± 0.10 mS cm⁻¹, respectively. The cation exchange capacity was estimated to be 7.6 ± 0.26 and 45 ± 0.14 cmol·kg⁻¹ in the ChM and SS samples, respectively. In the ChM sample total organic carbon content was $24.93 \pm 3.2\%$, which is nearly twice as large as that in the SS sample ($12.36 \pm 4.1\%$), whereas total nitrogen content was estimated to be $0.33 \pm 0.03\%$ and $0.10 \pm 0.01\%$ for ChM and SS samples, respectively. Using scanning electronic microscopy and laser particle size distribution analysis, it was shown that the SS sample was more homogeneous in its structure and consisted of particles having a lower size of 1 to 200 μm with particles of 10 to 100 μm being the most frequent, while the ChM sample was nonhomogeneous and its particle size varied between 2 and 2000 μm. To observe the influence on plants, 1% of biochar was added to soil, and wheat seeds were planted. The germination index estimated for soil treated by SS biochar was estimated to be 97%, while that of soil treated by ChM biochar was lower at about 78%.

1. Introduction

Currently the world faces several serious problems: CO₂ emissions systematically increase, the amount of organic wastes grows, soil-carbon content decreases, and global climate changes – people are worried about global warming. In some regions, due to farming practices and intensive tillage soil organic carbon has decreased by 30 to 50%, as many fields have been cultivated for more than 100 years [1]. Herewith, both in big cities and in rural areas great amounts of organic wastes are generated, such as sewage sludges and different types of dung and manure. Thus, one of poultry plants in the city of Kazan (the Republic of Tatarstan, Russia) produces 50,000 tons of chicken manure every year. Another source of bulk wastes is sewage sludge forming in all wastewater treatment plants, where sewage is treated in aerotank at some stage. These types of organic wastes need additional treatment and cannot be used directly as organic fertilizers. The limiting factors of using them in plant growing are the content of toxic compounds (ammonium in chicken manure, organic matter decomposition products in SS), and possible content of pathogenic microflora. Biological methods of treating such wastes, such as anaerobic fermentation and composting are often expensive and long, and the quality of the end product is unstable. One of the



effective methods of recycling such wastes is the pyrolysis, as a result of which biochar and liquid pyrolysis fuel are produced. Biochar is produced from a biomass heated without oxygen or with little oxygen [2–4], it is a solid porous substance rich in carbon with an odorous surface, and it contains various functional groups. The specific surface area and the stability of biochar are high, as well as the amounts of oxygen contained in functional groups. The distinctive properties of biochar make it a promising new method of dealing with global problems: climate change mitigation (reduction of greenhouse gas), waste treatment, energy production, soil remediation improvement, modification of physical and chemical properties of soil and the improvement of soil properties, gaseous N emissions reduction, alteration of soil nutrient availability, reduction of nutrient leaching and increase of crop yields [5–15]. The use of biochar for the above mentioned purposes is possible if it possesses certain physical and chemical properties, which in their turn strongly depend on the raw material and the parameters of the carbonization process [11]. Biochar can be produced from many types of raw material: such as woodchips, byproducts of timber industry, industry, sludge, organic wastes, plant residues, and chicken manure [16–18]. The factors influencing the pyrolysis process products are: the temperature of reaction, heating rate, and processing time [2,11,14,17,19]. Generally, the higher the temperatures are, the lower is the yield of biochar (and the more is the amount of liquid and gas), but the better is its quality: the content of nutrients like N, P, and K, porosity and the surface area [2,14,17,19]. When the pyrolysis temperature increases, the yield of biochar and the content of organic compounds in it decreases, and the percentage of mineral substances and the syngas yield increases [11,20]. It happens because the increasing temperature of pyrolysis activates the process of the biomass organic constituents (such as lignin, cellulose, and hemicelluloses) transformation and release as gases and volatiles while mineral compounds, like Mg, Ca and P, remain, and their concentration in biochar therefore increases [21]. Mohammad et al. [20] and Zhang et al. [22] discovered that biochar yield and the yield of acidic functional groups reduced, when the pyrolysis temperature increased, and the yield of the main functional groups, ash content, pH, and carbon stability became higher. Higher pH at high pyrolysis temperatures was explained by the decrease of organic functional groups, like –COOH and –OH. The highest bio-oil yield was observed at about 500°C, as at higher temperatures cracking occurs [11,20]. The usual pyrolysis temperature range is 200 to 800°C [23,24]. The processes of pyrolysis can be slow or rapid depending on the rate at which the temperature increases [11]. Slow pyrolysis is characterized by long residence of pyrolyzed vapors in the reactor, when the temperatures are low, and such long vapor-phase reactions enhance the char yield [11,20]. Inganzo et al. [25] described the char obtained at the higher rate of temperature elevation (60°C/min compared to 5°C/min) as having low volatile substance content and a high ash yield (including fixed carbon). The researches came to the conclusion that the high rate of temperature elevation improves the quality of biochar. However, the rate of temperature elevation did not have such influence on the product quality at high pyrolysis temperatures [11,26]. That is why the usual aim of rapid pyrolysis is to produce the higher yield of a liquid product [11,27,28]. Short vapor residence time reduces the production of gas because of secondary cracking and liquid product yield remains higher, when the cooling is fast. Residence time in the process of pyrolysis influences the product composition [11]. Thus, biochar yield increases, when the time of pyrolysis increases [22]. Besides, residence time influences the specific surface area of biochar and its pore characteristics.

