

Original Research

Influence of H₂O₂ Modification on the Adsorptive Properties of Birch-Derived Biochar

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Abstract

Biochar, which is rich in aromatic carbon and minerals, is a product of biomass pyrolysis at temperatures ranging from 350°C to 1000°C in oxygen-limited environments. In recent years biochar has generated much interest in the field of water treatment in view of low production costs, availability of the feedstock (e.g., lignocellulosic biomass waste) and adsorptive properties. The aim of this study was to evaluate the effect of modifying biochar with H₂O₂ on its adsorptive characteristics. The novelty of this study was investigating the influence of H₂O₂ modification process parameters (concentration of H₂O₂ solution, biochar particle size, rotation during modification) on the physico-chemical properties of biochar, such as bulk density, elemental composition, moisture, ash content, pH, electrical conductivity, cation exchange capacity, specific surface area, and content of oxygen-containing functional groups. We found that 30% concentration of H₂O₂ solution, rotation at 3 rpm, and particle size 0.4-1 mm favor the modification process.

Keywords: engineered biochar, modified biochar, adsorption, pyrolysis

Introduction

Due to population growth and rapid development of industrialization, the spread of a wide range of potentially toxic elements (PTEs) in surface water and groundwater has become a critical issue worldwide. PTEs persisting in wastewater include heavy metals, inorganic compounds, organic pollutants and other complex compounds. The most common cationic PTEs in wastewater, like Pb(II), Zn(II), Cu(II), Cr(III, IV, VI),

Ni(II), and Cd(II), are long-term pollutants and cannot degrade naturally. If present in excessive concentrations, they may be hazardous to human health and inhibit plant growth. The Baltic Marine Environment Protection Commission (HELCOM) has referred these metals to its list of priority contaminants.

A variety of treatment technologies are available with different degrees of success to control and minimize wastewater pollution with PTEs. The usual concentration of these metals in wastewater solution is low (Cr 0.2-18 mg/l, Cd 0.3-17 mg/l, Pb 0.001-2.0 mg/l, Ni 0.2-79 mg/l, Zn 0.6-370 mg/l, Cu 0.005-9.9 mg/l), therefore conventional methods (e.g., reverse osmosis, membrane, micro-, ultra- and nanofiltration, coagulation-

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flocculation, flotation, chemical precipitation, ion exchange, and electrochemical methods) may be not efficient for removing low concentrations of PTEs from wastewater (less than 100 mg/l), expensive or generate toxic sludge. Comparatively, adsorption is considered a better and more economical alternative in wastewater treatment because of the removal of PTEs at low concentrations, flexibility in design and operation. Biochar is one of the alternative sorbents to commercial activated carbon (AC), and could be produced from wastes [1, 2] or by-products [3]. Prices for biochar worldwide vary between 0.08 to 13.5 \$/kg [4], while the cost of commercial AC in the world market varies between 2.2-5 \$/kg [5]. In comparison, silica gel costs 0.6-0.8 \$/kg, activated alumina 0.8-2.8 \$/kg, and molecular sieve zeolite 1-3 \$/kg [6]. Primary biochar has gained much interest in carbon sequestration and soil amendment [7], but in recent years many researchers have applied biochar for PTE removal from aqueous solutions [8-10].

Various mechanisms like complexation, electrostatic attraction and ion exchange control adsorption of PTEs on the biochar. Adsorption of cations by biochar is mainly controlled by electrostatic attraction and ion exchange [8]. Carboxylic functional groups on the surface of biochar are responsible for the adsorption of cationic PTEs from wastewater. Carboxylic groups are slightly acidic in nature, and in the basic or neutral aqueous solutions carry a common negative charge, which is able to interact with the cationic metals. Authors of [11] showed that the oil palm biochar with lower specific surface area exhibited a higher adsorption capacity than the rice husk biochar for the As(III, V), suggesting that oxygen-containing functional groups are more important than the surface area of the biochar. It has been suggested [12] that the removal of Pb(II), Cu(II), Ni(II), and Cd(II) was mainly controlled by interactions between metal ions in solution and hydroxylic and carboxylic functional groups on the hydrochar's surface.

In order to increase the efficiency of biochar as an alternative adsorbent for water purification, it is necessary to modify the biochar surface to enhance its ability to adsorb cationic metals. Thus, modified biochar showed enhanced Pb sorption ability with a sorption capacity of 22.82 mg/g, which was comparable to that of commercial activated carbon and was more than 20 times that of untreated biochar (0.88 mg/g) [12]. In recent years modification of biochar has been made through various methods, e.g., acid/base treatment, carboxylation, amination, treatment with organic solvents, surfactant modifications, coating of biochar, impregnation of mineral oxides, steam activation, gas purging, and magnetization [13]. Some methods include the use of strong acids and bases such as phosphoric acid and potassium hydroxide [14]. However, many of these processes are expensive on a large scale or produce deleterious byproducts. Recently it has been shown that hydrochar (biomass converted to a solid

carbon rich material through hydrothermal conversion) treated with H_2O_2 had an increased capacity to adsorb metals from solution [12]. H_2O_2 is a strong oxidant that is relatively inexpensive and environmentally friendly. After being used for modification of the biochar, it would not remain in the biochar materials as adverse residues since H_2O_2 decomposes into H_2O and O_2 [15]. In addition, the activation of the biochar surface with a solution of H_2O_2 is more efficient than with the acids. Acids form salts that can block the pores of the biochar, and limit penetration of metals into the pores. Hence, fewer metal ions can be adsorbed into the pores of the biochar as there will be fewer available pores. Studies show that treatment with H_2O_2 leads to an increase in the number of carboxylic groups and an increase in the cation exchange capacity of the biochar [16].

