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-
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 hydroxyl and carboxylic functional groups on the biochar’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 H₂O₂, had an increased capacity to adsorb metals from solution [12]. H₂O₂ 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 H₂O₂ decomposes into H₂O and O₂ [15]. In addition, the activation of the biochar surface with a solution of H₂O₂ 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 H₂O₂ 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 H₂O₂ (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 H₂O₂ 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-H₂O₂ 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 10ºC/min until the desired pyrolysis temperature of 450±5ºC 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±3ºC), and a 1–10-mm-diameter fraction was separated by sieves (Retsch, Germany). Biochar yield (%) was calculated according to:

\[ Y_{bc} = \frac{W_2}{W_1} \times 100\% \]  

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

**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:

\[ BD = \frac{m_{biochar}}{V_{biochar}} \]
...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 biomass 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 CH$_3$COONH$_4$ ($\geq$98%). The biochar was transferred in a filter paper-fitted Buchner funnel. The biochar was gently washed four times with 25 ml additions of CH$_3$COONH$_4$. The leachate was discarded and the biochar was washed with eight separate additions of CH$_3$CH$_2$OH (95%) to remove excess saturating solution. The adsorbed NH$_4^+$ was extracted by leaching the biochar with 1 M KCl ($\geq$99.5%). The biochar was removed and the leachate was transferred into volumetric flasks and diluted at up to 250 ml volume with an additional 1 M KCl. The concentration of NH$_4^+$ was determined in the KCl extract by colorimetry using ammonia calibration curve and measuring absorption intensity at the wavelength k = 400 nm with spectrophotometer in 1 cm length cells, and concentration of NH$_4^+$ was calculated using the Nessler method. Also, NH$_4^+$ was determined in the original KCl extracting solution (blank) to adjust for possible NH$_4^+$ contamination in this reagent. Cation exchange capacity was calculated using equation (1.3):

$$CEC = \frac{NH_4N_{extract} - NH_4N_{blank}}{14}$$

...where $CEC$ is the cation exchange capacity, cmol/kg; $NH_4N_{extract}$ is ammonium ion concentration in the extract, mg/l, and $NH_4N_{blank}$ 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 Callidus software, 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±2)°C for 24 h:

$$FH = \frac{m_e - m_r}{m_e} \times 100$$

...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°C/min to 106°C in oxygen atmosphere to constant mass.
- Temperature increase 5°C/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 4000-450 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$_2$O$_2$ solution and $r$ indicates that modification was made using rotation.
Results and Discussion

Influence of H$_2$O$_2$ 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 H$_2$O$_2$ increased bulk density of the biochar, confirming that there was almost no weight loss from the H$_2$O$_2$ 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/m$^3$, when hydrochar was modified with 10% of H$_2$O$_2$ solution. Results on bulk density of birch biochar are lower in comparison to those of [1] for woodchips pyrolyzed at 450ºC - 440 kg/m$^3$.

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 H$_2$O$_2$ 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 m$^2$/g), which exceeds BET SSA of unmodified biochar almost 15 times (20.11 m$^2$/g). Results on BET SSA are lower than those of birch-activated carbon – 400 m$^2$/g [23]. B3%-G biochar had the lowest BET SSA (50.7 m$^2$/g), which exceeds BET SSA of unmodified biochar only in 2.5 times (20.11 m$^2$/g). [19] showed higher results for unmodified birch than indicated in the current study – 73.19 m$^2$/g. In comparison, BET SSA of rise straw biochar, modified with KOH was 179.7 m$^2$/g, HNO$_3$ – 87.2 m$^2$/g, H$_2$SO$_4$– 56.9 m$^2$/g, H$_2$O$_2$ – 110.9 m$^2$/g, and KMnO$_4$– 122.9 m$^2$/g [24]. The results on BET SSA from this study are similar to the CaO-treated woody AC (265.13 m$^2$/g for N$_2$ activated and 314.57 m$^2$/g for CO$_2$ activated) and exceed KOH-treated woody AC (35.23 m$^2$/g for N$_2$ activated and 167.68 m$^2$/g for CO$_2$ activated) [25].

