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Effect of Modification with $FeCl_3$ and $MgCl_2$ on Adsorption Characteristics of Woody Biochar

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Abstract. Due to high specific surface area, well-developed porous structure and surface functionality biochar has a potential for being used as low-cost adsorbent for adsorption of organic and inorganic contaminants from aqueous solutions. Higher adsorption capacity and selectivity for metals could be further developed after modification of properties of biochar through physical ("designed biochar") and chemical ("engineered biochar") modification techniques. Wood waste of three types [aspen (*Populus tremula L.*), pine (*Pinus sylvestris L.*) and fir (*Picea abies L.*)] were selected to produce the biochar under slow pyrolysis conditions at 450 °C for 2 h with the heating rate of 10 °C/min. Mg and Fe-particles, acting as potential sorption sites for adsorption of metals, were added into the biochar through modification of the biochar with metal salts $MgCl_2$ and $FeCl_3$. The aim of the study was to investigate the effect of chemical modifications of woody biochar with $MgCl_2$ and $FeCl_3$ on the adsorption characteristics of the biochar. The engineered biochar with improved physico-chemical and sorptive properties was evaluated as potential adsorbent of metals from aqueous solutions. Such characteristics of the biochar, as density, porosity, pH, cation exchange capacity, electrical conductivity, moisture content, ash content, water holding capacity, total organic carbon were analyzed. Modifications followed by increasing of moisture and ash content. While carrying out the future adsorption experiment, significantly decreased pH and electrical conductivity of the engineered biochar should be taken into account. Increased cation exchange capacity of the engineered biochar promotes enhanced adsorption of metals.

Keywords: engineered biochar, woody feedstock, adsorbent.

Conference topic: Environmental protection.

Introduction

Water pollution is a serious problem for the entire world, because it threatens the health for humans, plants and animals. Metallurgical and wastewater treatment plants, coal combustion processes, transport, using of phosphorous and mineral fertilizers create problem of water contamination with potentially toxic elements (PTE). For instance, PTE like Cr (III) and Cd (II) as parts of inorganic complexes are metals of great concern in wastewater and sewage sludge. Cr is of great interest, and Cd belongs to Priority list of Chemicals (HELCOM 2013). In 2016 Environmental Working Group (EWG) found cancer-causing Cr (VI) even in tap water from 31 of 35 cities it tested, thus theatening to 200 mln of Americans. Over the last 15 years, due to the intensive industrial exposure of Cadmium into surface water, the number of aquatic species included in Cadmium National Recommended Ambient Water Quality Criteria (AWQC) has increased from 149 to 224 (EPA 2016). Metals are long-term contaminants and can not degrade in natural way. Conventional wastewater treatment methods (e.g. reverse osmosis, membrane, micro-, ultra- and nanofiltration, flocculation, chemical precipitation) may have some significant disadvantages, like incomplete removal, expensiveness due to excessive energy, manual labor, operations and maintenance requirements, production of toxic sludge (Khurma *et al.* 2013). One of the low-cost natural sorbents based on the principles of sustainable development is biochar. The functional groups such as hydroxyl, carboxyl, ether, amide, amine, alkayl, alkyne, alkine and carbonyl are responsible for accumulating contaminants from water and wastewater. The atomic ratios such as H/C (aliphatic), O/C and N/C (polar index) are related to the specific properties of the biochar (Ahmed *et al.* 2016). The criteria, describing the ability of a biochar to facilitate the effective adsorption of metals, are given in Figure 1. When compared with activated carbon (AC), biochar could be produced from wastes (Baltrėnaitė *et al.* 2016a) at lower temperatures in a shorter time period and costs 3 times lower (platform for global wholesale trade www.alibaba.com). Despite of the lower microporosity and surface area of the biochar in comparison to activated carbon, adsorption characteristics of the biochar could be improved by modification techniques.