In this study, biochar derived from birch wood was produced via pyrolysis at 450°C and then treated with 3, 15 and 30% solutions of H_2O_2 (W/W). According to [17], lignocellulosic feedstock is the most valuable raw material in terms of its accessibility and waste management reasons, therefore, woody feedstock was chosen. Birch wood was pyrolyzed to produce the biochar sample materials due to it being plentiful and locally available. The highest treatment temperature (HTT) of 450°C was chosen for pyrolysis due to it being one of the most common HTTs used for slowpyrolysis, and is neither so low of a temperature that would result in incomplete conversion of the biomass (torrefaction), nor so high a temperature that there is little retained oxygen functionality through pyrolysis. Biochar was crushed according to sizes of commercial carbon: powder less than 1 mm and pieces 1-3 mm. The biochar samples were treated with H_2O_2 solution to test the effect of partial oxygenation on biochar with respect to specific surface area and content of oxygen-containing functional groups. This research also elucidates the elemental composition of the biochar samples of both pre- and post- H_2O_2 treatments in order to evaluate the possible change in biochar through partial oxygenation processes.

As adsorption is a surface phenomenon, principal characteristics of the material for adsorption include increased specific surface area (SSA) of adsorbent, and respectively porosity of the adsorbent. Among physical properties, bulk density of the biochar (as it shows the mechanical strength of the biochar) and Brunauer-Emmett-Teller (BET) specific surface area (the most common characteristic to show the efficiency of biochar for adsorption) were selected for investigation. In order to investigate the content of oxygen-containing functional groups, cation exchange capacity (CEC) and Fourier-transform infrared spectroscopy (FTIR) were selected to test. According to [17], basic chemical characteristics such as C, O, H, N, ash, moisture content, pH, and electrical conductivity were chosen to test as well, as they may influence adsorption.

It has been experimentally established that a higher efficiency of saturation of solid particles with a reagent is achieved when rotation is applied [18], because during this process the contact surface between solid particles and reagent is higher. In order to maintain continuous stirring of H₂O₂-solution, a special device for modification was developed. Modifications with/without rotation were made.

The aim of the study was to evaluate the effect of modification of biochar with H₂O₂ on the adsorptive properties of biochar. The following tasks were set: 1) to investigate optimal parameters (e.g., biochar particle size, concentration of solution, rotation) for the highest content of carboxylic groups on the surface of biochar; and 2) to compare physico-chemical properties of modified and unmodified biochar.

Materials and Methods

Selection of Feedstock

For the experiments, woody feedstock was selected due to high lignin content, that will result in higher yield of biochar, i.e., birch contains 19±0.18% of lignin. In terms of waste management reasons and biochar morphology (BET specific surface area and porosity) [19], birch (*Betula pendula*, occupying 17.5% of forest area in Lithuania [20]) was chosen. Birch was obtained in February 2017 from a private household in the Ignalina region of Lithuania (55°20'52"N 26°14'27"E). Birch wood was cut into pieces of 0,5 m long with a cross-section area diameter of 20 cm. The weight of each piece was 10 kg. Samples were put into plastic bags to keep conditions constant.

Biochar Production

The method described in [21] was used. Air-dried feedstock of birch was wrapped in aluminum foil in order to create an oxygen-limited environment. An E5CK-T muffle furnace was used with a heating rate of approximately 10°C/min until the desired pyrolysis temperature of 450±5°C was reached. The slow pyrolysis process was performed for 120 min under atmospheric pressure. At the end of the production process, the samples were left to cool down in the muffle furnace overnight.

The obtained biochar was ground after being cooled down to ambient temperature (20±3°C), and a 1–10-mm-diameter fraction was separated by sieves (Retsch, Germany). Biochar yield (%) was calculated according to:

$$Y_{bc} = \frac{W_2}{W_1} \times 100\% \quad (1)$$

...where W_1 is the dry mass of the feedstock (g) and W_2 is the dry mass of biochar (g).

