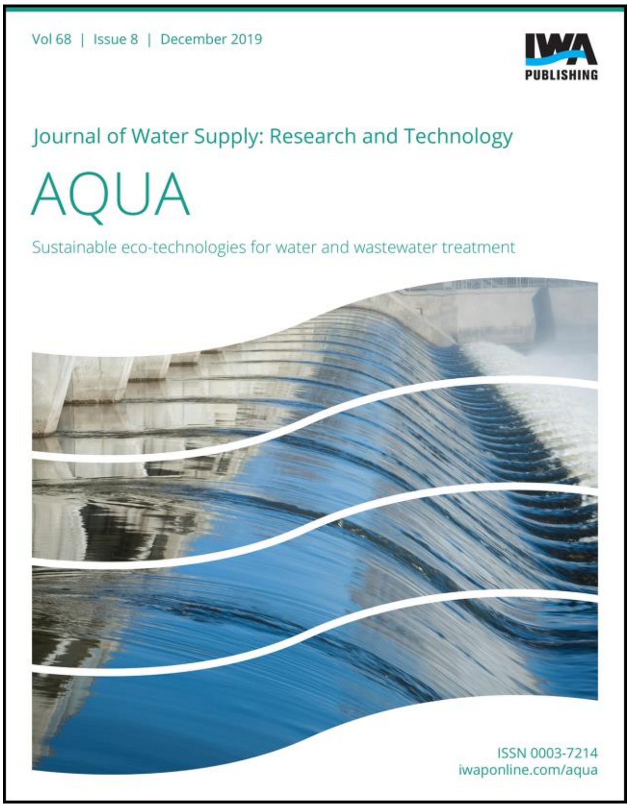
Vol 68 | Issue 8 | December 2019
IWA PUBLISHING
Journal of Water Supply: Research and Technology
AQUA
Sustainable eco-technologies for water and wastewater treatment
ISSN 0003-7214
iwaponline.com/aqua

Technogenic metallic elements in biomass and their effects on biomass product properties

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ABSTRACT

Availability of clean water and sustainable management of water are among the 17 global 'Sustainable Development Goals,' established by the United Nations. The increasing technogenesis-related pollution causes increases the concentrations of many metallic elements (MEs) throughout the biosphere. The syngenetic bio-incorporation of MEs changes the biomass's chemical and physical composition and impacts the quality of products, e.g. biochar (BC). This has impacts upon BCs potential for adsorption of water pollutants. While direct, engineered modification of BC can improve its adsorption characteristics, the more indirect alterations of BC composition, based on syngenetic elements, also modifies BCs adsorption functionality. The objective of this study was to identify the characteristics of syngenetically accumulated MEs in ligneous biomass on the adsorptive properties of the BCs derived from such modified biomasses. The authors of this paper investigated the syngenetic pathway of MEs into the ligneous biomass and provided an overview of the forms and quantities of MEs in the biomass and their transformation to BC. The early results of the effects of syngenetic MEs on the adsorptive properties of BC from ligneous biomass are presented. The results suggest that additional syngenetical MEs result in increases in the adsorptive properties of the resultant biomass-derived BCs.

Key words | adsorption, biochar, metallic elements, syngenetic elements, technogenesis

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INTRODUCTION

According to the World Health Organization, 2.1 billion people live without safe water at home. Contaminated water can transmit diseases such as diarrhea, cholera, dysentery, typhoid, and polio. Contaminated drinking water is estimated to cause 502,000 diarrheal deaths each year. At least 10% of the world's population has been documented to consume food irrigated by wastewater, which usually contains contaminants such as metallic elements (MEs) (e.g. Cu is a typical metal in wastewater (Shen 2019)), and organic contaminants (WHO 2017).

Both natural sources (such as soil erosion, urban runoff, aerosols, and particulates) and anthropogenic sources (metal finishing and electroplating processes, mining extraction operations, textile industries, nuclear power (Zeng *et al.* 2018; Oluwatuyi *et al.* 2019)) of MEs entering waterbodies are driven by intensive technogenesis and increased consumption of society. The need for environmentally friendly biotechnologies for the removal of organic and inorganic water pollutants was investigated (Rene *et al.* 2018) with the focus on sustainably produced adsorbents for the removal of water pollutants (Begum *et al.* 2018; Feng *et al.* 2018; Rai *et al.* 2018).

With the increase in gross domestic product (GDP) and human population by about 225% and 72% respectively since 1994, the world extraction of MEs increased by over 75%. As a result, since 1,983 the emissions of MEs to the biosphere, including waterways, have increased by a factor of 1.5–3. The stocks and flows of the global cycles of Ag, Al, Cr, Co, Fe, Ni, Pb, and Zn comprise over 98% of the

doi: 10.2166/aqua.2019.082

total mass of MEs mobilized by human activities by the turn of the 21st century (Rauch & Pacyna 2009).

The increase in MEs extraction intensifies the problem development of higher water contamination loads, which, in turn, lead to the increases in MEs biophilicity and bioaccumulation (Lietuvninkas 2012; Baltrėnaitė *et al.* 2016, 2018). The ways such technogenic substances are entering biomass during growth has the features of syngeneity and, therefore, can be called syngenetic. Therefore, MEs are subjected to a new – syngenetic – way of entering biomass.

The growing demand for organic products in the market promotes their use in various fields, including environmental engineering. One such product is biochar (BC) and its use in adsorption systems. Being of natural origin (i.e. produced via pyrolysis from organic biomass), such adsorbents are subject not only to adsorption efficiency requirements, but also to requirements of multi-functionality, cascading usage. For example, biochar, which resembles activated carbon, is produced for the adsorption of pollutants from biowaste (an advantage in waste management), it is relatively cheap, locally available, sustainable, promotes nutrient recycling, improves soil properties (when applied to reduce bioavailability of metals in soil), and stimulates healthy soil microbial diversity (Wu *et al.* 2016).

While artificial modification of BCs with MEs can highly improve its adsorptive characteristics (Wei *et al.* 2018) (also for adsorption of MEs from aqueous solution), syngenetically, incorporated MEs may affect BC composition, which enhances the adsorption of water contaminants by BCs as well as decreases BCs modification costs. For example, BC, made of tomato biomass with naturally increased Mg content, adsorbed approximately two times greater amounts of phosphates than BCs from biomass of tomatoes grown in the 'normal way' (Yao *et al.* 2013). It showed that natural or syngenetic entrance of MEs into biomass can be beneficial for altering properties of biomass products. When considering more engineered biomass products, syngeneity of MEs can be advantageous in designing BCs.

The novelty of the paper is the analysis of MEs syngeneity effects on the adsorptive properties of BCs made from this modified biomass. Such BCs can be used in water engineering applications, e.g. removal of contaminants from water.

The authors of this paper investigated the problems associated with the increasing rate of MEs accumulation in living matter in general, with a special focus upon accumulations of MEs in the biomass of ligneous plants. The authors reviewed the advantages of bioaccumulation of syngenetic MEs having technogenic origins, in the biomass of ligneous plants and its product (biochar, BC) from an environmental (water) engineering perspective.

This paper is divided into three parts.

The first two sections review the ways and quantities of MEs that enter the biomass of the ligneous plants. Ligneous biomass was selected to document MEs syngeneity effect for BC adsorptive properties because ligneous biomass is preferred for BC production as plant parts rich in ligneous substances, such as bark, roots and branches, are viewed as waste instead of being used for the production of higher value products. The second part of the paper focuses on the forms and quantities of MEs present during transformation of ligneous biomass into BC.

The BCs produced from ligneous biomass were selected for this research. They are widely produced from different types of biomass for which syngenetic entrance of MEs is especially high.

The BCs have been widely studied for their potential to adsorb water pollutants. Moreover, the syngeneity affected properties of BCs to be utilised in water decontamination processes.

The third part of the paper ('The influence of syngenetic elements on the pyrolysis') provides the preliminary results of the effects of syngenetic MEs on BCs' properties for adsorption of water pollutants. The focus is on the physico-chemical properties which may increase the adsorptive features of BCs.

This research provides new insights. First, it introduces new – syngenetic – origins of MEs entrance into biomass and extends the systematic understanding of origins of MEs. Second, it describes and presents preliminary research results on the syngenetic MEs' impacts on the characteristics of BCs and how those changes impact the absorptive capacities of BCs.

SYNGENETIC METALLIC ELEMENTS AND THEIR PLACE IN CLASSIFICATION BASED ON ORIGIN

The mechanisms of the accumulation of chemical (and metallic) elements (MEs) into the biomass of the ligneous plants vary extensively. Vassilev *et al.* (2012) presented a classification of the biomass containing MEs according to their origin, place and time of generation. These MEs originated from natural (authigenic and detrital) and anthropogenic processes, taking place during pre-syngenesis, syngenesis, epigenesis and post-epigenesis of biomass according to the main formation processes and locations, as well as the times and mechanisms of the formation processes.

The MEs can be integrated into biomass from the aerogenic and edaphic sources as early as during the plant's growth. Aerogenic sources of MEs are usually the stationary or mobile emission sources from which MEs are transported in the form of aerosolic particles. The particles of aerogenic origin primarily include finely dispersed products of chemical ashing of rock (clay minerals) and organic or mineral soil components. Both of them can adsorb MEs, while in organic soil components (i.e. decomposed plants and humus), these components may originate from plants which concentrated the MEs. Thus, MEs can be incorporated within aerosol particles due to the processes taking place on the Earth's surface, such as mineralization, deflation, and evapotranspiration.