Various biochar modification techniques in terms of enhanced adsorption of metals are oriented towards changing the biochar surface properties: increasing specific surface area, pore volume, content of carboxylic (mainly oxygen-containing) functional groups. Treatment of biochar with solutions of metal salts (i.e. engineering of the biochar) not only protonates the charged sites but also replaces the natural mix of ionic species present in the bio-

mass with protons. It was found that seaweed treated with $MgCl_2$ showed 73% of Cr(III) uptake in comparison to unmodified one (65%) (Aravindhan *et al.* 2004). There were successful attempts to modify biochar with Fe (Hu *et al.* 2015; Samsuri *et al.* 2013) or Mg (Yao *et al.* 2013; Usman *et al.* 2013). Fe-modified biochar showed significant Pb and Cd removal as Fe-particles on the biochar surface served as sorption sites for electrostatic attraction (Zhang *et al.* 2013). Agrafioti *et al.* (2014) observed 95% removal of Cr on Fe-modified biochar through electrostatic attraction. Yao *et al.* (2013) indicated that Mg particles on the surface of the Mg-modified biochars acted as sorption sites in 88.5% of phosphate removal. Moreover, modified biochar exhibited higher specific surface area and porosity in comparison to unmodified biochar (Komnitsas, Zaharaki 2016), that characteristics also influence adsorption of contaminants. Fristak *et al.* (2016) modified wood chips with $Cu(OH)_2$, $FeSO_4$, $MgCl_2$, KCl, $Mg(OH)_2$, $AlCl_3$ (30% w/w) and observed that sorption efficiency for As was the highest from $AlCl_3$-biochar (prepared at 400 °C), for P – from $Mg(OH)_2$ (prepared at 400 °C). Therefore, surface modification of biochar with metal salts followed by inreasing of porosity, specific surface area of biochar, oxygen-containing functional groups, enhances adsorption of metals.

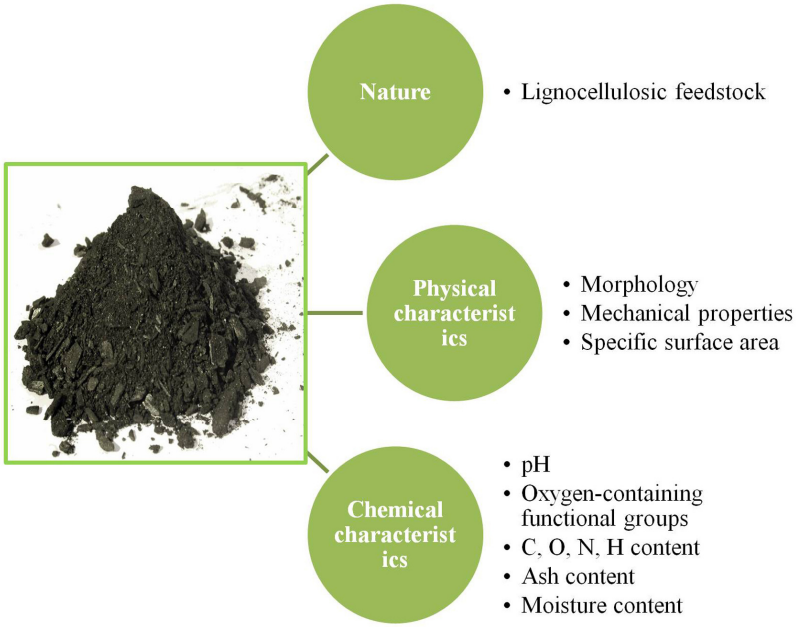

Fig. 1. The criteria for selecting the biochar for adsorption of metals

According to the European Biochar Certificate, lignocellulosic feedstock is the most valuable raw material in terms of its accessibility and waste management reasons. *Pinus sylvestris L.* and *Betula pendula L.* woody biochar was used in biofiltration systems for removal of volatile compounds from the air (Baltrėnas *et al.* 2015, 2016). Properties of wood, that can influence the adsorption of metals, include lignin, water content, mineral composition, morphology and pore structure. In comparison to the other types of waste, the woody feedstock results in higher yield of biochar due to higher lignin content (Baltrėnaitė *et al.* 2016b, 2016c).

