

REVIEW ARTICLE

A review of lignocellulosic biochar modification towards enhanced biochar selectivity and adsorption capacity of potentially toxic elements

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Biochar, which is rich in aromatic carbon and minerals, is a product of biomass pyrolysis at temperatures ranging from 350°C to 1000°C in oxygen-limited environments. In recent years biochar has generated much interest in the field of water treatment in view of low production costs, availability of the feedstock (e.g. lignocellulosic biomass waste) and adsorptive properties. This review incorporates researches on artificial and natural modifications of biochar towards adsorption of potentially toxic elements on biochar. The aim of this study was to provide a comprehensive review of recent research findings and theory developments on the existing modifications of biochar for adsorption of potentially toxic elements (i.e. inorganic compounds) from aqueous solutions. Factors affecting adsorption of potentially toxic elements by lignocellulosic biochar and modification techniques for lignocellulosic biochar towards enhanced adsorption of potentially toxic elements were analyzed. The novelty of this study is discussion of the natural modifications of biochar and smart properties of biochar towards adsorption of potentially toxic elements. Recommendations are offered for modifying the lignocellulosic biochar to produce designed, engineered or smart biochar with high adsorption capacity for potentially toxic elements.

Key words: engineered biochar; adsorption; lignocellulosic biomass; pyrolysis

Introduction

According to European Biochar Certificate 2015, biochar 'is a heterogeneous substance rich in aromatic carbon and minerals. It is produced by pyrolysis of the sustainably obtained biomass under controlled conditions with clean technology and is used for any purpose that does not involve its rapid mineralization to CO₂ and may eventually become a soil amendment'.

At the beginning of biochar research, it aroused much interest as a soil amendment because of its potential for carbon sequestration and soil quality improvement. After physical, chemical and biological properties of biochar (Sun et al., 2014) and production technologies (Nartey and Zhao, 2014) were investigated, biochar research shifted from soil improvement to application in health sciences and engineering. Biochar could be a new low-cost adsorbent for removal of inorganic compounds (e.g. potentially toxic elements). It can be produced from wastes (e.g. lignocellulosic biomass) and is cheaper than activated carbon because it is produced through single-stage pyrolysis at 350–1000 °C and does not need additional costs in the activation process. Activation is the second stage in the production of activated carbon and occurs in the temperature range of 600–1200 °C in the presence of oxidizing gas, e.g. CO₂ or steam, which results in the formation of a well-developed micropore structure. Therefore, biochar requires less energy for production than activated carbon (Azargohar and Dalai, 2006) and can be used as an alternative adsorbent to remove potentially toxic elements (PTE) from water solutions (Inyang et al., 2012) and air (Baltrėnaitė et al., 2016a). It demonstrated the ability to remove Cr (Dong et al., 2011), Cd, Cu, Pb and Zn (Komkienė and Baltrėnaitė, 2016). Table 1 shows the cost comparison of biochar and other adsorbents used in water treatment.

Table 1. Cost comparison of porous adsorbents for water treatment.

	Adsorbent	Price (2016), \$/ton
1	Biochar	430-2000
2	Activated carbon	1200-2500
3	Silica gel	600-800
4	Activated alumina	800-2800
5	Molecular-sieve zeolite	1000-3000
6	Activated bentonite	200-2200

Silica gel is cheaper than biochar because it has lower specific surface area values and silanol groups on its surface instead of oxygen-containing functional groups. Therefore, application of biochar in adsorption of PTE from aqueous solutions is better. Activated alumina and molecular-sieve zeolite possess the same adsorption capabilities as activated carbon and are the most expensive owing to the complexity of their production. The price of biochar is highly variable and depends on the region of production. In 2013 the mean price of biochar was 2.65 \$/kg and ranged from 0.09 \$/kg in the Philippines to 8.85 \$/kg in the UK. For blended biochar the mean price was 3.29 \$/kg, ranging from 0.08 \$/kg in India to 13.48 \$/kg in the US (Jirka and Tomlinson, 2013).