Another way MEs enter into biomass is by edaphic origin such as via fertilizers and other soil amendments. They are assimilated and accumulated in the plants as they grow. This path of accumulation MEs in biomass is referred to as a syngenetic mechanism. This implies that the classification of MEs according to their origin offered by Vassilev *et al.* (2012) should be supplemented by the data on MEs of technogenic (authigenic) origin, while their penetration into biomass takes place when a plant is growing (i.e. it is syngenetic) (Figure 1).

With the increase in the intensity of technogenesis, the penetration of MEs into biomass is increasing due to a higher load of MEs in the biosphere. Therefore, syngenetic entrance of MEs into biomass has a growing importance because of the potential effects on biomass and BCs' characteristics.

AMOUNTS AND PHASES OF SYNGENETIC METALLIC ELEMENTS FOUND IN LIGNEOUS BIOMASS

The presence of MEs in ligneous biomass varies depending on their type, species and the availability of MEs in the soil. The differences in local characteristics of the soil, hydrology,

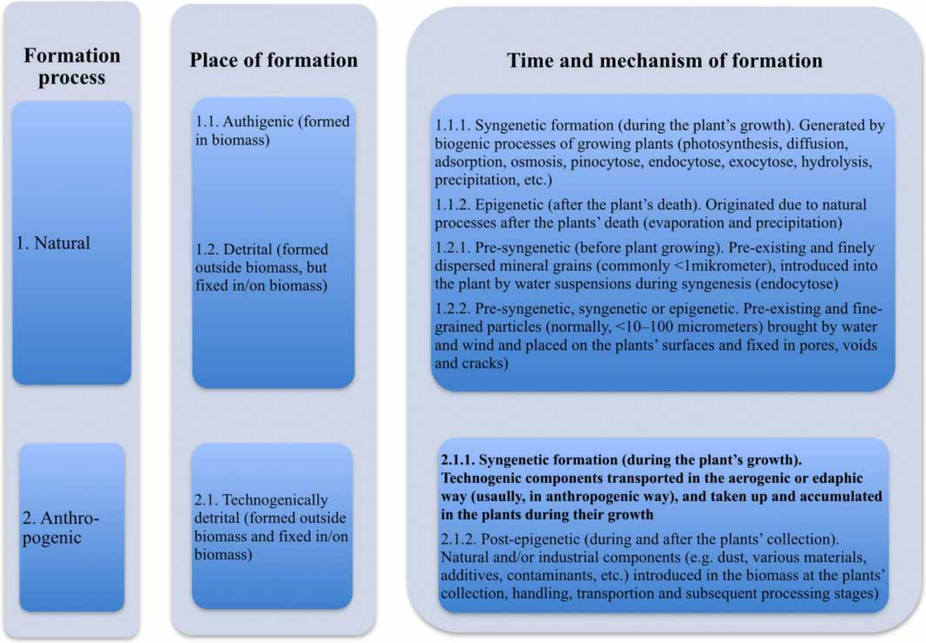


Figure 1 | The origin of metallic elements in ligneous biomass. New – syngenetic – types of metallic elements' entrance into biomass are provided in bold (adapted from Vassilev *et al.* 2012).

Table 1 | Bioaccumulation of chemical elements (according to Lietuvninkas 2012).

Level		Coefficients, K_{ba}				
		100*n	10*n	n	0.n	0.0n–0.00n
Accumulation	Energetic	Br, Cl, I, P, S				
	High		B, Ca, K, Mg, Na, Se, Sr, Zn			
Capture	Medium		Ag, As, Ba, Co, Cu, F, Ga, Hg, Mo, Mn, Ni, Pb, Ra, Sn			
	Weak or very weak		Al, Be, Cd, Cr, Cs, Fe, Li, Nb, Rb, Sb, Sc, Si, Ta, Th, Ti, U, V, W, Y, Zr			

Note that the value of n is from 1 to 9.

and the degree of exposure to air pollutants result in various degrees of MEs immobilization, assimilation and bioaccumulation by ligneous plants. Biomass of ligneous plants is 90% of the biomass of terrestrial living matter, while the latter is 99.5% of the mass of living matter (Lietuvninkas 2012). Therefore, bioaccumulation as a phenomenon is important in the case of ligneous plants. The most extensive results and summary on bioaccumulation levels of MEs in living matter in natural conditions are given in Table 1. It is clear that MEs, which are considered potentially toxic (Cr, Cu and Pb), are accumulated at the level 1–0.001*n (where n is a factor with values from 1 to 9) compared to those of the substrate (Table 1).

These limits are corrected by the substrate's pollution, thereby reflecting the increase in the intensity of penetration of MEs into biomass (Baltrėnaitė & Baltrėnas 2019). The changes in the chemical background and the resulting increases in the amounts of MEs in the ligneous plants can be observed in the cases of pollution of edaphic and aerogenic origins. The results revealed that the load of MEs of aerogenic origin was more specific for the accumulation of Ni and Pb emissions, while the load of the edaphic origin was more characteristic for Cu, Cd and Zn emissions (Baltrėnaitė *et al.* 2018).

The global increase in metal concentration in soil and terrestrial biomass from 1990 to 2009 can be observed from data provided in Table 2. The increase in soil Cu, Pb and Cr concentrations by 1.95, 2.7 and 1.44 times, respectively, can be detected. Using data of metal concentration in soil and biomass, the coefficient of bioaccumulation of metals in biomass can be calculated. This coefficient, calculated on the global level, reflects uptake of metals by biomass as affected by long-term metal contamination of soil and indicates the global changes in metal circulation in soil–plant systems.

Table 2 | Global mean metal (Cu, Zn, Pb, Ni, Cr) concentrations (data in 1990 and 2009) in soils and terrestrial biomass and coefficient of metal bioaccumulation by biomass, mg/kg (Saet *et al.* 1990; Rauch & Pacyna 2009)

	Cu	Zn	Pb	Ni	Cr
Soil (Saet *et al.* 1990)	20	50	10	40	90
Soil (Rauch & Pacyna 2009)	39	48	27	25	130
Terrestrial biomass (ash) (Rauch & Pacyna 2009)	96	720	188	22	18.8
Coefficient of metal bioaccumulation	2.5	15	6.96	0.88	0.14

The coefficient of bioaccumulation of Pb increased by about two times and, consequently, it changed places with Cu and became more important with respect to bioaccumulation in global biomass:

Global biomass bioaccumulation sequence (calculated for data of 2009): $Zn_{15}Pb_{6.96}Cu_{2.5}Ni_{0.88}Cr_{0.14}$.
Global biomass bioaccumulation sequence (in 1990 by Saet *et al.* 1990): $Zn_{19.6}Cu_{9.1}Pb_{3.7}Ni_{1.5}Cr_{1.0}$.

Taking into account that Pb is not essential for living organisms' metabolism and in fact it is toxic and carcinogenic, it is important to note that the increasing bioaccumulation coefficient gives cause for societal concern (Markert *et al.* 2015). Therefore, due to the development of technogenesis, the amount of MEs of anthropogenic origin of releases of Cu, Cr, Pb and Zn into the biosphere will be increasing even more rapidly and will potentially have more negative impacts upon the biosphere and upon human health (Rauch & Pacyna 2009).

Accumulation of MEs in trees due to bioaccumulation, which is a non-equilibrium process, involves the following steps of the element's transport:

a. diffusion of the ME on the surface of the cell;
b. sorption (including adsorption and absorption);
c. binding to the groups on the surface of the cell (passive or active);
d. binding in the organic-metallic form (in this way, metal is excluded from the metabolic processes) (Chojnacka 2010).

The MEs are incorporated into the inorganic matter of the ligneous biomass in any or all of three solid states: crystalline, semi-crystalline and amorphous states (Vassilev *et al.* 2012). The inorganic components in ligneous biomass are typically various salts of carbonates, silicates, phosphates, and oxalates (predominantly, in the bark), in free ionic phase or as cations bound to acidic groups. They are minor constituents of the ligneous materials and, naturally, their total concentrations (measured from the ash) rarely exceed the 1% level (Ivaska & Harju 1999).

The phases of inorganic compounds were studied by Keown *et al.* (2008), Doshi *et al.* (2009), Meyer *et al.* (2012), Vassilev *et al.* (2012, 2014) and Leijenhorst *et al.* (2016) and a summary of the information is presented in Figure 2. The MEs phases in ligneous biomass vary, depending on the element. The most simple species is a free ion dissolved in fluids within the biomass's inner structure. More complex phases include salts in mineral form (e.g. sodium chloride), covalent bonding between inorganic elements and organic structures, solid salt structures embedded on the cell wall or bonded inside the organic matrix, forms of impurities in amorphous or semi-crystalline cellulose, or in sulfate, nitrate or in small (<2 μm) crystal structures.

Meyer *et al.* (2012) suggested that ligneous materials should have more positive associations with respect to divalent MEs ions than to monovalent ions. They found that cellulose can bind more MEs than lignin. Considering ligneous plants as representatives of the living matter, forming the largest biomass, it is evident that accumulation of MEs in ligneous biomass will increase with more intensive technogenic loads of MEs. More divalent MEs are expected to be accumulated in the ligneous biomass than univalent MEs.