To assess the potential of using biochar as a soil improver it is necessary to evaluate the initial characteristics of biochar. We've chosen biochar produced from such organic wastes as chicken manure (ChM) and sewage sludge (SS) as the targets of research.

2. Material and Methods

We've chosen two types of biochar as the targets of research: i) biochar produced from chicken manure, and ii) biochar produced from sewage sludge. Both types of biochar were produced in an industrial pyrolysis plant in the city of Naberezhnye Chelny (the Republic of Tatarstan, Russia), using the method of rapid pyrolysis at the temperature of 550°C and the retention time of 8 min. The pH of the biochar was determined with the help of a pH-410 meter and its electrical conductivity (EC) – with the help of a conductmeter Anion 4100 – 10g of biochar in 100 ml of deionized water were suspended [29]. Moisture was measured according to the weight loss by drying wet samples at 105°C [30]. The CEC for the biochar samples was determined in this research using a modified barium chloride compulsive exchange method

(Skjemstad). Wet oxidation with potassium dichromate [31] was used to determine TOC and the TKN was determined by the Kjeldahl method [32]. Ash content was measured by means of burning a biochar sample in a muffle furnace at 550°C for 3 hours [33]. The extraction method in the solution of 0.1 M K₂SO₄ outlined by Chefetz et al. [34] was used to determine the DOC values of each sample. A 0.5-ml sample of solution was taken after extraction and it was analyzed immediately by dichromate oxidation in accord with the tube digestion procedure elaborated by Nelson and Sommers [35]. Total metal content, P, S, and B content was determined using a Shimadzu ICPE – 9000 (Japan) atomic absorption spectrophotometer after sample extraction by digestion with concentrated HNO₃ using the photometric method of PND F 16.1:2:3.11-98 [36].

Biochar particle size was determined using the Microtrack BlueWave laser particle analyzer in accord with ISO 13320-1 [37]. The size of pores and the form of particles were determined using the method of electronic microscopy. To realize this, the sample on a chuck was put into the chamber of Quorum Q 150T ES vacuum apparatus. Conductive layer apply by technique cathode sputtering using alloy Au/Pd by quantity proportion 80/20. The thickness of alloy is 15 nm. Measuring was carried out by using a Merlin Carl Zeiss field-emission high-resolution scanning electron microscope. Observation photo of morphology surface apply at accelerating voltage of incident electron 5 kV and current probe 300 pA in order to minimum modify sample. In the test with oats (*Avena sativa*) biochar was added to the soil in an amount of 10 % by weight. The germination test was carried out on gray forest soil (Haplic Greyzem). Each of 5 pots was sown with 10 oat seeds and after 10 days, the percentage germination, biomass and root length were determined. The soil without added biochar was used as the control. The germination index (GI) was evaluated in accord with Zucchini et al., 1981 using the following equation:

$$GI (\%) = \frac{\text{Seed germination Sample } (\%) * \text{Root Length Sample } (\text{mm})}{\text{Seed germination Control } (\%) * \text{Root Length Control } (\text{mm})} \times 100$$

All measurements were realized in triplicate. All tables present the values and the standard deviations.