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

<table>
<thead>
<tr>
<th>Type of biochar</th>
<th>BET, m$^2$/g</th>
<th>Average pore diameter, nm</th>
<th>Total pore volume, cm$^3$/g</th>
<th>Total micropore volume, cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>20.11</td>
<td>4.497</td>
<td>0.023</td>
<td>0.010</td>
</tr>
<tr>
<td>B30%-P</td>
<td>264.9</td>
<td>2.329</td>
<td>0.154</td>
<td>0.116</td>
</tr>
<tr>
<td>B30%-G</td>
<td>236.4</td>
<td>2.477</td>
<td>0.146</td>
<td>0.081</td>
</tr>
<tr>
<td>B15%-P</td>
<td>152.3</td>
<td>2.893</td>
<td>0.11</td>
<td>0.091</td>
</tr>
<tr>
<td>B15%-G</td>
<td>121.9</td>
<td>3.239</td>
<td>0.099</td>
<td>0.142</td>
</tr>
<tr>
<td>B3%-P</td>
<td>82.8</td>
<td>3.39</td>
<td>0.079</td>
<td>0.048</td>
</tr>
<tr>
<td>B3%-G</td>
<td>50.7</td>
<td>3.51</td>
<td>0.059</td>
<td>0.032</td>
</tr>
<tr>
<td>B30%r-P</td>
<td>321.7</td>
<td>2.269</td>
<td>0.183</td>
<td>0.111</td>
</tr>
<tr>
<td>B30%-G</td>
<td>310.4</td>
<td>2.333</td>
<td>0.181</td>
<td>0.171</td>
</tr>
<tr>
<td>B15%r-P</td>
<td>301.5</td>
<td>2.31</td>
<td>0.174</td>
<td>0.172</td>
</tr>
<tr>
<td>B15%r-G</td>
<td>289.9</td>
<td>2.29</td>
<td>0.166</td>
<td>0.165</td>
</tr>
<tr>
<td>B3%-r-P</td>
<td>277.0</td>
<td>2.33</td>
<td>0.161</td>
<td>0.158</td>
</tr>
<tr>
<td>B3%-r-G</td>
<td>205.8</td>
<td>2.44</td>
<td>0.126</td>
<td>0.119</td>
</tr>
</tbody>
</table>
Influence of $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ solution corresponds to a higher decrease in $pH$. Therefore, the highest $pH$ had B3%-P biochar among all modified types of biochar, the lowest – B3%-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.

Modification with $\text{H}_2\text{O}_2$ 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%-P 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)
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 $\text{H}_2\text{O}_2$ 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%r-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 $\text{H}_2\text{O}_2$ increased oxygen content. Biochar modified with rotation had higher oxygen content than biochar modified without rotation. Our results on oxygen content exceed those results from [15], where unmodified pinewood biochar had 7.36% of O, and $\text{H}_2\text{O}_2$-modified biochar had the following content: 3% modification – 7.15% of O, 20% modification – 7.18% of O, and 30% modification – 7.43% of O.

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 $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$-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 $\text{H}_2\text{O}_2$ increased nitrogen content. Biochar modified with rotation had higher nitrogen content than biochar modified without rotation. Our results correspond to [15], where $\text{H}_2\text{O}_2$-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).