EFFECT OF COMPOSITION OF FEEDSTOCK AND CONDITIONS OF PYROLYSIS ON THE ACCUMULATION AND FORMS OF METALLIC ELEMENTS IN BIOCHAR AS AN EXAMPLE OF TYPE OF LIGNEOUS BIOMASS PRODUCT

The growing demand for (natural) organic products in the market fosters new uses/demands. An example of such

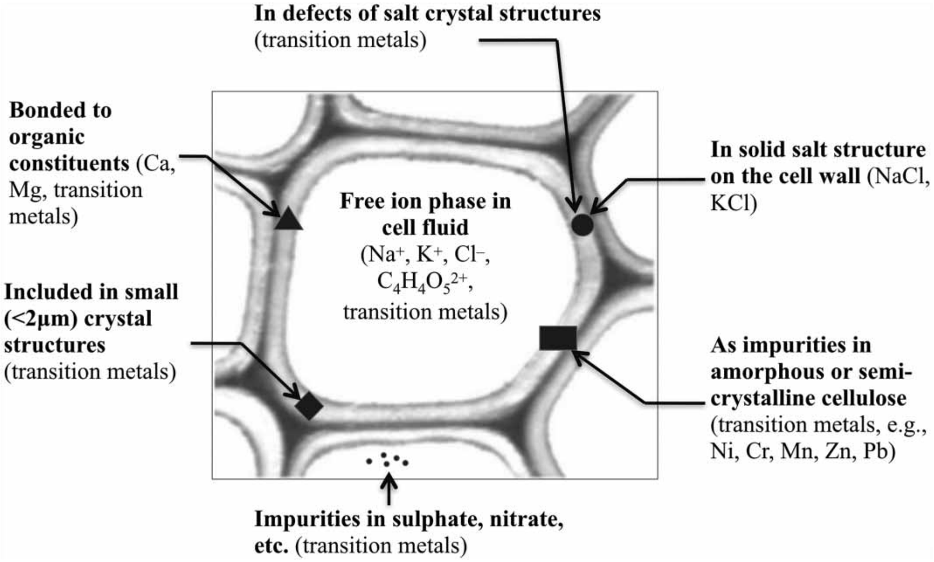


Figure 2 | The phases of the metallic elements in ligneous biomass.

products is BCs which are produced via pyrolysis. It was found that for climate change mitigation, the BC production from lignocellulosic biomass has higher potential for energy production than direct biomass combustion. (Woolf *et al.* 2010).

However, BCs are too valuable to be used to only meliorate soil immediately after its production. They should be used for another useful purpose at least once before being added to the soil. Among the innovative environmental applications, BCs have been used to absorb contaminants in environmental protection engineering systems (Srinivasan & Sarmah 2014).

Also, pyrolysis was proposed as an alternative method to dispose of the MEs' contaminated biomass, such as phytoremediation biomass waste or impregnated wood waste (i.e. wood impregnated with Cu, Cr, and As salts for preservation purposes).

The MEs concentrated in BCs show the potential of adding the practical value for char, which can be used in environmental pollution control technologies.

Subsequent subsections of this article describe the effects of pyrolysis conditions and the composition of feedstock on BCs properties. The role of syngenetic elements is also emphasized in the discussion.

Degradation phases of structural components of biomass

Wood is formed predominantly of lignocellulosic structural components with various infiltrated substances. The content and composition of structural components in ligneous plants affect the amount and quantity of pyrolysis products as well as the concentrations of infiltrated components, such as MEs. Extractive-free softwoods, in general, contain 70–75% holocellulose (the total carbohydrate portion includes true cellulose and hemicellulose), the total carbohydrate portion, including true cellulose and hemicelluloses, and 25–30% lignin. Extractive-free hardwoods contain about 75–82% holocellulose, and 18–25% lignin. The holocellulose of hardwoods usually contains more cellulose than that of softwoods, being considerably richer in pentosans rather than hexosans (as in the case of softwoods) (Stamm 1964). The lignin content depends on the strength of the bound fibers in plants, i.e. woody plant species are richer in lignin due to tightly bound fibers, while herbaceous plants have more loosely bound fibers and, consequently, lower lignin content. Up to 40% of bark is made of lignin. Lignin is the most stable component of the plant's matrix, due to its aromatic nature and tendency to condensation (Azarov *et al.* 1999). Lignin content, composition, and distribution varies among the taxa of trees. In different species of ligneous plants, the lignin content can range from 15 to 36% of the dry weight of the wood (Zobel & van Buijtenen 1989).

Lignin decomposes within the range of 280–500 °C. With the higher content of lignin in softwoods, they tend to give higher BC yields than hardwoods. Lignin from coniferous trees was found to be more stable than lignin of deciduous trees, and the former produces a larger percentage of BC per kg of input materials (Brebu & Vasile 2010).

Cellulose is the main component of ligneous biomass that consists of long polymers of cellulose chains. The aggregation of these chains provides a crystalline structure that is highly inert and inaccessible to some chemicals. Cellulose usually constitutes approximately 50% of dry wood. Cellulose mainly contributes to the production of tar, while lignin is primarily converted into BC and a small amount of water on pyrolysis. However, at a relatively low temperature, cellulose degrades into stable anhydrocellulose which yields high amounts of BC, but at higher temperatures (>350 °C), the cellulose decomposes to produce volatile products (Demirbas 2007).

Unlike cellulose, hemicellulose has a branched structure based on pentose and hexose sugars, while its molecular weight is low. Its content varies from 20 to 40%. Hemicellulose is most sensitive thermally and so decomposes faster, therefore hemicellulose conversion to biochar starts at 200 °C.

Primary pyrolysis involves the degradation of the three major components of wood and converting the biomass into liquid (bio-oil or bio-crude), solid (char/BC) and gaseous fractions (syn-gas). The thermal decomposition patterns of the lignocellulosic structures during the pyrolysis process are summarized in three distinct steps (Table 3).

The products of the primary reactions, e.g. char and volatiles, usually catalyze the secondary reactions. If the purpose is to maximize the char yields, low temperature and low heating rates should be applied (Brewer *et al.* 2009). The target product of slow pyrolysis is BC, but this

Table 3 | Thermal decomposition patterns of the lignocellulosic structures during the pyrolysis process (Demirbas & Arin 2007; Tripathi *et al.* 2016)

Type of process	**Heating and drying**	**Devolatilization**		**Secondary reactions**
Temperature	**100–200 °C**	**200–300 °C**	**200–650 °C**	**>650 °C**
Process description	In this phase, the wood temperature rises to 100 °C, moisture evaporates; the wood particle becomes chemically inert. At around 160 °C, dehydration is accomplished, elimination of volatiles, bond breakage, the formation of free radicals, carbonyl, carboxyl and hydroperoxide groups take place	In the devolatilization of the pyrolysis process, gas (carbon dioxide, carbon monoxide and condensable vapors) and tar species leave the solid matrix of the wood (hemicellulose). At the end of this stage, a porous biochar structure is left. At <300 °C, the governing process is the reduction in the degree of polymerization of cellulose. The thermal degradation of hemicellulose starts in the temperature regime of 200–260 °C. After decomposition of the polymer into soluble fragments, the conversion into monomers takes place which further degrade into volatile products. In comparison to cellulose, decomposition of hemicellulose results in more volatiles, less tar and biochar. At the beginning of the pyrolysis (250–300 °C) process, most of the volatiles are released at a rate 10 times higher than that of the next step	The degradation of cellulose increases and reaches a peak around 320 °C. At that temperature the reaction products are mainly volatiles. The degradation rate of lignin increases at temperatures higher than 320 °C. It is followed by a rapid increase in the carbon content of biochar. In the second step, at >300 °C, the formation of biochar, tar and gaseous products takes place. The major component of tar is levoglucosan that vaporizes and then degrades with the increasing temperature. When lignin is heated to >400–450 °C, only about 50% volatilizes and the rest remains as biochar	Tar produced during the decomposition of the wood can decompose further. Tar decomposition is suggested to be catalyzed by the solid matrix of the fuel, resulting in biochar creation on the pore walls.

is always obtained together with an almost equal percentage of liquid and gaseous products. Slow pyrolysis takes several hours to complete; the process is characterized by slower heating rates (1–20 °C/min), relatively long solid and vapor residence times (5–30 min) and, usually, a lower temperature than that maintained in the fast pyrolysis. If a low temperature (compared to the temperature used in the combustion process, around 1,273 K) is adopted, MEs do not volatilize and are accumulated in the solid pyrolysis fraction (char and ash). At the same time, a reduction in the weight and volume of the ME contaminated biomass is obtained (Lievens *et al.* 2008).

In summary, lignin content is higher in ligneous biomass in comparison to herbaceous plants and among the tree species softwoods in general they contain about 5% higher lignin content than hardwoods. Lignin is the most charring biomass component and biochar is the most abundant component in the products of ligneous biomass pyrolysis.

Cellulose mainly contributes to the production of tar, but at low temperatures it degrades to rather stable compounds, contributing to a high production of char. Therefore, softwoods with some of their morphological parts (e.g. bark) provide the best feedstock for BC production because of the lignin content. The MEs associated with lignin structures have a higher potential to be retained in the char.

Temperature effects

The pyrolysis temperature is of prime importance for the transfer of MEs from the feedstock to BC. The operating temperature of 400–600 °C was found to be adequate to disintegrate the organic structures of biomass, but low enough to avoid volatilization of the inorganics (Leijenhorst *et al.* 2016). It has been shown that alkali earth MEs (Mg, Ca), transition MEs (Cu, Fe, Cd, Ni, Co, Cr, Zn, Mn) and post-transition MEs (Pb, Al) predominantly remain on/in the BC. For the alkali MEs (K, Na), the entrainment of solid BC particles to pyrolysis oil is the primary pathway, although K and Na are also transported primarily by the reactions with volatiles.

The results of research by Lievens *et al.* (2008, 2009); Kan *et al.* (2016) and Kovacs & Szemmelveisz (2017) documented that MEs can be divided into those that are mainly released during decomposition stage (250–475 °C) (i.e. Sc, Cr, Ti, V, Ni from the transition ME group) and those that are mainly released at high temperatures (900–1,300 °C) (i.e. Zn, Cu, Mn from the transition MEs group), thus reflecting their different roles in organic structures. Based upon these findings, the major quantities of alkali MEs (K, Rb, Cs), transition elements (Zn, Cu, Mn) and high-field strength elements (Mo, Ag, Cd) can be expected to be found in the slow pyrolysis BC (~450 °C production temperature) (Table 4).