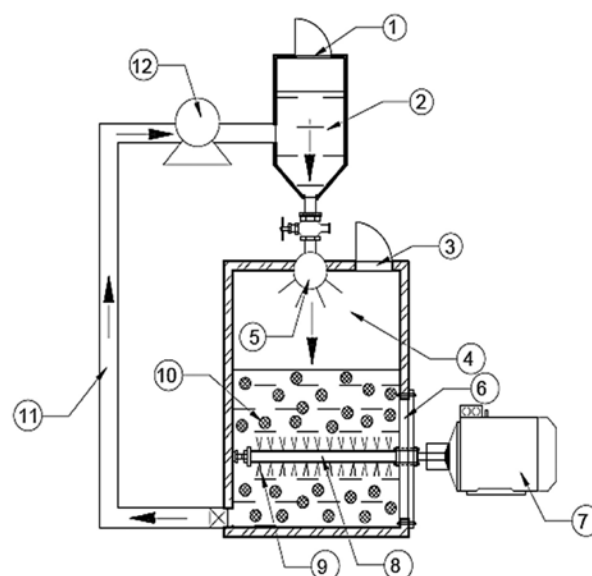


Fig. 1. Device for modifying the biochar with H₂O₂: 1) opening, 2) tank for H₂O₂, 3) opening, 4) modifying tank, 5) spray, 6) opening, 7) motor reducer, 8) rotary driven flexible roller, 9) brush, 10) biochar, 11) tube, and 12) vacuum pump; arrows indicate the water flow, which is regulated by vacuum pump.

Biochar Modification

The biochar was crushed by pressing, and two fractions (according to commercial size of the activated carbon adsorbent) were separated by sieving: <1.0-mm-diameter (powder form of adsorbent) and 1-3-mm-diameter (granular form of adsorbent). For modification process, solution H₂O₂ (30%) was used, and three types of solutions were prepared: 3, 15, and 30% of H₂O₂. The biochar was added to modifying solutions with a ratio of 25% w/w. In one case, there was no rotation, in other cases biochar with solution was stirred at 3 rpm for 2 h in a self-made device according to [22] (Fig. 1). Then the biochar was filtered through a cellulose acetate membrane filter with particle retention 1.06 μm.

This device for modifying biochar with H₂O₂ solution is economically efficient and sustainable [22]. It contains an additional stirring mechanism to increase the contact surface of the biochar with the solution. The purpose of the invention was to activate the biochar surface, and thus improve the adsorption properties of the biochar for the adsorption of cationic metals.

Physical Properties of Biochar

Bulk density (analogue VDLUFA-Method A 13.2.1) of the biochar of particle size <1 mm and 1-3 mm was measured in accordance with EBC guidelines [17]. The samples of biochar were filled into a graduated cylinder and the mass was determined by weighing:

$$BD = \frac{m_{\text{biochar}}}{V_{\text{biochar}}} \quad (2)$$

...where BD is bulk density (kg/m^3), m_{biochar} is mass of the biochar sample (kg), and V_{biochar} is volume of the biochar sample in cylinder (m^3).

The specific surface area of lignocellulosic biochar was determined using nitrogen gas sorption measurements at 77 K and Brunauer-Emmett-Teller (BET) theory with Nova 4200 E-Series, Quantachrome Instruments (US) at the Latvian State Institute of Wood Chemistry. 100 mg of each crushed biochar sample was put on vacuum degasation (300°C , 17-24 h) overnight and cooled down.

Chemical Properties of Biochar

pH was determined by an instrumental method using a glass electrode in a 1:5 (volume fraction) suspension of 0.4 mm fraction of the biochar in deionized water (level III according to LST EN ISO 3696:1996) [21]. After shaking the suspension for 1 h and after allowing the suspension to stand for 1 h, the pH was measured using a Mettler Toledo seven multi pH meter (Germany).

Cation exchange capacity (CEC) was determined using ammonium acetate [21]. 25 grams of biochar were allowed to soak overnight after being thoroughly shaken with 125 ml of 1 M $\text{CH}_3\text{COONH}_4$ ($\geq 98\%$). The biochar was transferred in a filter paper-fitted Buchner funnel. The biochar was gently washed four times with 25 ml additions of $\text{CH}_3\text{COONH}_4$. The leachate was discarded and the biochar was washed with eight separate additions of $\text{CH}_3\text{CH}_2\text{OH}$ (95%) to remove excess saturating solution. The adsorbed NH_4 was extracted by leaching the biochar with 1 M KCl ($\geq 99.5\%$). The biochar was removed and the leachate was transferred into volumetric flasks and diluted at up to 250 ml volume with an additional 1 M KCl. The concentration of $\text{NH}_4\text{-N}$ was determined in the KCl extract by colorimetry using ammonia calibration curve and measuring absorption intensity at the wavelength $\lambda = 400$ nm with photocolimeter in 1 cm length cells, and concentration of $\text{NH}_4\text{-N}$ was calculated using the Nessler method. Also, $\text{NH}_4\text{-N}$ was determined in the original KCl extracting solution (blank) to adjust for possible $\text{NH}_4\text{-N}$ contamination in this reagent. Cation exchange capacity was calculated using equation (1.3):

$$CEC = \frac{NH_4N_{\text{inextract}} - NH_4N_{\text{inblank}}}{14} \quad (3)$$

...where CEC is the cation exchange capacity, cmol_c/kg ; $NH_4N_{\text{inextract}}$ is ammonium ion concentration in the extract, mg/l ; and NH_4N_{inblank} is ammonium ion concentration in the blank, mg/l .