3. Results and Discussion

To assess the possibility of using biochar as soil improver it was necessary to evaluate its physical and chemical properties and its influence on plants. The data is presented in Table 1. One of very important parameters influencing the quality of biochar as soil improver is its pH. The biochar pH depends on the raw material and the production conditions. Most commonly biochar pH is greater than 7, so biochar is alkaline [2]. That is why using biochar as a soil improver can neutralize soils that are acidic [38]. Herewith, the lowest pH values are observed in biochars produced from dung and manure [2]. Our results coincide with those of other researches. Thus, the chicken manure biochar (ChM sample) has pH value of 5.80±0.21, which is 1.6 lower than the pH of the SS sample. The pH of biochar depends on the ash content – the higher ash content is the higher is pH [4,39]. Some researchers [2,40,41] have found a relationship between ash content and the value of pH: biochars with high ash content often have high pH. Our samples prove those results, as ash content in the SS sample is higher (54.85±0.06%), and its pH is higher as well (7.40±0.24). In whole, the data obtained coincide with those described by other researches, that is, the chicken manure biochar pH varies between 5.8 and 10.16 [42,43], and sewage sludge biochar pH – between 7.7 and 9.54 [18]. In the study realized by Cely et al. [42] chicken manure biochar with the ash content of 20.24% was analyzed.

The ChM sample electrical conductivity was 6 times higher than that of the SS sample, being 6.42±0.30 mS cm⁻¹ and 1.02±0.10 mS cm⁻¹, correspondingly. Being the product of pyrolysis, biochar is characterized by low moisture content (6.75±0.10% and 7.57±0.10% for ChM and SS samples, correspondingly). Thus, in the research carried out by Li et al. [44] moisture content for chicken manure biochar was determined as 10.2%, and for sewage sludge biochar – 3.59 to 9.53%.

It was found out that the biochar cation exchange capacity (CEC) affects the fertility of soil [2]. The biochar CEC also influences on the soil CEC, improving its physical and chemical properties, that is why it was important to assess the CEC of the samples we obtained. So, ChM sample CEC is 7.6±0.26 cmol kg⁻¹, and SS sample CEC is 45±0.14 cmol kg⁻¹. The CEC of the biochar produced from different types of biomass can differ greatly, depending on the type of pyrolysis (its temperature being the most important factor) and the initial substrate, and is 2 to 516 cmol·kg⁻¹ [2,18]. Biochar samples we have analyzed were

produced in the same conditions, thus, only the characteristics of the initial substrate influenced the difference in the CEC value. When biochar is introduced back into the soil, the functional groups on its surface are oxidized and superficial CEC increases [45,46]. The maximum CEC is observed in the biochar with the largest surface area [47]. The values of CEC for chicken manure biochar described by other researches vary between 9.14 and 66.8 cmol kg⁻¹ [42,43] and the CEC values for sewage sludge biochar vary between 2.36 and 30 cmol kg⁻¹ [18].

Table 1. Characteristics of biochar

Sample	ChM	SS
pH	5.80±0.21	7.40±0.24
EC, mS·cm ⁻¹	6.42±0.30	1.02±0.10
Moisture, %	6.75±0.10	7.57±0.10
CEC, cmol·kg ⁻¹	7.6±0.26	45±0.14
Ash, %	33.85±1.06	54.85±0.06
TOC, %	24.93±3.2	12.36±4.1
DOC, mg·g ⁻¹	0.30±0.02	0.20±0.01
TKN, %	0.33±0.03	0.10±0.01
P mg·kg ⁻¹	2125.00±15.59	5250.00±12.15
S mg·kg ⁻¹	4900.00±17.45	5583.33±14.12
B mg·kg ⁻¹	5.63±0.23	14.33±2.10
Al mg·kg ⁻¹	386.25±5.10	7350.00±24.10
Cd mg·kg ⁻¹	1.88±0.21	7.42±0.20
Ca mg·kg ⁻¹	5412.50±2.56	12541.67±52.45
Co mg·kg ⁻¹	0.53±0.10	51.83±0.92
K mg·kg ⁻¹	6525.00±13.24	2475.00±27.45
Mg mg·kg ⁻¹	2550.00±3.45	3241.67±1.58
Na mg·kg ⁻¹	675.00±1.22	199.58±1.21
Cr mg·kg ⁻¹	23.75±0.59	155.00±1.65
Cu mg·kg ⁻¹	73.38±0.12	90.00±0.22
Fe mg·kg ⁻¹	1762.50±1.23	13583.33±45.12
Mn mg·kg ⁻¹	312.50±3.10	433.33±2.87
Ni mg·kg ⁻¹	7.50±0.24	35.33±2.97
Pb mg·kg ⁻¹	11.25±0.59	31.25±1.64
Zn mg·kg ⁻¹	292.50±2.12	608.33±5.46
Mo mg·kg ⁻¹	0.46±0.02	0.71±0.01
GI, %	78	97