In summary, the temperature regime of degradation of all three wood components takes place and overlaps between 400 and 450 °C. Low temperature (400–450 °C), low heating rate (1–20 °C/min) and relatively long solid and vapor residence times (>30 min) are the conditions for maximizing the char yield and retaining metals (including Zn, Cu, Mn, Cd) in the char.

Table 4 | The release of chemical elements at two stages of pyrolysis (adapted after Thy *et al.* (2017) and Stals *et al.* (2010))

	The amount of release, %	
Type of element	**Decomposition of the organic matrix (250–475 °C)**	**After decomposition of the organic matrix, high temperature (900–1,300 °C)**
Anions (C, S, Cl)	75–90	
Alkali MEs (K, Rb, Cs)		85–90
Alkali earth elements: (Mg, Sr)	70–90	
Transition elements:		
Sc, Cr, Ti, V, Ni	75–80	
Zn, Cu, Mn		80–90
High-field strength elements:		
Y, Zr, Nb	60–70	
Mo, Ag, Cd		70–90
Rare earth elements: (La)	< 20	
Potentially volatile and toxic elements: (As, Se, Sb, Hg)	60–90	
EPA criteria pollutants:		
Cu, Cd, Tl, Pb		45–90
Cr, Ni	90	

Amounts and forms of metallic elements in BC

A thorough analysis of the composition of BC obtained from the feedstock of natural origin focused on the concentration of MEs in BC was performed by Hilber *et al.* (2017). In the case where the total concentration of the potentially toxic elements is low, the bioavailability and accessibility of toxic elements are low.

Table 5 shows the concentrations of MEs in BC produced from noncontaminated and contaminated feedstock. The sources of the feedstock contamination were wood processing (both mechanical and chemical) and ligneous-based waste materials. It can be stated that, first, BC obtained from non-polluted feedstock did not exceed the limiting values with respect to MEs' content specified by the European Biochar Certificate. A tendency of exceeding a limiting value is characteristic of BC (more exactly, a pyrogenic carbonaceous product) made of ligneous waste or another type of processed wood waste material in the case of all MEs (except Pb). The recommended limit values were exceeded 2–4 times which shows the potential of MEs to increase within the wood waste material.

As presented above, the direct involvement of BC components in natural flows could only increase the intensity of technogenic flows, however, it can be used in a safer way if used as a feedstock for the production of other products, where MEs as the constituent parts have beneficial roles, for example, in the production of adsorbents with specific features influenced by the presence of syngenetic MEs.

Second, BC obtained at the temperature of 400–450 °C demonstrated relatively higher concentrations of MEs (except for Cu) than BC produced at the temperature range of 700–750 °C. This is in agreement with the observations of Thy *et al.* (2017) where the largest amounts of MEs (Cu, Cd, Pb and Zn) evaporate at the temperature of 1,000 °C and above, and only Cr and Ni are characterized by more intense volatilization at a temperature of about 500 °C. Following the findings, in slow pyrolysis BC (~450 °C of the production temperature), the major quantities of MEs considered as potentially toxic (Zn, Cu, Cd) can be expected to be found.

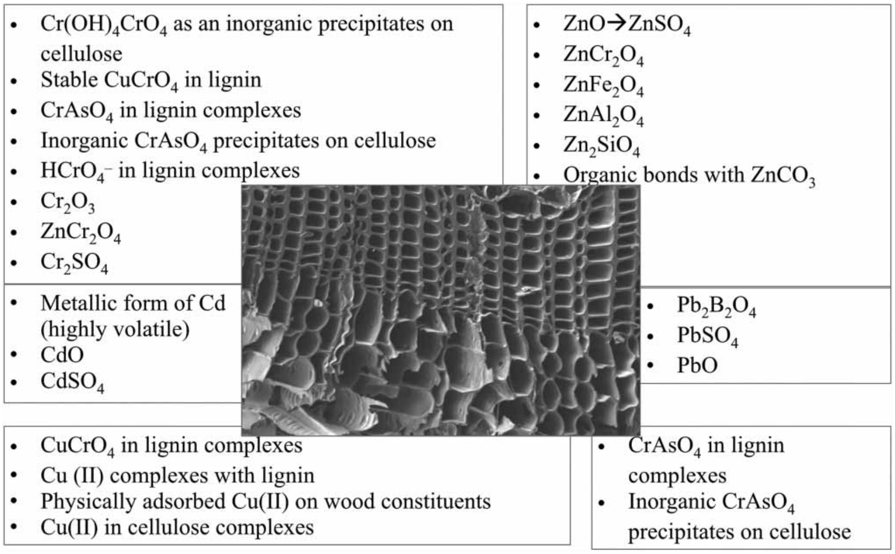
Figure 3 presents the major MEs (Zn, Pb, Hg, Ni, Cu, Cd, Cr, As) phases found in biochar after pyrolysis. The formation of MEs phases are highly dependent on the characteristics of MEs themselves and the behavior of them during thermal treatment. The behavior features of the most relevant MEs are described below.

Zn appears to be less volatile than Pb and Cd. Zn remains stable in mineral form, e.g. $ZnCr_2O_4$, $ZnFe_2O_4$, $ZnAl_2O_4$, Zn_2SiO_4 (Janse *et al.* 2000). Cellulose and hemicellulose degraded at 200 °C producing phenolic compounds and organic acids. Organic acids could react with Zn carbonate. At temperatures of 200–400 °C, cellulose, hemicellulose and other organic materials are decomposed. The volatilization of Zn is dependent on the type of thermally treated biomass.

During pyrolysis, the stable form of Pb is the solid sulphide. PbO appears in solid form and its presence in

Table 5 | The concentrations of MEs (mg/kg in dry weight) in BC produced from ligneous biomass from different sources

Type of biochar feedstock	Production temperature, °C	Pb	Cu	Zn	Cd	Cr	Ni	Refs
Wood control	400–450	0.26–6.22	2.97–85.5	20.9–252	0.04–0.27	0.62–25.8	0.83–17.8	Baltrėnaitė *et al.* (2016)
Wood control	700–750	0.55–0.58	3.71–8.86	10.7–17.9	0.01–0.90	1.02–7.47	1.49–10.8	Baltrėnaitė *et al.* (2016)
Processed wood and wood waste	400–450	8.07–39.3	22.4–382	118–1,269	0.16–6.32	24.3–227	17.9–88.1	Usevičiūtė & Baltrėnaitė (2019)
Processed wood and wood waste	700–750	9.03–33.1	32.7–452	141–1,209	0.02–0.18	17.2–97.1	18.3–52.7	Baltrėnaitė *et al.* (2016)
Wood from contaminated area	450	1.5–1.8	18.1–21.7	50.6–286.5	0.017–0.029	12.6–13.2	6.5–9.3	Chemerys & Baltrėnaitė (2018)
Basic quality biochar	–	150	100	400	1.50	90	50.0	EBC (2012)
Premium quality biochar	–	120	100	400	1.00	80	30.0	EBC (2012)



- $Cr(OH)_4CrO_4$ as an inorganic precipitates on cellulose
- Stable $CuCrO_4$ in lignin
- $CrAsO_4$ in lignin complexes
- Inorganic $CrAsO_4$ precipitates on cellulose
- $HCrO_4^-$ in lignin complexes
- Cr_2O_3
- $ZnCr_2O_4$
- Cr_2SO_4

- $ZnO \rightarrow ZnSO_4$
- $ZnCr_2O_4$
- $ZnFe_2O_4$
- $ZnAl_2O_4$
- Zn_2SiO_4
- Organic bonds with $ZnCO_3$

- Metallic form of Cd (highly volatile)
- CdO
- $CdSO_4$

- $Pb_2B_2O_4$
- $PbSO_4$
- PbO

- $CuCrO_4$ in lignin complexes
- Cu (II) complexes with lignin
- Physically adsorbed Cu(II) on wood constituents
- Cu(II) in cellulose complexes

- $CrAsO_4$ in lignin complexes
- Inorganic $CrAsO_4$ precipitates on cellulose

Figure 3 | List of metallic element phases which are found in biochar produced at a temperature of about 750 °C. The image in the figure presents the structural view (magnification 300×) of biochar.

liquid form is expected above the char oxidation zone, where the temperature exceeds the melting point of PbO (887 °C). These forms of $Pb_2B_2O_4$ and $PbSO_4$ were found in the solid pyrolysis product. The higher pyrolysis temperature promoted the transformation of amorphous Fe/Mn hydroxides into more crystalline forms (Janse *et al.* 2000). Lievens *et al.* (2008) concluded that Pb compounds are less receptive to volatilization at pyrolysis temperatures of 400 °C than Cd compounds.

Following Dell'Antonia (2013), Ni is a nonvolatile ME under pyrolysis conditions up to 705 °C. Its emissions can be observed only if the pyrolysis reactor used releases ME-bearing particles due to high gas velocities. With respect to release, Cu does not pose any problems. When the pyrolysis temperatures were increased to 200 °C, the organic part of biomass decomposed and Cu formed a very stable complex with organic matrixes. However, in the temperature range of 300–500 °C, thermally treated biomass' aromaticity increased and Cu could not form the Cu-organic complexes (Janse *et al.* 2000). Lievens *et al.* (2008) concluded that Cu compounds are less volatile at pyrolysis temperatures of 400 °C than Cd compounds.