The aim of the study was to investigate the effect of chemical modifications of woody biochar with $MgCl_2$ and $FeCl_3$ on the adsorption characteristics of the biochar.

Materials and Methods

Selection of biochar feedstock

Wood waste of three tree species was selected for biochar production from supermarket of building materials UAB "Vedrana": pine (P), fir (F) and aspen (A). Due to local availability, cost-effectiveness and the prevalence of coniferous trees in Lithuania, pine and fir [pine and fir occupy 33.1% and 19.7% of forest area in Lithuania (Ministry of Environment of Lithuania 2015)] were chosen. Aspen [occupies 3% of forest area in Lithuania (Ministry of Environment of Lithuania 2015)] was chosen among deciduous trees. Pine and fir contain 25–33% of lignin, aspen – 20–23% of lignin. Moreover, these tree species have different natural characteristics that can be helpful for further investigation of adsorption: bioaccumulation of nutrients (Mg, Fe), water, lignin content, C, O, N, H, S contents.

Biochar production

As regards biochar production, a method described in the work by Mancinelli *et al.* (2016) was followed. Air dried feedstock was placed in open crucibles, weighed, and wrapped in aluminium 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. Each of the production combinations (the three types of feedstock at one pyrolysis temperature) was repeated three times. At the end of the production process, the samples were left to cool in the muffle furnace overnight. Three types of biochar samples were produced: (1) Pine biochar produced at conditions of slow pyrolysis; (2) Fir biochar produced at conditions of slow pyrolysis; (3) Aspen biochar produced at conditions of slow pyrolysis. The obtained biochar was grounded 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 as follows:

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

where: W_1 − the dry mass of the feedstock, g; W_2 − the dry mass of biochar, g.

Biochar modification with $FeCl_3$ and $MgCl_2$

The biochar was grounded and 0.4-mm-diameter fraction was separated by 400-µm sieve (Retsch, Germany). For modification process, two types of solutions were prepared: 0.37 M $FeCl_3 \cdot 6H_20$ and 1 M $MgCl_2 \cdot 6H_20$. The biochar was added to modifying solutions with ratio 30% w/w and rotated (RS12 Rotoshake, Gerhardt) at 12 rpm for 2 h. Then the biochar was filtered through cellulose acetate membrane filter (ALBET LabScience, Germany) with particle retention 0.45 µm.

Physical properties of biochar

Skeletal density (analogue VDLUFA-Method A 13.2.1) was measured in accordance with EBC guidelines (EBC 2012). The sample was filled into a graduated cylinder and the mass was determined by weighting. The density in kg/m^3 was calculated from the mass and the volume of the sample.

The morphology of pine and aspen biochar was determined at Scientific Institute of Thermal Insulation of Vilnius Gediminas Technical University using mercury porosimeter Quantachrome Poremaster PM-33-12.

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 (Komkiene, Baltrėnaite 2016). After shaking the suspension for 1 h and after allowing deionized water to stand for 1 h, the pH was measured using Mettler Toledo Seven Multi pH meter (Germany).

Cation exchange capacity (CEC) was determined using ammonium acetate (Komkiene, Baltrenaite 2016). Twenty-five grams of biochar was allowed to stand overnight after being thoroughly shaken with 125 ml of 1 M NH_4OAc. The biochar was transferred in filter paper-fitted Buchner funnel. The biochar was gently washed four times with 25 ml additions of NH_4-OAc. The leachate was discarded and the biochar was washed with eight separate additions of 95% CH_3CH_2OH to remove excess saturating solution. The adsorbed NH4 was extracted by leaching the biochar with 1 M KCl. The biochar was removed and the leachate was transferred to a volumetric flask to dilute to 250 ml volume with additional 1 M KCl. The concentration of NH_4–N was determined in the KCl extract by colorimetry (from composed ammonia calibration curve by measuring absorption intensity at k = 400 nm with photocolorimeter in 1 cm length cells, concentration of NH_4–N was calculated using Nessler method. Also NH_4–N was determined in the original KCl extracting solution (blank) to adjust for possible NH_4–N contamination in this reagent. Cation exchange capacity was calculated using Eqn (2):

$$CEC = \frac{NH_4N_{inextract} - NH_4N_{inblank}}{14}, \quad (2)$$

where: CEC − cation exchange capacity, $cmol_c$ /kg; $NH_4N_{in\ extract}$ − ammonium ion concentration in the extract, mg/ l; $NH_4N_{in\ blank}$ − ammonium ion concentration in the blank, mg /l.