Electrical conductivity (EC) according to DIN ISO 11265 was measured by adding 20 g of the sample into 200 ml of deionized water and shaking it for 1 hour, followed by filtration of the solution. The conductivity was then measured in the filtered water [17].

C, O, N, and H contents were determined using a Eurovector EuroEA3000 elemental analyzer with dedicated Callidussoftware, allowing for the most exact determination of C, N, H and O in the samples. All types of biochar were ground into fine particles of 0.4 mm diameter. Each sample was packed into an aluminum foil container and weighed (mass of the sample tended to be less than 1 mg). Analysis was performed in three basic steps: sample combustion at high temperature, fast separation of the resultant gaseous species and TCD detection. Determination of Oxygen content was performed on the same instrument in pyrolysis mode by a quick change of configuration. O/C, H/C and N/C ratios were calculated.

Moisture content was determined following the method described in [17]: the sample of the air-dried and crushed (grain size < 1 mm) sample was weighed and dried in air atmosphere at $(106 \pm 2)^\circ\text{C}$ for 24 h:

$$FH = \frac{m_e - m_r}{m_e} \times 100 \quad (4)$$

...where FH is moisture content (%), m_e is mass of the sample before drying (g), and m_r is mass of the sample after drying (g).

To determine ash content (550°C) [17] two heating programs were used:

- Heating with a rate of $5^\circ\text{C}/\text{min}$ to 106°C in oxygen atmosphere to constant mass.
- Temperature increase $5^\circ\text{C}/\text{min}$ up to 550°C in oxygen atmosphere and holding this temperature for 60 min to constant mass.

Content of oxygen-containing functional groups on the biochar surface was determined using FTIR spectroscopy at the Latvian State Institute of Wood Chemistry. 2 mg of each sample were crushed and pressed. Spectrum One (Perkin Elmer, UK) instrument and KBr pellet technique were used (1% solid in KBr) in the range of $4000\text{-}450$ cm^{-1} , resolution: 4 cm^{-1} , number of scans: 64.

Quality Assurance and Statistical Analysis

Each sample was prepared and analyzed in triplicate. The measurements were carried out three times and the mean of the results of measurement were calculated. The statistical analysis was performed using the Excel program. The results of mean values with values of the 95% confidence interval (CI) were presented in graphical expression of the results. The standards of calibration were used to calibrate devices in 2017. The quality of experiments was assured by blank samples such as KCl (for determining CEC).

Biochar was marked as follows: first letter B means biochar, last letter P or G means powder or granular fraction, respectively. Numbers 3, 15, 30% indicate concentration of H_2O_2 solution and r indicates that modification was made using rotation.

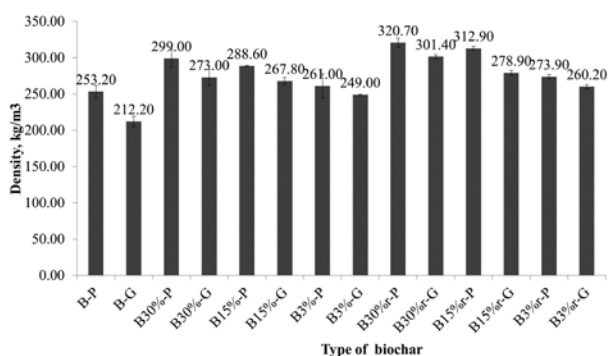


Fig. 2. Density of the unmodified and modified biochar; error bars represent 95% confidence interval.

Results and Discussion

Influence of H₂O₂ Modification on Physical Properties of Biochar

Density of the unmodified and modified biochar are summarized in Fig. 2.

Higher bulk density is associated with higher mechanical strength. The bulk density is related to the mechanical strength, which is the characteristic used to define the biochar ability to withstand wear and tear during its use. In adsorption systems, the media should remain stable with time. Modification with H₂O₂ increased bulk density of the biochar, confirming that there was almost no weight loss from the H₂O₂ treatment. Biochar, modified with rotation, had a higher bulk density than biochar, modified without rotation. Biochar with powder particle size (0.4-1 mm-diameter) had higher bulk density than biochar with granular

particle size (1-3 mm-diameter). [12] reported an increase in bulk density from 240 to 250 kg/m³, when hydrochar was modified with 10% of H₂O₂ solution. Results on bulk density of birch biochar are lower in comparison to those of [1] for woodchips pyrolyzed at 450°C - 440 kg/m³.

The effect of modification on structural properties of biochar is shown in Table 1.

It is known that adsorption of PTEs through complexation, electrostatic attraction and ion exchange is affected by micropores with pore sizes less than 2 nm [8]. Modification with H₂O₂ increased BET-specific surface area (SSA). Biochar, modified with rotation, had a higher BET SSA than biochar, modified without rotation. Biochar with powder particle size (<1 mm) had higher BET SSA than biochar with granular particle size (1-3 mm).