Cadmium compounds were reduced to Cd^0, which volatilized at temperatures higher than 600 °C. The thermodynamically stable chemical forms of Cd (sulphide, CdS, and chloride, $CdCl_2$) were found. The most significant result refers to volatilization: Cd entirely vaporizes in the form of vapor Cd and, in a smaller quantity, as the chloride $CdCl_2$. The gaseous species can condense on the surface of particles transported in the fumes, therefore, Cd and $CdCl_2$ are likely to be found in the ashes as $CdSO_4$ (Janse *et al.* 2000).

Dell'Antonia (2013) concluded that during the pyrolysis of sewage sludge at $T > 600$ °C the transfer of Cd to the off-gas is expected. On heating at temperatures of 200–400 °C, the ligneous biomass decomposes and produces organic matter that can easily bond to Cd. When the pyrolysis temperature increased to 500 °C, the organic matter in biomass turned to more aromatic compounds and could not bond to Cd. Lievens *et al.* (2008) found that the Cd compounds are more sensitive to volatilization at pyrolysis temperatures of 400 °C than Cu, Pb and Zn compounds. The volatilization of Cd increases with increases in temperature. It has been found that a certain amount of Cr is released from the pyrolysis reactor gaseous CrO_2Cl_2, or as solid Cr_2O_3 and $ZnCr_2O_4$.

The final stable species are $ZnCr_2O_4$ and Cr_2SO_4. The Cr stays in the solid form, irrespective of the conditions of composition and temperature. No gaseous species are predicted for Cr (Mènard *et al.* 2006). As concluded by Van den Broeck *et al.* (1997) from the speciation experiments, it appears that the major part of Cr in the pyrolysis residues is bound to carbonate, oxidized wood components and organic matter. A non-negligible amount of Cr is found in the exchangeable fraction.

Temperature and residence time highly affect the amount of As released during the pyrolysis. Helsen *et al.* (2013) carried out a thermogravimetric study of the hydrated Cr arsenate and revealed that thermal degradation results in the development of solid Cr_2O_3 and gaseous O_2, H_2O and As_4O_6, also indicating that As $(^{5+})$ is reduced to As $(^{3+})$ because As_2O_3 is volatilized at a temperature below 200 °C. Char and pyrolysis vapors form a reducing environment, thereby influencing the behavior of MEs oxides.

Zhurinsh *et al.* (2005) found that, in pyrolysis of CCA-treated wood, As losses depend on the final temperature of pyrolysis; its content in the condensed pyrolysis products reaches only 2% from the total As amount, while As evaporation in the batch process begins under 200 °C.

To summarize, MEs are present in inorganic precipitates on cellulose (in the case of Cr, Cu), lignin (Cr, Cu) or in the form of oxides (for Cr, Cd, Cu, Zn, Pb), sulphates (Cd, Pb, Cr, Zn) or sulphides (for Pb). A reduction in the weight and volume of the MEs contaminated biomass is obtained, therefore, the concentration of the MEs increases. Low pyrolysis temperatures keep larger amounts of organic matter which results in higher amounts of organically bound MEs present (e.g. Zn, Cr). These conditions are favorable for less volatile MEs to be kept in the char (e.g. Pb with a melting point >887 °C, Ni, Cd which volatilize at temperatures higher than 600 °C). Most of the As and a large percentage of the Hg are released during low temperature pyrolysis because of their low temperature of volatilization, such as <200 and <500 °C respectively. The MEs stability in BC were determined during leachability studies. Low moisture content and higher oxygen content in the feedstock (about 5%) must be kept to keep BC yield higher. Keeping maximum reducing conditions in the reactor can result in 2–3 times higher amount of MEs in the BC.

Retention and leachability of metallic elements in biochar

Several studies have demonstrated that MEs present in the feedstock are stabilized during the production of BC (Lu *et al.* 2012). Based on the comparison of two leaching procedures (ASTM method vs BSI method) used to study charcoal ME content in the solution, Helsen *et al.* (1997) suggested that there was a stronger connection between Cr and the BC compared to that in the feedstock (i.e. CCA-treated wood).

According to Stals *et al.* (2010), with the increasing processing temperatures the weakest bound and chemically less stable compounds were not retained in the BC, analyses of MEs (Cd, Pb and Zn) presence in the EDTA extract from the chars produced at different pyrolysis temperatures (350, 450, and 550 °C) revealed that ME compounds are more resistant to lixiviation at 550 °C. According to Lu *et al.* (2011), the stabilization of MEs in the sludge-derived BC is associated with the pyrolysis process.

The amounts of the six examined MEs (Zn, Cr, Ni, Cu, Cd and Pb) washed out from various types of the BC found on railway sleepers were not considerable. Their amount compared to the original amount of the elements of various types of BC ranged from 0.07 to 11.28% of the amount originally present in the sleepers (Usevičiūtė & Baltrėnaitė 2019).

As found by Mancinelli *et al.* (2016), the most suitable temperature for reducing MEs leachability during pyrolysis depends on the MEs in question. The temperature of 450 °C was especially effective in stabilizing Cr and Ni in the BC as these MEs did not tend to leach. According to Lievens *et al.* (2009), it is important to note that, due to the low operating temperature, MEs are enriched in the BC/ash fraction of various pyrolysis products. This suggests that pyrolysis can be a means of reducing MEs (Zn, Pb, Cd, Cr, Ni, Cu) availability in contaminated feedstock.

Other factors (residence time, heat flux, thermal conductivity, reactor matrixes)

This research team investigated the influence of the particles' shape (spherical, cylindrical and flat) at the surface temperature of 550 °C. They found that spherical particles have the shortest conversion time, based on the higher surface/volume ratio. However, for small particle diameters (smaller than 20 mm), the rate of the reaction was dominant and various particles' shapes had a nearly equal time of conversion (Encinar *et al.* 2000).

The solid heat carrier in the pyrolysis reactor can affect the distribution of MEs in the pyrolysis products. According to Lievens *et al.* (2008), the sand matrix used in the pyrolysis reactor promoted the retention of Cd at 500 and 600 °C, and Cu at 600 °C, in the char/ash obtained from Maatheide birch contaminated by MEs. At the temperature of 400 °C, the volatilization of the compounds of MEs (Cd, Cu, Pb, and Zn) was not affected by various kinds of the solid heat matrixes, sand or fumed silica, while the solid heat matrix retains Cu and Pb.

A very large amount of moisture reduces the heating rate and, as a result, more time is required for achieving the pyrolysis temperature. In the pyrolysis of wood with 5 and 20% moisture content, it was found that the biomass with a smaller amount of moisture caused the formation of a large amount of residue (Fang *et al.* 2014). Demirbas (2007) found that the increase in the moisture content in wood reduced the BC yield. The presence of oxygen is another factor, influencing the reactivity of biomass during pyrolysis, which affects the pyrolysis product yield and its composition (Gani & Naruse 2007).

Comparing mass percentage of MEs in the bottom ash from incineration and the pyrolysis of the contaminated biomass (i.e. hyperaccumulators), Lu *et al.* (2012) found that volatile MEs (e.g. Cd, Pb and Zn) tend to accumulate in the bottom ash if the reducing conditions were used. The recoveries in the bottom ash of MEs, such as Cd, Pb and Zn, were about 2–3 times smaller under incinerations condition than those observed under pyrolysis conditions at 550 °C. Therefore, if the transfer of MEs (e.g. Cd, Zn, Pb) to the gaseous phase should be avoided, an oxidizing atmosphere should not be used.

The thermal conductivity of wood varies, depending on the direction of the heat flow with respect to the grain, as well as with the temperature, density, and moisture content. The heat transfer takes place via the complex interaction between the transfer mechanisms, such as conduction, convection, and radiation. However, when the direction of gas flow is perpendicular to the heat flux direction, the cooling effect will not occur. Grain orientation in wood needs to be taken into account due to the resulting anisotropicity (Mènard *et al.* 2006).

Effect on equilibrium, kinetics, rate limiting factors and thermodynamics during adsorption of others MEs

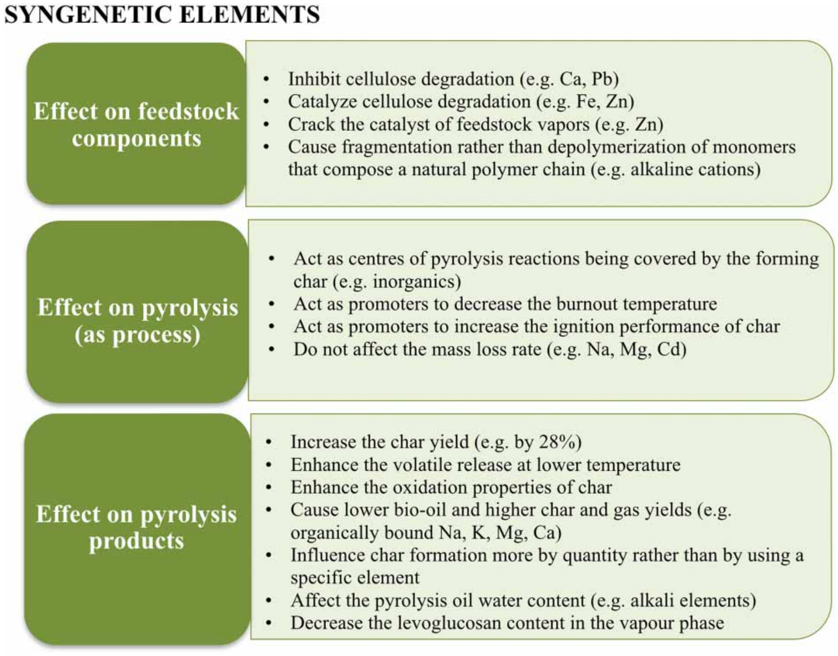
Information on syngenetically modified biochar and impact on adsorption of MEs is scarce while more studies are available on artificially modified BC. Artificially added metals to BC are referred to chemical modification of BC by metal salts to produce BC-based functional materials (Wu *et al.* 2017; Wei *et al.* 2018). It was determined that the chemically modified BCs have a better adsorption effect on contaminants in wastewater. These types of BCs showed high affinity for MEs. Although both Freundlich and Langmuir isotherm models (Xia *et al.* 2016) fitted the adsorption data better than other equilibrium models, there are observations which indicate that syngenetic-MEs-modified BC may precondition the double layer adsorption of MEs facilitated by varying orientation of solutes (Baltrėnaitė-Gedienė *et al.* submitted). The results of adsorption kinetics mostly followed the pseudo-second-order model, which is based on the assumption that the rate-limiting step may be chemical sorption involving valence forces through the sharing or exchange of electrons between contaminants and BC (Ho & Mckay 1999).