<table>
<thead>
<tr>
<th>Type of biochar</th>
<th>O, %</th>
<th>C, %</th>
<th>H, %</th>
<th>N, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-P</td>
<td>8.00±0.120</td>
<td>82.96±3.330</td>
<td>9.01±0.230</td>
<td>0.027±0.005</td>
</tr>
<tr>
<td>B-G</td>
<td>7.76±0.330</td>
<td>84.15±3.640</td>
<td>8.06±0.110</td>
<td>0.025±0.005</td>
</tr>
<tr>
<td>B30%-P</td>
<td>17.50±1.270</td>
<td>70.50±2.460</td>
<td>11.81±0.240</td>
<td>0.192±0.090</td>
</tr>
<tr>
<td>B30%-G</td>
<td>16.85±1.240</td>
<td>73.98±2.650</td>
<td>9.00±0.780</td>
<td>0.166±0.070</td>
</tr>
<tr>
<td>B15%-P</td>
<td>15.21±1.290</td>
<td>74.45±2.420</td>
<td>10.23±0.480</td>
<td>0.102±0.009</td>
</tr>
<tr>
<td>B15%-G</td>
<td>13.14±1.270</td>
<td>77.09±2.290</td>
<td>9.68±0.440</td>
<td>0.085±0.010</td>
</tr>
<tr>
<td>B3%-P</td>
<td>9.23±0.280</td>
<td>80.16±2.280</td>
<td>10.57±0.680</td>
<td>0.033±0.008</td>
</tr>
<tr>
<td>B3%-G</td>
<td>8.40±0.190</td>
<td>81.54±3.180</td>
<td>10.03±0.570</td>
<td>0.028±0.005</td>
</tr>
<tr>
<td>B30%r-P</td>
<td>19.50±0.930</td>
<td>66.51±2.230</td>
<td>13.78±0.890</td>
<td>0.210±0.097</td>
</tr>
<tr>
<td>B30%r-G</td>
<td>18.77±1.260</td>
<td>68.22±2.620</td>
<td>12.82±0.220</td>
<td>0.183±0.086</td>
</tr>
<tr>
<td>B15%r-P</td>
<td>15.69±1.280</td>
<td>70.65±2.190</td>
<td>13.54±0.430</td>
<td>0.112±0.098</td>
</tr>
<tr>
<td>B15%r-G</td>
<td>13.34±1.410</td>
<td>74.31±2.240</td>
<td>12.25±0.850</td>
<td>0.091±0.008</td>
</tr>
<tr>
<td>B3%r-P</td>
<td>9.57±0.290</td>
<td>78.44±2.920</td>
<td>11.93±0.520</td>
<td>0.053±0.007</td>
</tr>
<tr>
<td>B3%r-G</td>
<td>8.66±0.280</td>
<td>79.70±2.480</td>
<td>11.60±0.110</td>
<td>0.037±0.006</td>
</tr>
</tbody>
</table>
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 \( \text{H}_2\text{O}_2 \) increased H/C, N/C and O/C ratios. Biochar, modified with rotation, had higher ratios than biochar, modified without rotation. Respectively, B30%-P biochar had the highest ratios (H/C = 0.212, N/C = 0.0003, O/C = 0.293).

Cation exchange capacity (CEC) of different types of biochar is presented in Fig 7. Modification with \( \text{H}_2\text{O}_2 \) increased CEC of the biochar. Biochar modified with rotation had higher CEC than biochar modified without rotation. Respectively, B30%-P biochar had the highest CEC (30.11 cmol/kg). For comparison, unmodified hydrochar [15] had 17.95 cmol/kg, modified with 3% \( \text{H}_2\text{O}_2 \) solution - 23.3 cmol/kg, 20% \( \text{H}_2\text{O}_2 \) solution - 25.43 cmol/kg, 30% \( \text{H}_2\text{O}_2 \) solution - 31.37 cmol/kg. For comparison, 90 min ozone activation increased CEC of the pine wood 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.

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Cation exchange capacity (CEC) of different types of biochar is presented in Fig 7. Modification with \( \text{H}_2\text{O}_2 \) 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 the biochar materials. Respectively, B30%-P biochar had the highest CEC (30.11 cmol/kg). For comparison, unmodified hydrochar [15] had 17.95 cmol/kg, modified with 3% \( \text{H}_2\text{O}_2 \) solution – 23.3 cmol/kg, 20% \( \text{H}_2\text{O}_2 \) solution - 25.43 cmol/kg, 30% \( \text{H}_2\text{O}_2 \) solution - 31.37 cmol/kg. For comparison, 90 min ozone activation increased CEC of the pine wood 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].

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

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

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

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 H\(_2\)O\(_2\). From Fig. 8 peaks at 1500-1750 cm\(^{-1}\) corresponded to carboxylic groups, while peaks at 3250-3500 cm\(^{-1}\) corresponded to hydroxyl and aminofunctional groups on the biochar surface. Modification with H\(_2\)O\(_2\) increased content of carboxylic groups, especially in cases of rotation during modification. With the increasing percentage of H\(_2\)O\(_2\)-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 H\(_2\)O\(_2\) modification can activate birch-derived biochar and increase cation exchange capacity 6-fold (from 5.15 cmol/kg to 30.11 cmol/kg) and BET-specific surface area 15-fold (from 20.11 m\(^2\)/g to 321.7 m\(^2\)/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) H\(_2\)O\(_2\) modification influences other physicochemical 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 H\(_2\)O\(_2\) 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 H\(_2\)O\(_2\) solution 30%. Additionally, modification time of 2 h should be maintained, biochar-to-solution ratio 25% w/w.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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