Electrical conductivity of biochar according to the EBC guidelines (DIN ISO 11265) was measured by adding 20 g of the biochar to 200 ml deionized water and shaking it for 1 hour, followed by filtration of the solution. The conductivity of biochar was measured then in the filtrated water.

Moisture content according to the EBC guidelines (DIN 51718):
1) raw moisture using Eqn (3):
The sample was spread evenly in a drying bowl crucible, weighed with 0,1 g accuracy and dried in an oven at (40±2) °C until the mass is constant.

$$FG = \frac{m_E - m_R}{m_E} \times 100, \quad (3)$$

where: FG − raw moisture, %; m_E − mass of the sample before drying, g; m_R − mass of the sample after drying, g.
2) hygroscopic moisture using equation 4:
A subsample of the air-dried and crushed (grain size < 1 mm) sample was weighed and dried in oxygen atmosphere at (106±2) °C to constant mass.

$$FH = \frac{m_E - m_R}{m_E} \times 100, \quad (4)$$

where: FH − hygroscopic moisture, %; m_E − mass of the sample before drying, g; m_R − mass of the sample after drying, g.
3) moisture content using equation 5:

$$W_t = FG + FH\frac{100 - FG}{100}, \quad (5)$$

where: Wt − water content, %; FG − raw moisture, %; FH − hygroscopic moisture, %.

To determine ash content (550 °C) according to the EBC guidelines (DIN 51719) of biochar two heating programs were used:

- heating with a rate of 5 °C / min to 106 °C under oxygen atmosphere to constant mass (dry mass Dm <0.05%).
- temperature increase with 5 °C / min to 550 °C under oxygen atmosphere, and hold this temperature for 60 min to constant mass (Dm <0.05%).

Water holding capacity (WHC) according to the EBC guidelines (DIN ISO 14238-2011) was measured by soaking the 2 mm fraction of the material in deionized water for a period of 24 hours. After this, the material was placed on a dry sand bed for 2 hours for removing free water. The saturated material was weighed and then dried at 40 °C in a compartment dryer. After drying the material was weighed again for estimate the water holding capacity.

Total carbon (TC) was determined according to Komkiene and Baltrėnaite (2016) using Total Organic Carbon Analyzer TOC-V (SHIMADZU, Japan). Samples of biochar were dried at room temperature, sieved through a 2-mm sieve, crushed, and homogenized. 20 mg of each biochar sample weighed in the combustion cell was placed in the combustion chamber.

Quality assurence and statistical analysis

Each analysis was prepared and analysed in duplicates. The measurements were carried out three times and the average of the results of measurement errors was calculated. The statistical analysis was performed using Excel program. The results of arithmetic mean values with values of relative errors were presented in graphical expression of the results. The standards of calibration were used to calibrate devices in each year. The quality of experiments was assured by blank samples such as deionized water (for NH_4–N) and KCl (for pH).

Results

Physico-chemical characteristics of the pine, fir and aspen biochar are summarized in Table 1. Water-holding capacity (WHC) is an ability of biochar to retain water. According to diameter (d), pores are classified as micropores (d < 2 nm), mesopores (2 nm < d < 50 nm) and macropores (d > 50 nm) (Lehmann, Joseph 2015). Mercury intrusion porosimetry (MIP) is a suitable technique to describe meso- and macroporous structure, in our case pores with diameter higher than 6.449 nm. Smaller-diameter pores should be investigated by N_2 adsorption at low temperatures.