Based on the results of the thermodynamic studies, Van Vinh *et al.* (2015) found that Zn-modified BC exhibited the spontaneous and exothermic nature of the As(III) adsorption process (indicated by the negative free energy (ΔG°) value and positive ΔH° value (31.10 kJ/mol), respectively). The positive values of ΔS° (0.141 kJ/mol/K) showed an increase in randomness at the solid/solution interface during the adsorption of As(III) on modified BC.

INFLUENCE OF SYNGENETIC ELEMENTS ON PYROLYSIS

In the previous sections, the changes in the ME forms depending on the pyrolysis conditions were discussed. On the other hand, MEs have an impact on pyrolysis conditions as well. The typical behavior of syngenetic elements, influencing the feedstock, pyrolysis and pyrolysis products, are shown in Figure 4.

Some of the introduced MEs ions support higher temperature of cellulose decomposition: the top temperatures of



SYNGENETIC ELEMENTS

Effect on feedstock components

- Inhibit cellulose degradation (e.g. Ca, Pb)
- Catalyze cellulose degradation (e.g. Fe, Zn)
- Crack the catalyst of feedstock vapors (e.g. Zn)
- Cause fragmentation rather than depolymerization of monomers that compose a natural polymer chain (e.g. alkaline cations)

Effect on pyrolysis (as process)

- Act as centres of pyrolysis reactions being covered by the forming char (e.g. inorganics)
- Act as promoters to decrease the burnout temperature
- Act as promoters to increase the ignition performance of char
- Do not affect the mass loss rate (e.g. Na, Mg, Cd)

Effect on pyrolysis products

- Increase the char yield (e.g. by 28%)
- Enhance the volatile release at lower temperature
- Enhance the oxidation properties of char
- Cause lower bio-oil and higher char and gas yields (e.g. organically bound Na, K, Mg, Ca)
- Influence char formation more by quantity rather than by using a specific element
- Affect the pyrolysis oil water content (e.g. alkali elements)
- Decrease the levoglucosan content in the vapour phase

Figure 4 | The effect of syngenetic elements on the feedstock, pyrolysis and pyrolysis products.

cellulose decomposition are moved to a higher zone, when the MEs of the ligneous biomass are washed out, and to the lower temperature zones, when approximately 2% (by weight) ash is introduced to demineralized wood (Meyer *et al.* 2012): Ca^{2+} – (increase by 4 °C), Zn^{2+} – (decrease by 4 °C), Fe^{3+} – (decrease by 9 °C), Pb^{2+} – (increase by 1 °C). Fe and Zn tend to catalyze the cellulose degradation, while Ca and Pb inhibit it by moving the top temperature to higher temperature ranges (Meyer *et al.* 2012).

Inorganics not only affect BC and gas formation, but also influence the distribution of compounds forming the biooil and tars. The formation of levoglucosan (LG) (the key product of low volatility that forms tars) was found to be acid-catalyzed degradation of cellulose. The rate of cellulose-to-LG conversion was decreased when MEs were added to the feedstock, while the cellulose-to-LG conversion rate ranged between 29% (Na) and 62% (Mg).

Ash significantly increases the release of volatile BC at lower temperatures (300–350 °C) of BC pyrolysis. Both the primary and secondary reactions of volatile products are affected by the presence of inorganics (Zaror *et al.* 1985; Antal & Varhegyi 1995), and the heterogeneously catalyzed oxidation of volatiles can explain the weight loss increase in the presence of ash (Loffler *et al.* 2002). DeGroot & Shafizadeh (1983) concluded that the catalytic and inhibiting properties of inorganics affected the oxidation properties of BC, but not its structure.

Koppolu *et al.* (2004) found that BC yields are affected by the ME used to dope the feedstock, but no variations were observed depending on the type of salt (acetate or citrate) used for its preparation. The char yields can be ranked in increasing order as follows: Cu < Co < Zn < Ni < Cr < untreated feedstock. Koppolu *et al.* (2004) found a difference in the amounts of char produced from a feedstock impregnated with different MEs. The average char yield from the feedstock doped by Zn acetate (21.2%) was the highest, followed by Cu acetate (18.05%) and Ni acetate (17.15%). Hence, using different MEs changed BC yields by 4.05% at most.

Due to the presence of alkaline cations in the process of fast pyrolysis of biomass, the fragmentation rather than depolymerization of the monomers that compose the natural polymer chains can be observed (Mohan *et al.* 2006). The presence of intrinsic or ion-exchanged inorganic materials (e.g. Ca and K) in biomass catalyzes the pyrolysis reactions such as biomass decomposition and the BC forming reactions (Yaman 2004).

In the work of Stals *et al.* (2010), the lower water content of the bio-oil obtained using a hot-gas filter accounted for the decreased char particles' presence and the related alkali ME load, thus avoiding alkali ME catalysis effects on the breakdown of molecules from the condensable form into smaller ones (Fahmi *et al.* 2008).

In the process of pyrolysis, inorganics act as centers of the pyrolysis reactions and are covered by the forming char. Furthermore, a higher content of Ca, K, and Mg in the original feedstock could accelerate the pyrolytic reactions of the lignocellulosic components and the carbonization irrespective of the pyrolysis temperature, since lower oxygen and higher carbon content in the BC from *Acacia saligna* produced at 380 °C was detected compared to that obtained from sawdust at 450 °C (Agblevor & Besler 1996).

Raveendran *et al.* (1995) investigated the influence of mineral matter on the pyrolysis characteristics of wood and twelve other types of biomass. They found that demineralization increased liquid yields and decreased gas yields for all the biomass samples studied.

Kinata *et al.* (2012) concluded that treating wood with ME ions has a significant effect on its thermal degradation process. TGA and the pyrolysis experiment have shown that the presence of Cr, Cu, B in the salts of CCB results in the production of low tar and high charcoal yields.

Meyer *et al.* (2012) found that the changes in the properties of ligneous biomass and the cellulose, which is the main cell wall constituent of ligneous biomass, can bind more MEs than lignin alone. This implies for higher content of MEs to be kept in pyrolyzed biomass product which have not yet undergone thermal stages of cellulose destruction. The ME binding capacity of ligneous constituents is higher in the case of Pb and Cd than in the case of the alkali earth and alkaline MEs. The presence of Zn, Pb, Ca and Fe ions slightly changed the disintegration temperature of cellulose, while Cd, Na and Mg ions did not affect the mass loss rate during pyrolysis. The BC formation was affected mainly by the quantity rather than by the quality of the introduced ME ions. The LG yield of ligneous biomass pyrolysis was affected by the type, rather than by the total amount of the added MEs. Both ash and the added MEs acted as promoters during BC combustion by reducing the burnout temperature and increasing the ignition process of BC.

According to Beliy & Udoratina (2014), in the context of using pyrolysis as a preliminary stage of gasification, the use of Zn and Sn chlorides as catalysts seems to be the best solution because it greatly reduces the thermal degradation onset temperature and the activation energy, as well as increasing the BC yield. Sharma *et al.* (2015) described the main ways in which catalysts affect the pyrolysis processes. The degradation temperature of ligneous biomass constituents may significantly decrease when a catalyst is used. Catalysts promote the formation of coke due to dehydration reactions (mainly due to the high acidity of catalysts).

Tripathi *et al.* (2016) concluded that the acidic catalysts increase the BC yield and reduce the tar production, while the basic catalysts usually reduce the BC yield. Acidic catalysts, such as $ZnCl_2$ and ZnO, not only stimulate the BC production but also improve its characteristics. In summary, MEs presence in biomass has direct effects on pyrolysis products and indirect effects by changing pyrolysis conditions and, therefore, they affect the formation of the final pyrolysis product quality.

In relation to the BC properties for enhanced adsorption capacity, the following MEs effects are of primary interest. For example, enhancing the oxidation properties of BC can: (i) favor formation of oxygen-containing functional groups, which are the key factors for complexation reactions during adsorption; (ii) decrease the burnout temperature limiting the volatilization of MEs; (iii) enhance the volatile release at lower temperatures that can favor the development of porosity; (iv) modify the catalyzing effect on cellulose degradation (known for Fe and Zn); (v) increase of BC yield that favors retention of MEs originally precipitated in the cellulose.