Respectively, B30%-r-P biochar had the highest BET SSA (321.7 m²/g), which exceeds BET SSA of unmodified biochar almost 15 times (20.11 m²/g). Results on BET SSA are lower than those of birch-activated carbon - 400 m²/g [23]. B3%-G biochar had the lowest BET SSA (50.7 m²/g), which exceeds BET SSA of unmodified biochar only in 2.5 times (20.11 m²/g). [19] showed higher results for unmodified birch than indicated in the current study - 73.19 m²/g. In comparison, BET SSA of rice straw biochar, modified with KOH was 179.7 m²/g, HNO₃ - 87.2 m²/g, H₂SO₄-56.9 m²/g, H₂O₂ - 110.9 m²/g, and KMnO₄-122.9 m²/g [24]. The results on BET SSA from this study are similar to the CaO-treated woody AC (265.13 m²/g for N₂ activated and 314.57 m²/g for CO₂ activated) and exceed KOH-treated woody AC (35.23 m²/g for (N₂ activated and 167.68 m²/g for CO₂ activated) [25].

Table 1. Specific surface area and pore characteristics of the biochar produced from lignocellulosic feedstock.

Type of biochar	BET, m ² /g	Average pore diameter, nm	Total pore volume, cm ³ /g	Total micropore volume, cm ³ /g
B	20.11	4.497	0.023	0.010
B30%-P	264.9	2.329	0.154	0.116
B30%-G	236.4	2.477	0.146	0.081
B15%-P	152.3	2.893	0.11	0.091
B15%-G	121.9	3.239	0.099	0.142
B3%-P	82.8	3.39	0.079	0.048
B3%-G	50.7	3.51	0.059	0.032
B30%-r-P	321.7	2.269	0.183	0.111
B30%-r-G	310.4	2.333	0.181	0.171
B15%-r-P	301.5	2.31	0.174	0.172
B15%-r-G	289.9	2.29	0.166	0.165
B3%-r-P	277.0	2.33	0.161	0.158
B3%-r-G	205.8	2.44	0.126	0.119

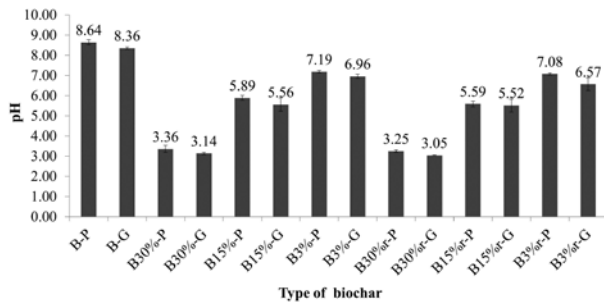


Fig. 3. pH of unmodified and modified biochar; error bars represent the 95% confidence interval.

Influence of H₂O₂ Modification on Chemical Properties of Biochar

pH of the unmodified and modified biochar are summarized in Fig 3.

pH of the modified biochar was lower in comparison to unmodified biochar (8.64 for powder fraction and 8.36 for granular fraction), which could be attributed to the weak acidic nature of the created carboxyl surface functional groups. [12] reported a decrease in pH from 6.2 to 4.4, when hydrochar was modified with 10% of H₂O₂ solution. Biochar, modified with rotation, had even lower pH than biochar modified without rotation. Biochar with powder particle size (<1 mm) had higher pH than biochar with granular particle size (1-3 mm), because lower particle size favors modification with solution. A higher concentration of H₂O₂ solution corresponds to a higher decrease in pH. Therefore, the highest pH had B3%-P biochar among all modified types of biochar, the lowest – B30%-r-G biochar.

Electrical conductivity indicates the capacity to transport electricity. EC depends on the inorganic content of the biochar and thus could be used to calculate the salinity of the material [26]. Lower conductivity is associated with the higher degree of aromatic condensation in char [27]. Electrical conductivity of the unmodified and modified biochar are summarized in Fig. 4.

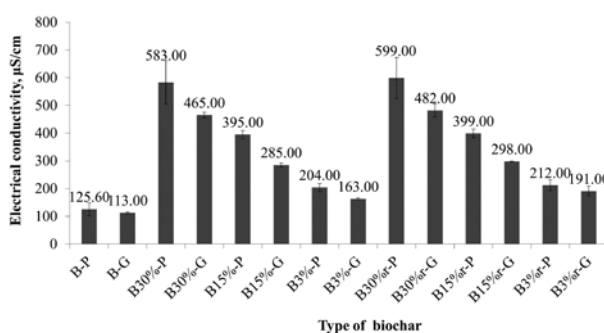


Fig. 4. Electrical conductivity of the unmodified and modified biochar; error bars represent the 95% confidence interval.