Table 1. Physico-chemical characteristics of the biochar

Characteristics / Type of biochar	Yield, %	Bulk density, g/cm^3	Apparent density, g/cm^3	TOC, %	WHC, %	Total porosity, %	Pore surface area, m^2/g	Pore volume, cm^3/g
P450	25.0	1.4	0.5	88.8	11.8	81.3	8.6	1.5
F450	23.9	n.a.	n.a.	88.4	13.2	n.a.	n.a.	n.a.
A450	19.6	1.7	0.6	85.4	16.5	79.2	5.6	1.1

TOC – total organic carbon, WHC – water holding capacity.

Prepared in the same conditions, biochar of the different type differ in yield: aspen biochar has the lowest yield because of lower amount of lignin in the aspen feedstock. Moreover, aspen biochar has the lowest total organic carbon content because of lower amount of carbon in the aspen trees than conifer species. Though, aspen has the highest WHC, that could be attributed to the finer structure of aspen biochar. The total porosity of pine was slightly bigger

than of aspen, promoting the better adsorption of contaminants. The same tendency for physico-chemical characteristics of woody biochar was observed in Komkiene and Baltrėnaite (2016).

Effect of the modification of woody biochar with $FeCl_3$ and $MgCl_2$ on characteristics of the biochar

Results on skeletal density are presented in Figure 2.

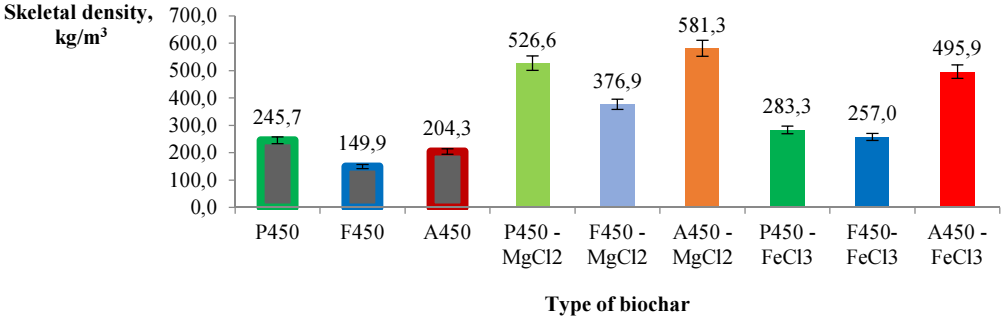

Fig. 2. Skeletal density of the biochar before and after modifications ± relative errors

Both types of modification increased the density of the biochars because of adding of Mg or Fe. Modification of biochar with $MgCl_2$ increased density in almost 2 times in comparison with unmodified biochar. Modification of biochar with $FeCl_3$ influenced density slightly in comparison with $MgCl_2$ modification, because of lower concentration of solution, though the density of $MgCl_2$ is lower than $FeCl_3$ (2.32 g/cm^3 and 2.9 g/cm^3, respectively).

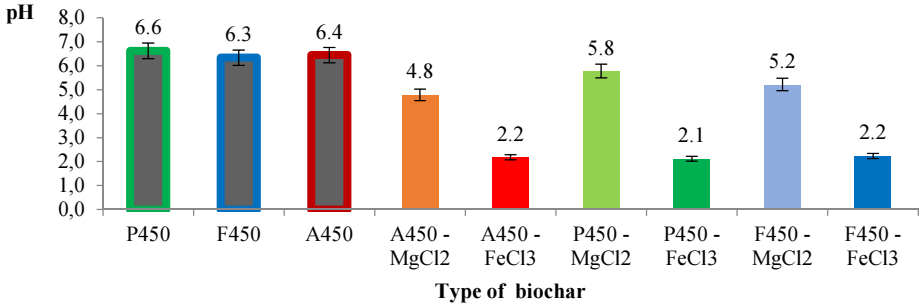

Fig. 3. pH of the biochar before and after modifications ± relative errors

Both type of modification decreased pH of the biochars because of adding of Mg or Fe (Fig. 3). Principally, $MgCl_2$ originated from $Mg(OH)_2$ (a weak base) and HCl (a strong acid). $FeCl_3$ can be considered as a salt of $Fe(OH)_3$ (a weak base) and HCl (a strong acid). Hence, aqueous solutions of $FeCl_3$ and $MgCl_2$ were acidic. pH electrode is sensitive to hydrogen ion activity, that means that modification decreased the hydrogen content.