The Fe and Zn catalyze the cellulose degradation by reducing degradation temperature by 4–9 °C, while Pb and Ca shift the cellulose degradation temperature to higher temperatures by 1–4 °C. Some MEs were put in the following sequence according to their impact on BC yields: Zn > Cu > Ni. It is interesting that the temperature of pyrolysis and presence of MEs in the feedstock have reciprocal effects. The lower temperature (400–450 °C), low heating rate (1–20 °C/min) and relatively long solid and vapor residence times (>30 min) are the conditions for maximizing the char yield and keeping MEs (including Zn, Cu, Mn, Cd) in the biochar (as presented above under 'Temperature effects'). On the other hand, the presence of MEs in the feedstock has impacts on the temperature of the biomass (namely, its component, cellulose) decomposition, e.g. Zn tends to catalyze (decreasing the temperature by 4 °C), while Pb suspends (increasing the temperature by 1 °C) the cellulose degradation and, therefore, increasing and decreasing, respectively, the kinetics of the pyrolysis reaction (as discussed later in this paper). High concentrations of MEs can accelerate the pyrolytic reactions and carbonization irrespective of the pyrolysis temperatures (Agblevor & Besler 1996).

IMPACT OF SYNGENETIC ELEMENTS ON THE ADSORBING CAPACITY OF BIOCHAR – FIRST FINDINGS

The changes in ligneous biomass composition undoubtedly have an influence on ligneous biomass products. Could these changes improve the physical or chemical characteristics of ligneous biomass products which are important in adsorption of water contaminants? Can these changes be associated with syngenetically accumulated MEs? Can the syngenetic elements improve the properties of ligneous biomass products or even enhance the environmental performance of the products towards removal of water pollutants?

The answers to these questions are provided with the findings presented in this paper. The authors clarified the effects of syngenetic MEs on ligneous biomass on the adsorptive properties of BCs, produced from lignin with syngenetically accumulated MEs (Cu, Cr, Pb, Zn, Ni, Cd).

Twenty test specimens were produced from lignin under two temperature regimes (400 and 700 °C) and pyrolysis durations (1, 2 and 4 h). The physico-chemical characteristics such as concentration of MEs (Cu, Cr, Zn, Pb, Ni, Cd), CEC, pH, PZC, and ash content were analyzed in the samples following methodologies described by Nguyen & Lehmann (2009) and Baltrėnaitė *et al.* (2017).

To evaluate the level of MEs concentration in the ligneous biomass, the concentration coefficients for MEs in the studied feedstock were calculated following the methods described in Markert *et al.* (2012) and Krastinytė *et al.* (2013) and using the background concentrations obtained by the authors from previous studies (Baltrėnaitė *et al.* 2012). They found that the concentration coefficients for MEs reached the value of 1.27 in the case of Pb, Cr and Zn; but they were higher than three in the case of Ni and Mn and exceeded 14 in the case of Cu. The values of concentration coefficients exceeding one indicates that the concentrations of MEs were especially pronounced in the case of Cu present in lignin and are higher than the background levels of MEs in ligneous materials.

The concentration coefficients for potentially toxic elements in the lignin indicating the elevation of elements over the background concentrations in biomass were calculated and found to be in the following order: Cu (14.28) > Ni (3.73) > Mn (3.3) > Cr (1.74) > Zn (1.65) > Pb (1.27).

The results presented in Table 6 show the concentrations of MEs determined in BC, which was produced from lignin feedstock at two temperature regimes. As expected, MEs concentration increased in most of the cases (except a slight reduction of Ni in BC at 450 °C and no difference for Cd in BC at 700 °C).

These facts separated the studied MEs into two groups:

1. The first group included MEs (Pb, Cu, Cr, Zn) where concentrations increased with the increase of the production temperature.

Table 6 | Concentration (mg/kg of dry weight, mean value ±SD, $n = 3$–4) of potentially toxic elements in BCs produced at difference temperature regimes and the concentration level of MEs in BCs as the ratio of concentration in the feedstock and the BCs produced at a particular temperature

	Pb	Cu	Ni	Cr	Zn	Cd
At 450 °C	5.54 ± 2.23	127.95 ± 23.4	7.21 ± 2.56	17.82 ± 6.01	224.0 ± 41.6	0.16 ± 0.14
Concentration level	×2.4	×1.3	×0.8	×1.5	×1.5	×3.5
At 700 °C	7.89 ± 1.32	185.53 ± 36.86	15.23 ± 9.23	28.01 ± 4.35	397.84 ± 74.19	0.05 ± 0.02
Concentration level	×3.5	×1.9	×1.6	×2.3	×2.7	×1.0

2. The second group included Cd which concentrated more in BC produced at 450 °C than in the BCs produced at 700 °C because Cd is the most volatile among the studied MEs (the boiling point of Cd is 767 °C).

Therefore, it can be concluded that most of the investigated MEs were concentrated in the BCs. The higher concentrations of MEs were typical in BC produced at 700–750 °C, but higher concentrations of MEs (including the more volatile elements) were retained in BCs at 450 °C. These findings were in line with the results obtained by Thy *et al.* (2017).

With the author's objective to study the effects of the syngenetic MEs on the adsorptive characteristics of BC, the key properties, including cation exchange capacity (CEC) (Beesley *et al.* 2015; Hilber *et al.* 2017) and point of zero charge (PZC), were analyzed because of their importance in studying the adsorption of water pollutants. The CEC indicates the level of how cations can be retained on the material of interest. The PZC is typically the pH value at which a studied material submerged in the solution exhibits zero net electrical charge on the surface. These parameters are relevant indicators of materials to quantify adsorptive capacities (Wongrod *et al.* 2019).

As shown in Table 7, in comparison to the reference BC, lignin BC was characteristic for higher MEs concentrations as well as higher amount of ash content and higher CEC value. The CEC value was higher in more than three times, the one for ash content – in about seven times. The mean concentrations of MEs in lignin BC were higher than in reference BCs by four times for Pb, 70 times for Cu, 10 times for Ni, 38 times for Cr, 1.7 times for Mn, 3.5 times for Zn and 3.8 times for Cd. The results show that lignin BC had higher-ash BCs which also had higher inorganic content that is typically formed from inorganic elements including MEs. The findings of higher MEs concentration, ash content and CEC values have correlative value (Figure 5) and confirmation of MEs influence on higher CEC level were also important. Our findings that high-ash biomass-derived BCs were characteristic for higher CEC values, were in agreement with those of Lehmann *et al.* (2011). The MEs impact on higher CEC values of BCs could be explained by the fact that much of MEs, which were present in BCs feedstock and in the BCs are in the form of oxides (Hilber *et al.* 2017) and might be replaced further (e.g. during pyrolysis) by the elements of lower charge and can increase the BCs' negative charge, therefore increasing CEC (Beesley *et al.* 2015). This phenomenon was explained for soil CEC by Birkeland (1999). The stronger correlation between Cu and CEC suggests the stronger influence of concentration level on CEC value and supports the hypothesis that MEs have impacts on the CEC as adsorptive characteristics (Figure 5). The supporting data were provided by Mohamed *et al.* (2017) who found that the increase of CEC in metal contaminated and BC amended soil is due to increased surface area and porosity.

Table 7 | Characterization of lignin and reference biochar in relation to syngenetic approach (mean values ±standard error)

Parameter	Lignin BC	Reference BC
Cation exchange capacity, $\mathrm{mmol_c/kg}$	117.5 ± 18.5	31.8 ± 2.7
Ash content, %	23.0 ± 2.2	2.9 ± 0.2
Pb, mg/kg DW	6.7 ± 0.6	1.6 ± 0.2
Cu, mg/kg DW	243.8 ± 90.4	3.4 ± 0.3
Ni, mg/kg DW	11.2 ± 2.2	1.1 ± 0.1
Cr, mg/kg DW	22.9 ± 2.1	0.6 ± 0.1
Mn, mg/kg DW	293.4 ± 26.6	169.2 ± 15
Zn, mg/kg DW	310.9 ± 31	91.1 ± 11.9
Cd, mg/kg DW	0.105 ± 0.032	0.027 ± 0.004

The other adsorption-relevant factor was the 'Point Zero Charge' (PZC) value which is considered as the total surface charge of the materials and is determined as the point on the pH scale where the sum of anion and cation exchanges are in equilibrium (Fiol & Villaescusa 2009). As the oxidation of the material increase, the PZC appears at lower pH values (Lu *et al.* 2013). PZC was determined by the salt addition method described by Mahmood *et al.* (2011). The ΔpH (the difference between final and initial pH) values were plotted against the initial values of pH and the PZC was determined as the initial pH at which ΔpH was zero. The ΔpH values varied based upon the biochar production temperatures, residence times and biochar types as presented in Figure 6.