Being the product of organic substrate pyrolysis, biochar is the source of carbon, but unlike initial sewage sludge and chicken manure, biochar mostly contains slow-releasing carbon, which makes it possible to use it as a long-term fertilizer. That is why it was important to assess the content of dissolved organic carbon (DOC) easily assimilable by microorganisms and total organic carbon. In the ChM sample TOC content was 24.93±3.2%, which is nearly twice as large as TOC content in the SS sample (12.36±4.1%), for which high ash content is registered. According to the results of the investigation, sewage sludge biochar C content varies in the range of 15.92 to 66.7% depending on the characteristics of the initial sewage sludge and the type of pyrolysis [18,44]. High organic matter content of 213.52 g kg⁻¹ [43] and high carbon content is particularly characteristic for biochar produced from dung and manure – 33.25-52.1% [18,43,44]. In both samples DOC content was low (0.2-0.3mg·g⁻¹), and in this connection their use as soil improvers won't lead to carbon sequestration.

The biochar samples obtained were characterized by low nitrogen content of $0.33 \pm 0.03\%$ and $0.10 \pm 0.01\%$ for ChM and SS samples, correspondingly. In whole sewage sludge biochar can contain 0.91 to 9.3 % of nitrogen, depending on the initial nitrogen content in the sewage sludge and the type of pyrolysis, and the highest concentration of nitrogen was marked for low temperature pyrolysis [17,44]. According to the data obtained by other researchers, chicken manure biochar is characterized by the nitrogen content of 1.62 to 5.03% [17,42–44,48]. Herewith it is considered that the typical N content in biochar is less than 5 wt% [2,44]. Biochar samples are rich in phosphorus ($2125.00 \pm 15.59 \text{ mg} \cdot \text{kg}^{-1}$ and $5250.00 \pm 12.15 \text{ mg} \cdot \text{kg}^{-1}$ in ChM and SS samples, correspondingly), which will help to use biochar as soil improver and to reduce the use of phosphate fertilizers.

Currently the Russian legislation has no legal framework in respect of the quality of biochar used as a soil improver. That is why we can compare the obtained product of recycling chicken manure and sewage sludge with GOST R 53765-2009 [49] regulating the use of poultry manure as organic fertilizer, with GOST R 54651-2011 [50] regulating the use of organic fertilizer produced from sewage and GN 2.1.7.2041-06 regulating maximum permissible concentrations (MPC) of chemical substances in soil. According to the data received, gross sulfur content in both samples of biochar exceeds the specified standard for soils (GN 2.1.7.2041-06). According to GOST R 54651-2011 [50] biochars obtained can be classified as fertilizers from group 2, as zinc ion content exceeds the specified standard in both samples. Compared to GOST R 53765-2009 [49] chicken manure biochar corresponds to all the standards, except for nitrogen content, which is connected with using the pyrolysis method to process the chicken manure.

The analysis of particle size was carried out using two methods: scanning electronic microscopy (Figure 1) and Microtrack Bluewave laser particle size analyzer.