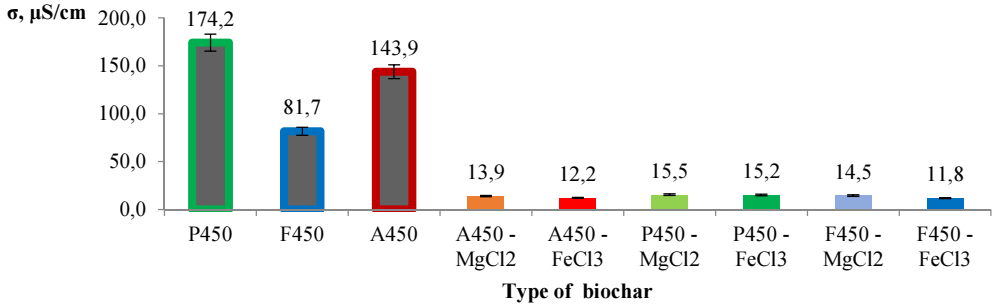

Fig. 4. Electrical conductivity of the biochars before and after modification ± relative errors

Both modifications reduced electrical conductivity of the biochars because of adding of Mg or Fe. High electrical conductivity is connected with the high mobility of hydrogen (Karato 2006), which was decreased after modification. Though the electrical conductivity of the biochar from different tree species had been different, after modification the values of electrical conductivity became almost equal.

Moisture content is shown in Table 2. Moisture content depends on raw moisture and hygroscopic moisture content.

Table 2. Moisture content of the biochar

Type of biochar / Type of moisture	P450	F450	A450	P450 -$MgCl_2$	F450 -$MgCl_2$	A450 -$MgCl_2$	P450 -$FeCl_3$	F450 -$FeCl_3$	A450 -$FeCl_3$
Raw moisture, %	2.1	2.1	4.7	7.0	8.2	6.7	9.3	9.3	8.7
Hygroscopic moisture, %	2.3	0.6	1.9	14.5	15.3	14.0	14.1	15.8	13.6
Moisture content, %	4.3	2.7	6.6	21.5	23.6	20.7	23.4	25.0	22.3

Hygroscopic moisture of the biochar increased after modification, because $FeCl_3$ and $MgCl_2$ are highly hygroscopic compounds. Moisture content of the modified biochars increased in comparison to unmodified biochars.

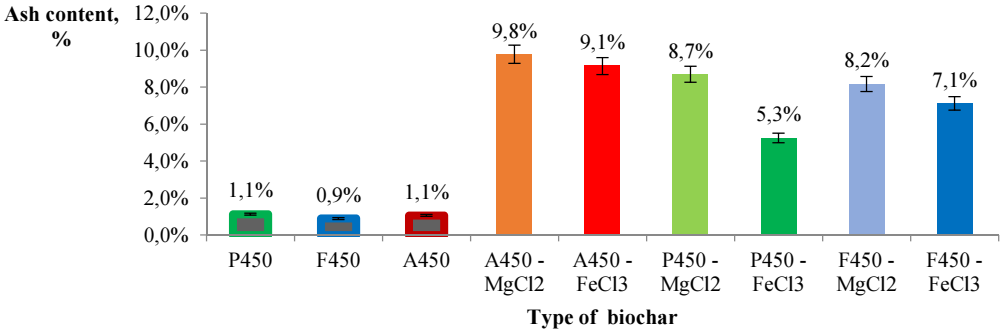

Fig. 5. Ash content of the biochar before and after modification ± relative errors

Ash content refers to the mineral content of the biochar. Ash content of the modified biochars increased, that suggested that activation with $FeCl_3$ and $MgCl_2$ was made (Fig. 5). Depending on modification type, in case of $MgCl_2$ ash content decreased in order A450 < P450 < F450, for $FeCl_3$ – A450 < F450 < P450.