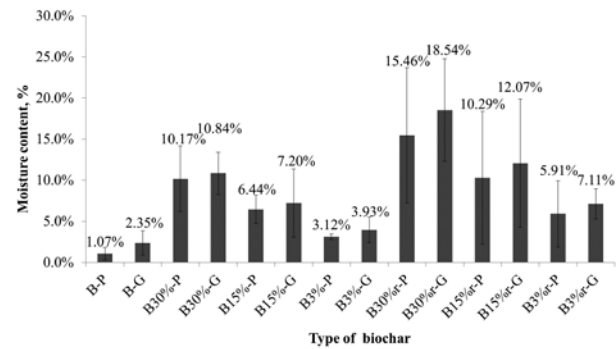


Fig. 5. Moisture content in the unmodified and modified biochar; error bars represent 95% confidence interval.

Electrical conductivity (EC) of the modified biochar was higher in comparison to unmodified biochar, which could be attributed to the increase in oxygen content. Biochar modified with rotation, had even higher EC than biochar modified without rotation. A higher concentration of H₂O₂ solution corresponds to a higher increase in EC. Therefore, the highest EC had B30%-r-P biochar among all modified types of biochar, the lowest – B3%-G biochar. Biochar with powder particle size (<1 mm) had higher EC than biochar with granular particle size (1-3 mm), because lower particle size favors modification with solution.

Excessive moisture in the biochar may block the pores, preventing the adsorption of PTEs by biochar. Moisture content in the unmodified and modified biochar is summarized in Fig. 5.

Modification with H₂O₂ increased moisture content. Biochar modified with rotation had the higher moisture content than biochar modified without rotation. Biochar with powder particle size (<1 mm) had lower moisture content than biochar with granular particle size (1-3 mm). The highest value for moisture was determined for the B30%-r-G biochar. The lowest moisture content among the modified types of biochar was determined for B3%-P biochar.

Ash is the residue that remains after combustion under specified conditions, which is composed primarily of oxides and sulfates. The ash fraction of biochar is enriched with inorganic non-crystalline (amorphous)

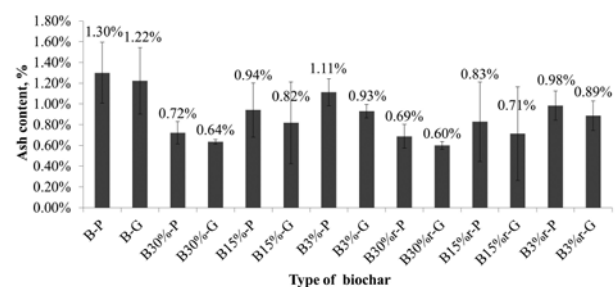


Fig. 6. Ash content in the unmodified and modified biochar; error bars represent 95% confidence interval.

and poorly to well-crystallized (mineral) constituents. The inorganic constituents of the ash fraction of biochar are usually metal carbonates, silicates, phosphates, sulfates, chlorides and oxy-hydroxides. Ash content in the unmodified and modified biochar are summarized in Fig. 6.

Modification with H₂O₂ decreased ash content of the modified biochar. Biochar modified with rotation had a higher ash content than biochar modified without rotation. Biochar with powder particle size (<1 mm) had higher ash content than biochar with granular particle size (1-3 mm). The highest values of ash had B3%-P biochar while the lowest had B30%-G biochar. On the one hand, minerals in ash can promote the adsorption of PTEs by serving as additional adsorptive sites [28]. On the other hand, metals from ash can block the pores, creating no space for adsorption of PTEs [29].

Once biochar is placed as a medium in the adsorption systems or in some other way exposed to the surrounding environment, one of the first modifications of their organic molecular structure to occur is functionalization of the surface with O-containing functional groups. COHN content the unmodified and modified biochar are summarized in Table 2.

According to [30], for hickory wood pyrolyzed at 450°C, oxygen content was 11.43%, which is lower than our results for unmodified biochar. A decrease of oxygen content may not favor the adsorption of PTEs, because it will cause the decrease of O/C ratio. Modification with H₂O₂ increased oxygen content. Biochar modified with rotation had higher oxygen content than biochar modified without rotation.

Obtained results on unmodified biochar are related to those in [30], for hickory wood pyrolyzed at 450°C,

where carbon content was 83.62%. An increase in carbon content may not favor the adsorption of PTEs, because it will cause the decrease of O/C ratio. Modification with H₂O₂ decreased carbon content. Biochar modified with rotation had the higher decrease in carbon content than biochar modified without rotation. Our results on carbon content exceed those results from [15], where unmodified pinewood biochar had 72.59% of C, and H₂O₂-modified biochar had the following content: 3% modification – 71.38% of C, 20% modification – 72.18% of C, and 30% modification – 71.43% of C.

An increase of hydrogen may not favor the adsorption of PTEs by biochar, because it will cause the increase of H/C ratio above 0.7. Modification with H₂O₂ increased hydrogen content. Biochar modified with rotation had higher hydrogen content than biochar modified without rotation. Our results on hydrogen content exceed those results from [15], where unmodified pinewood biochar had 3.86% of H, and H₂O₂-modified biochar had the following content: 3% modification – 3.61% of H, 20% modification – 3.83% of H, and 30% modification – 3.94% of H. [31] indicated 2.6% of hydrogen for hardwood biochar at 538°C, which is lower than obtained results for unmodified biochar.