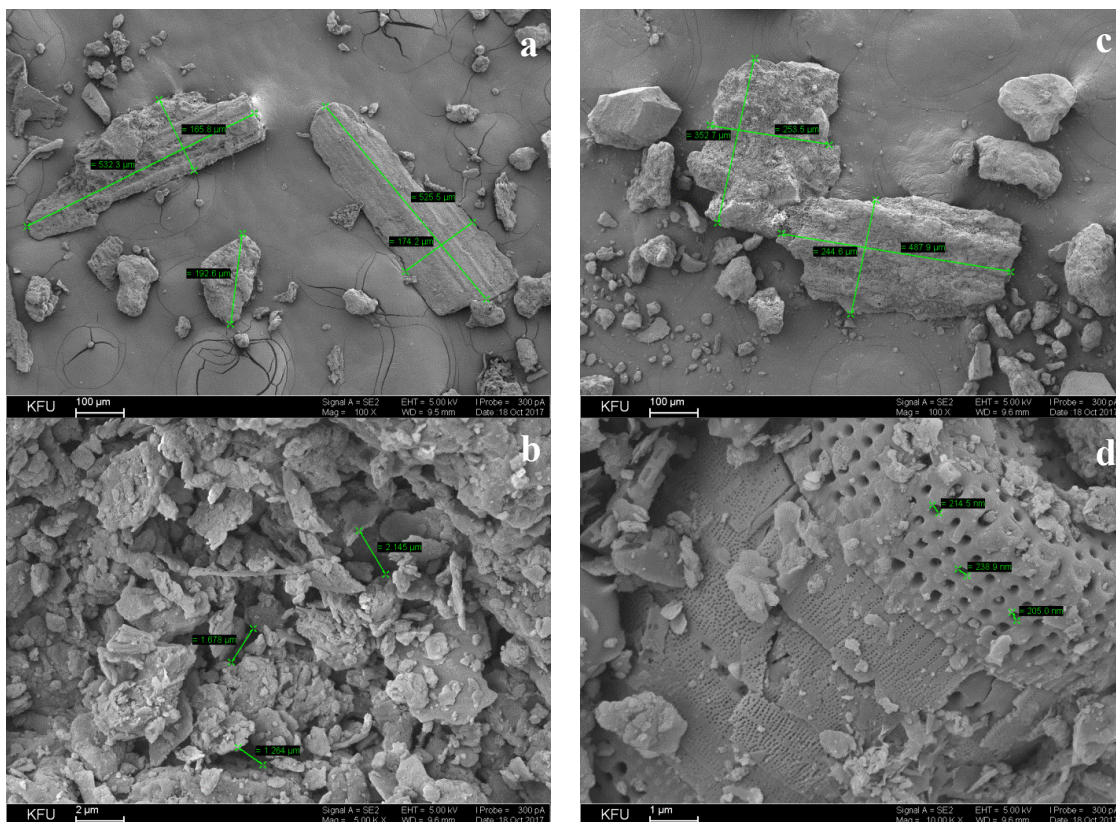


Figure 1. Scanning electron microscopic images of a) ChM (Bar=100μm), b) ChM (Bar=2μm), c) SS (Bar=100μm), d) SS (Bar=1μm)

Both methods showed that the SS sample is more homogeneous in its structure and consists of particles having lower size of 1 to 200µm, particles having the size of 10 to 100µm are more frequent. The ChM sample is nonhomogeneous and its particle size varies between 2 and 2000 µm. Particle size distribution in this sample is not normal.

It is worthwhile mentioning that the SS sample has a more prominent porous structure. The biochar specific surface area is of high importance as it increases its capacity to adsorb organic compounds and metal ions [18,48,51]. Generally, biochar that has a large specific surface area is characterized by a narrow micro-pore distribution, has good pore structure and possesses high adsorption capacity. Large specific surface area is the quality characteristic of biochar [2].

It is important to estimate the possibility of using biochar as soil improver taking into account its physical and chemical properties, but the characteristics received cannot provide an accurate forecast of the influence of biochar on the growth and development of plants. That is why the influence of the two types of biochar on the germination capacity, root and stalk length, and the biomass of wheat was assessed. According to the results received, the introduction of the SS sample into soil increased the length of above-ground sprouts by 23%; changes of germination capacity, root length and the biomass were unreliable. The germination index was 97%, which shows that there was no negative influence of biochar introduction. The introduction of ChM sample into soil lead to the shortening of root shoot; the changes of other parameters were unreliable. The germination index for the sample was 78%.

Conclusion

So, the two types of biochar obtained under the same pyrolysis conditions from different substrates not only differ in their chemical composition, but also in their physical structure. Such differences explain the fact that the introduction of sewage sludge biochar does not have negative influence on the growth and development of wheat, while as the introduction of chicken manure biochar into soil reduces the germination index of wheat.

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