The larger PZC values corresponded to the case of reference wood BCs (8.11) rather than to lignin-based BCs (<8). They were also larger for the BCs of 4-hour production (8.12) than for the BCs of 1- or 2-hour production (<8) and for the temperature of 700 °C (8.13) than for 450 °C

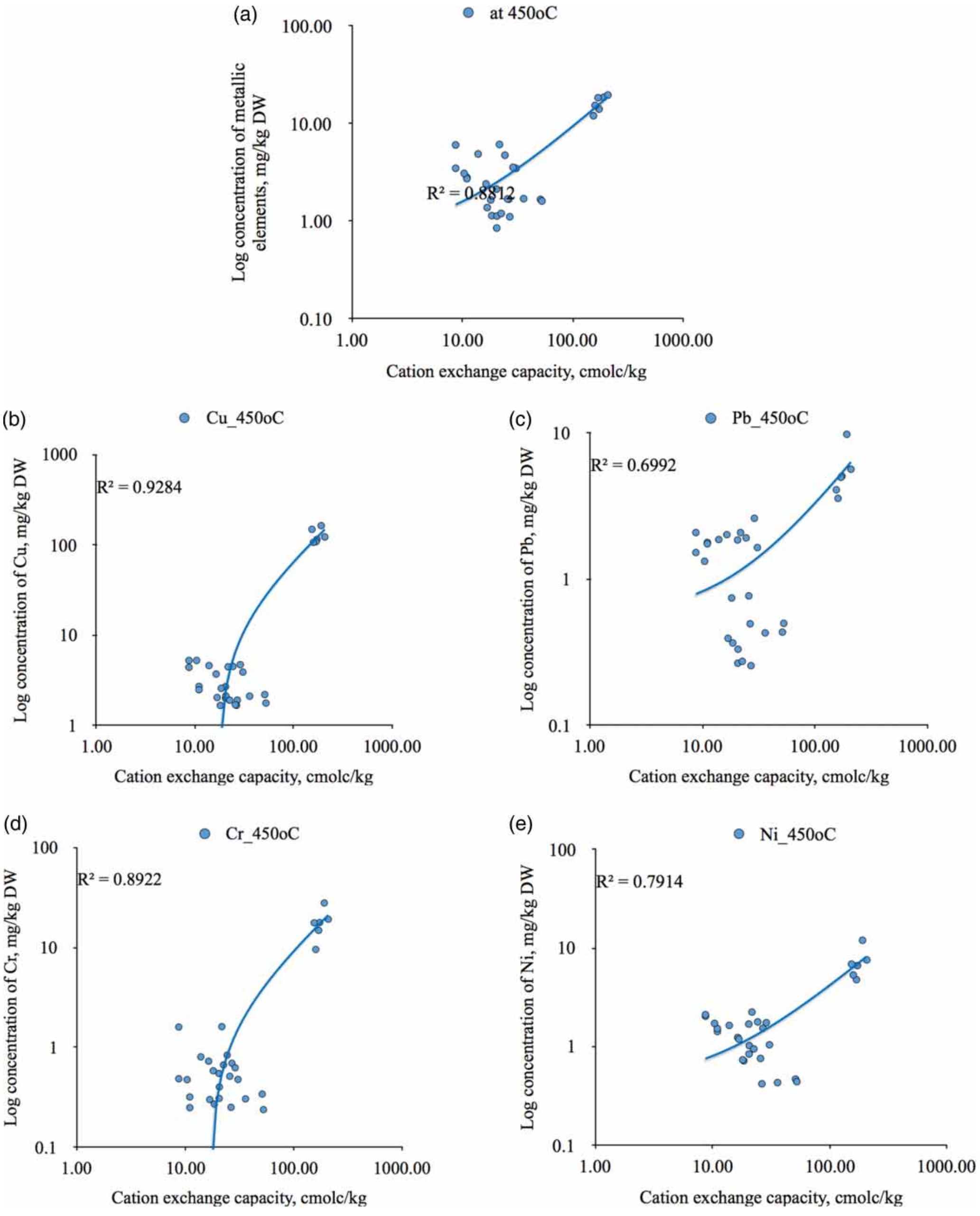


Figure 5 | Logarithmic relationship between cation exchange capacity and chemical element concentration in biochar: (a) for all chemical elements at 450 °C; (b) for Cu at 450 °C; (c) for Pb at 450 °C; (d) for Cr at 450 °C; (e) for Ni at 450 °C.

(<8). The high PZC values indicate that the adsorbent would be more positively charged and, in contrast, lower PZC values indicated that the adsorbent would be more negatively charged and therefore would attract more positively charged ions (Tang *et al.* 2019; Wongrod *et al.* 2019). In this study the BCs that have more potential to adsorb cationogenic elements (including studied MEs) were BCs obtained from lignin BCs under the pyrolysis conditions for 1 or 2 hours at 450 °C (Figure 6).

The preliminary experimental results reported in this paper documented that increased concentrations of MEs in lignocellulosic waste (lignin) are highly correlated with

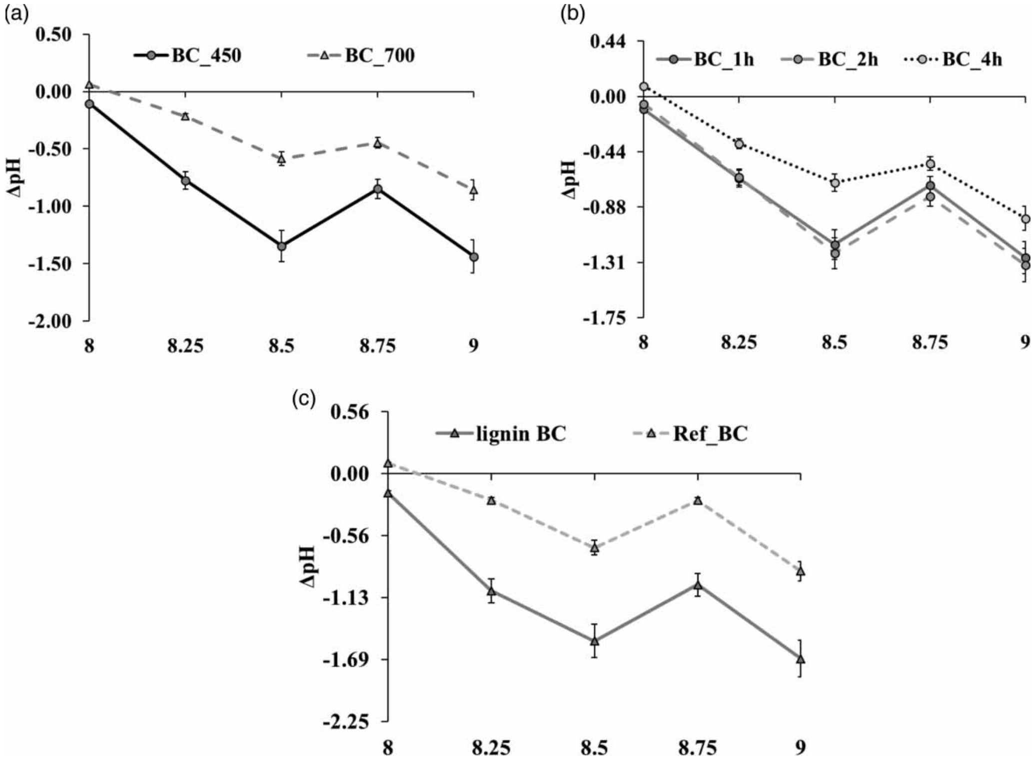


Figure 6 | The ΔpH versus initial pH of biochar produced: (a) at 450 and 700 °C; (b) at residence times of 1, 2 and 4 h; (c) for lignin BCs and reference wood BCs.

higher CEC and PZC of the produced BCs, which are important parameters to determine the adsorption capacity of BCs as well as other adsorbents.

There are at least two mechanistic dimensions involved in the dynamics of BC adsorption. First, MEs as inorganics are the principal components of the biomass ash. Increases in MEs concentration in biomass leads to higher portions of ash. Higher-ash mass leads to increases in CEC values because MEs in BCs are mostly in the form of oxides and can be easily replaced by elements of lower charge (Lehmann *et al.* 2011) and, therefore, increase the negative charge of BCs (Beesley *et al.* 2015; Hilber *et al.* 2017).

Second, the MEs have a potential to influence the pHpzc expressed in deltapH. The pHpzc allows one to hypothesize the ionization of functional groups and their interactions with MEs in solution (Bakshi *et al.* 2018). In this study BCs with higher MEs content had lower PZC values and they were able to form more negative surface charge which showed higher ability to adsorb cationogenic elements. The results of both indicators, CEC and PZC, support the potential of enhanced adsorption capacity for BCs produced from biomass with higher MEs and the syngenetic origin of MEs increases the potential of BCs with higher adsorptive features.

PRACTICAL APPLICATIONS AND FUTURE RESEARCH PERSPECTIVES

Some of the United Nations' efforts focus on working on ensuring availability and sustainable management of water, however, under the conditions of intensive technogenesis, the technophilicity of metallic elements and their entrance into water bodies increases. The need for clean drinking water and sustainable wastewater treatment facilities is high, especially in developing countries.

This research documented a new pathway of MEs entrance into biomass, therefore leading to nature-anthropogenized impacts of MEs on properties of biomass and its products.

From a practical perspective, the enhancement of BCs adsorption capacity by means of syngenetic MEs showed potential to use MEs affected BCs for adsorption purposes and increased economic benefits from the use MEs contaminated biomass. For example, instead of utilizing the MEs contaminated ligneous biomass, the products, such as BCs, with MEs impacted characteristics can be produced for removal of ME contaminants from polluted water. Further research of syngenetic MEs should be focused on other syngenetic MEs and their impacts on ligneous BCs characteristics.

The findings of this research support the observation that with increasing technogenesis, the syngenetically formed MEs will increasingly contribute to changes in the characteristics of biomass and its products, including BCs.

CONCLUSIONS

The BCs from ligneous plants are useful organic products for syngenetic elements to manifest their beneficial effects. At the pyrolysis temperature of 400–450 °C, most of the potentially toxic elements (including Zn, Cu, Mn, Cd) are retained within the BCs, and most of them are in the metal oxide forms, which in turn have an influence on BCs adsorptive properties. The increased concentrations of MEs in lignocellulosic wastes are highly correlated with higher CEC and PZC of their BCs, which results in higher adsorptive capacities of BCs. Among the studied MEs, syngenetic Cu was determined to correlate strongly with the CECs of the BCs.

ACKNOWLEDGEMENTS

The authors thank Dr Eglė Marčiulaitienė, Dr Mantas Pranskevičius and Dr Jelena Titova for providing analytical data. This research was funded by grants (No. S-MIP-17-83 and No. S-MIP-17-20) from the Research Council of Lithuania.

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First received 11 June 2019; accepted in revised form 6 October 2019. Available online 2 December 2019