A decrease of nitrogen may not favor the adsorption of PTEs on biochar, because it will cause the decrease of N/C ratio. Modification with H₂O₂ increased nitrogen content. Biochar modified with rotation had the higher nitrogen content than biochar modified without rotation. Our results correspond to [15], where H₂O₂-modified hydrochar had less than 0.5% of nitrogen. Three types of ratios, in particular O/C, H/C and N/C, were calculated to attribute biochar hydrophilicity, aromaticity and polarity level (Table 3).

Table 2. Hydrogen, nitrogen, carbon and oxygen content in the unmodified and modified biochar (n = 9, mean value±CI).

Type of biochar	O, %	C, %	H, %	N, %
B-P	8.00±0.120	82.96±3.330	9.01±0.230	0.027±0.005
B-G	7.76±0.330	84.15±3.640	8.06±0.110	0.025±0.005
B30%-P	17.50±1.270	70.50±2.460	11.81±0.240	0.192±0.090
B30%-G	16.85±1.240	73.98±2.650	9.00±0.780	0.166±0.070
B15%-P	15.21±1.290	74.45±2.420	10.23±0.480	0.102±0.009
B15%-G	13.14±1.270	77.09±2.290	9.68±0.440	0.085±0.010
B3%-P	9.23±0.280	80.16±2.280	10.57±0.680	0.033±0.008
B3%-G	8.40±0.190	81.54±3.180	10.03±0.570	0.028±0.005
B30%-r-P	19.50±0.930	66.51±2.230	13.78±0.890	0.210±0.097
B30%-r-G	18.77±1.260	68.22±2.620	12.82±0.220	0.183±0.086
B15%-r-P	15.69±1.280	70.65±2.190	13.54±0.430	0.112±0.098
B15%-r-G	13.34±1.410	74.31±2.240	12.25±0.850	0.091±0.008
B3%-r-P	9.57±0.290	78.44±2.920	11.93±0.520	0.053±0.007
B3%-r-G	8.66±0.280	79.70±2.480	11.60±0.110	0.037±0.006

Table 3. Hydrogen-, nitrogen- and oxygen-to-carbon ratios of biochar.

Type of biochar	Ratios		
	H/C \leq 0.7	N/C	O/C \leq 0.4
B-P	0.109	0.0003	0.096
B-G	0.096	0.0003	0.092
B30%-P	0.168	0.0027	0.248
B30%-G	0.162	0.0022	0.228
B15%-P	0.122	0.0014	0.204
B15%-G	0.126	0.0011	0.170
B3%-P	0.132	0.0004	0.115
B3%-G	0.123	0.0003	0.103
B30%r-P	0.207	0.0032	0.293
B30%r-G	0.188	0.0027	0.275
B15%r-P	0.192	0.0016	0.222
B15%r-G	0.165	0.0012	0.180
B3%r-P	0.152	0.0007	0.122
B3%r-G	0.146	0.0005	0.109

The correlation between higher O:C ratio and higher CEC was found. The decrease in the O/C and/or N/C ratios can indicate the increase in the hydrophobicity and the reduction of polar groups, therefore a decrease potential of adsorption of PTEs [32]. Modification by H₂O₂ increased H/C, N/C and O/C ratios. Biochar, modified with rotation, had higher ratios than biochar, modified without rotation. Respectively, B30%r-P biochar had the highest ratios (H/C = 0.212, N/C = 0.0032, O/C = 0.293).

Cation exchange capacity (CEC) of different types of biochar is presented in Fig 7.

Modification with H₂O₂ increased CEC of the biochar. Biochar modified with rotation had higher CEC than biochar modified without rotation. This increase in CEC can be attributed to an increase in the presence of acidic oxygen functional groups on the surface of

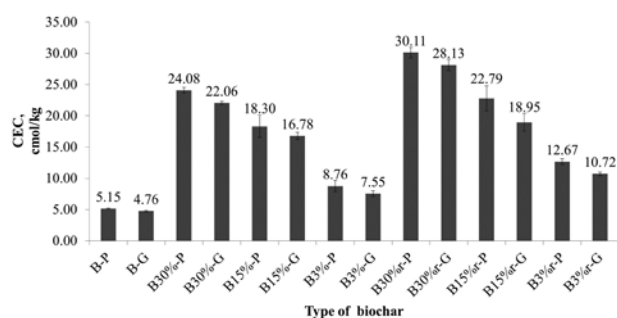


Fig. 7. Cation exchange capacity of modified and unmodified biochar; error bars represent 95% confidence interval.

the biochar materials. Respectively, B30%r-P biochar had the highest CEC (30.11 cmol/kg). For comparison, unmodified hydrochar [15] had 17.95 cmol/kg, modified with 3% H₂O₂ solution – 23.3 cmol/kg, 20% H₂O₂ solution - 25.43 cmol/kg, 30% H₂O₂ solution - 31.37 cmol/kg. For comparison, 90 min ozone activation increased CEC of the pinewood biochar from 15.39 to 32.69 cmol/kg [33]. Results on CEC exceeded some other adsorbents, e.g., bio-resin from arecanut husk with CEC 4.64 cmol/kg [34], sulphurised AC with 5.02 cmol/kg [35], wheat straw BC and AC with 7.42 and 4.27, respectively [36].