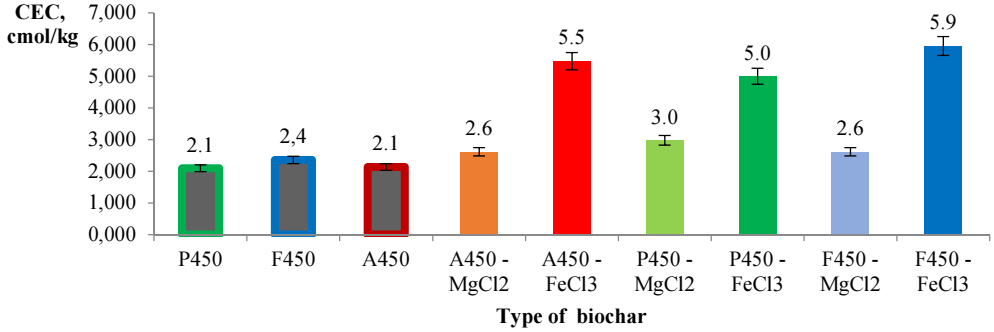

Fig. 6. Cation exchange capacity of the biochar before and after modification ± relative errors

Modification increased cation exchange capacity (CEC) of the biochars (Fig. 6). The highest CEC was observed in $FeCl_3$ modification, because the modication with $FeCl_3$ form more oxygen-rich functional groups were formed on the biochar, especially the C═O group, than $MgCl_2$ activation.

Increased cation exchange capacity of the engineered biochar suggested the increased amount of oxygen-containig functional groups, promoting enhanced adsorption of cationic metals through ion exchange. While carrying out the future adsorption experiment, significantly decreased pH and electrical conductivity of the engineered biochar should be taken into account. Ahmed *et al.* (2016) stated that modification method with metal salts influences physical and chemical properties of biochar, i.e. H/C, O/C and N/C molar ratios, CEC, ash content, facilitating enhanced removal of organic and inorganic contaminants, although with reduced pore volumes.

Even though most studies focus on investigating biochar properties and designing biochar for specific purposes, it is still difficult to establish specific process conditions to produce biochars with the desired characteristics because the relationship between the physical and chemical properties of biochar and its applicability in different fields need

to be further investigated. There is a need for adsorption technologies using biochar for metal sorption in soil (Baltrėnaitė *et al.* 2016d).

Conclusions

1) Unmodified aspen biochar showed lower values of yield (19.5%), porosity (79%) and TOC (85%) in comparison with conifer trees (23–25%, 81%, 88–89% respectively), but higher WHC (16.5% to 11–13%). Therefore, biochar from coniferous trees could be more suitable in adsorption of cationic metals.

2) Density of the biochars increased significantly after $MgCl_2$ modification. Results showed that modifications significantly decreased pH of the biochars, i.e. modification with $FeCl_3$ decreased pH of the biochar in 3 times, while $MgCl_2$ modification decreased pH on 20%. Properly, after modification electrical conductivity of the biochars decreased in 10 times. Increased ash content (in 9 times) showed the adding of Mg and Fe into the biochar. CEC increased because of adding of oxygen functional groups on the surface of biochar;

3) The most important characteristics for adsorption of cationic metals are pH, CEC, ash content. Hence, depending on the type of cationic metal, when the proper pH should be established, modified biochar with $MgCl_2$ or $FeCl_3$ could be applied regardless of tree specie. Coniferous trees showed higher ash content after $MgCl_2$ modification; in case of aspen there was no difference between treating agent. The highest CEC was observed after $FeCl_3$ modification of fir. Therefore, modifications could be made regardless of tree specie. Though, $MgCl_2$ produce higher ash content, $FeCl_3$ results in higher CEC.

4) Investigations on modification of different tree species should be continued. Due to its accessibility and low-cost production, natural ways of modification of biochar for enhanced adsorption of cationic metals should be developed, i.e. bioaccumulation of trace elements in wood, moisture and lignin content, C, O, N, H, S content.

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Disclosure statement

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