Effect of Modification on Surface Functionality of Biochar

FTIR was used in this study to describe the development and alterations in functional group chemistry of the studied types of biochar modified in different ways. The FTIR spectra of the types of the different types of biochar are presented in Fig. 8.

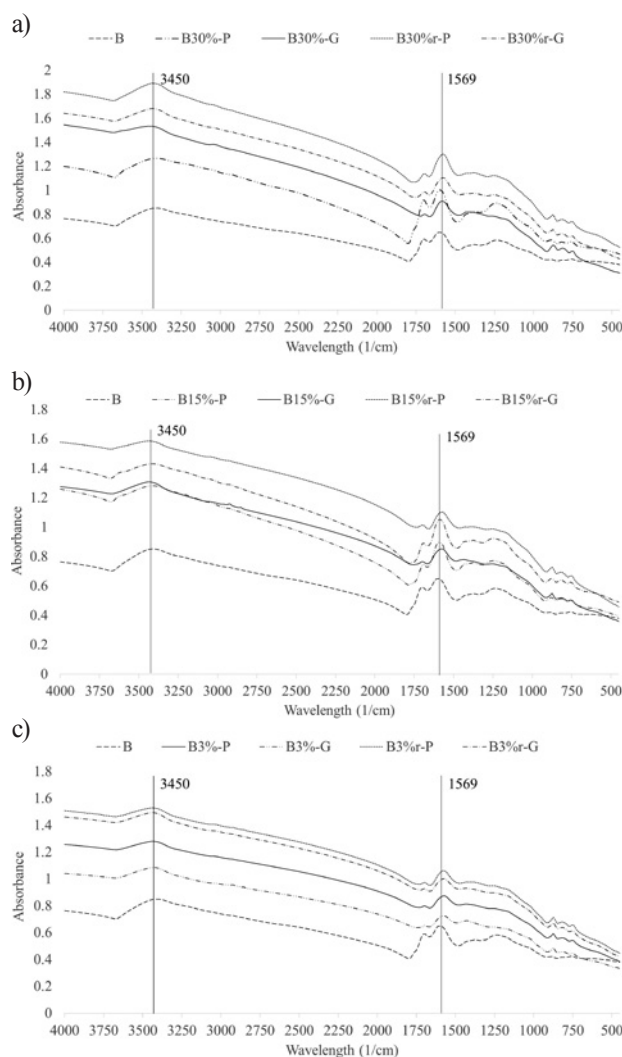


Fig. 8. FTIR spectra of modified and unmodified biochar (a, b, c).

The number of vacant sites on the surface of an adsorbent corresponds to the content of oxygen-containing functional groups, e.g., carboxylic and carbonyl groups. [15] stated that the peaks 1315 cm⁻¹ and 1700 cm⁻¹ corresponded to carboxylic acid functionality that increased after modification of biochar with H₂O₂. From Fig. 8 peaks at 1500-1750 cm⁻¹ corresponded to carboxylic groups, while peaks at 3250-3500 cm⁻¹ corresponded to hydroxylic and aminofunctional groups on the biochar surface. Modification with H₂O₂ increased content of carboxylic groups, especially in cases of rotation during modification. With the increasing percentage of H₂O₂-solution content of carboxylic and phenolic groups increasing, the highest peak for carboxylic groups was observed for 30%-modified biochar with rotation.

Conclusions

1) We found that H₂O₂ modification can activate birch-derived biochar and increase cation exchange capacity 6-fold (from 5.15 cmol_c/kg to 30.11 cmol_c/kg) and BET-specific surface area 15-fold (from 20.11 m²/g to 321.7 m²/g). Increases in cation exchange capacity can be attributed to the increase of acidic carboxylic functional groups on the surface of the biochar, as evidenced by FTIR and pH. Increases in specific surface area may be explained by the increase in micropore volume as a result of oxygenation of the biochar.

2) H₂O₂ modification influences other physico-chemical characteristics of the biochars. It increases density, electric conductivity, H/C, N/C and O/C ratios and reduces pH and ash content.

3) Rotation enhances the modification process. Thus, biochar modified with rotation has higher cation exchange capacity, specific surface area, density, electric conductivity, H/C, N/C and O/C ratios, but lower pH and ash content.

4) Biochar particle size influences the modification process. Thus, biochar with smaller particle size (0.4-1 mm) has higher density, pH, ash content, and specific surface area than biochar with particle size 1-3 mm modified in the same way.

5) Optimal parameters of H₂O₂ modification process to achieve the highest content of carboxylic groups on the surface of biochar were established on the base of the experimental data: rotation 3 rpm, biochar particle size 0.4-1 mm, concentration of H₂O₂ solution 30%. Additionally, modification time of 2 h should be maintained, biochar-to-solution ratio 25% w/w.

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Conflict of Interest

The authors declare no conflict of interest.

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