Increased environmental concerns have driven research on sustainable bioproducts, e.g. biosolvents, biogas, biodiesel and biosorbents. European Biochar Certificate stated that the most valuable material for biochar production is lignocellulosic biomass from agriculture and forestry owing to its composition. Lignocellulosic biomass is a promising alternative and renewable energy source that can be converted via the biomass pyrolysis process into liquid (bio-oil) and solid products (biochar), which are known to have a variety of applications. Cellulose, hemicellulose and lignin are the three main components of the structural composition of lignocellulosic biomass (see Fig. 1).

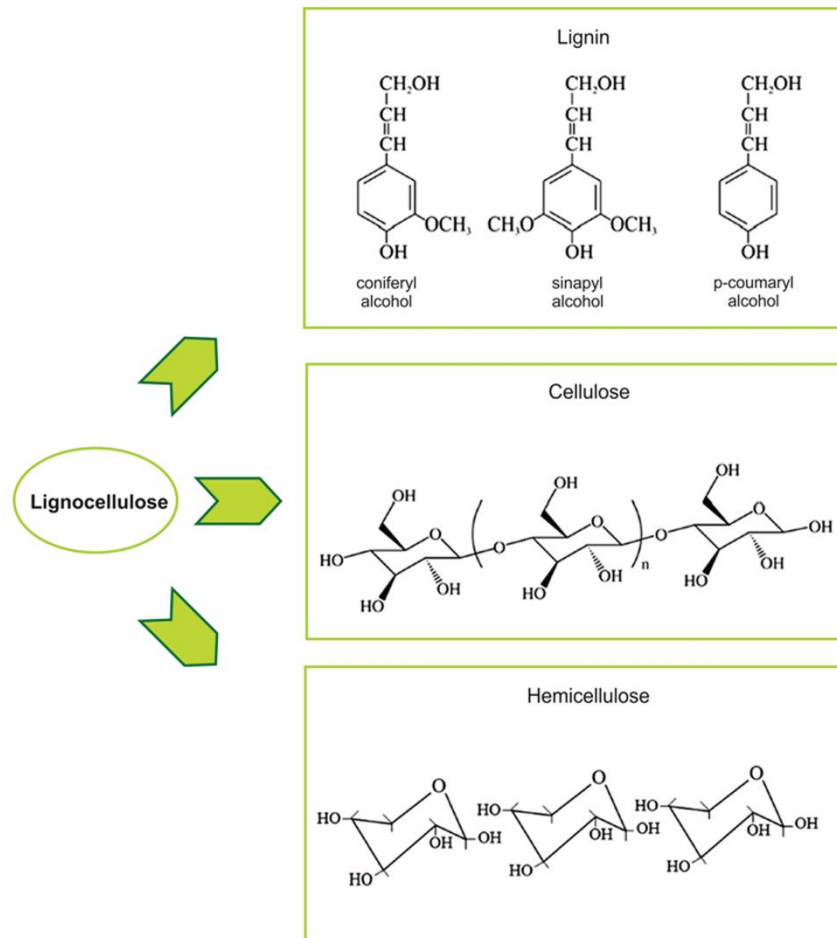


Fig. 1. The main components and structure of lignocellulose.

Depending on the type of biomass, the content of these components in lignocellulosic biomass is different; usually, cellulose constitutes 40–50%, hemicellulose 20–40% and lignin 10–40% of plant material. A small amount of ash and extractives is present as well. The lignin content depends on the strength of bound fibers in plants, i.e. woody plant species are richer in lignin because of tightly bound fibers, while herbaceous plants have more loosely bound fibers and, consequently, a lower lignin content (Stefanidis et al., 2014). In Table 2 various types of lignocellulosic biomass are presented.

In terms of waste management, plant biomass residues are of great importance because they can be used further in biofiltration systems and energy generation. The lignocellulosic residues include agricultural and wood residues (Nanda et al., 2013). Mitchell et al. (2013) examined several physical and chemical properties of lignocellulosic municipal waste biochars produced by slow pyrolysis at 480°C. Biochars produced from demolition wood, paper towel and newsprint were found to have properties that were similar to unprocessed wood biochars.

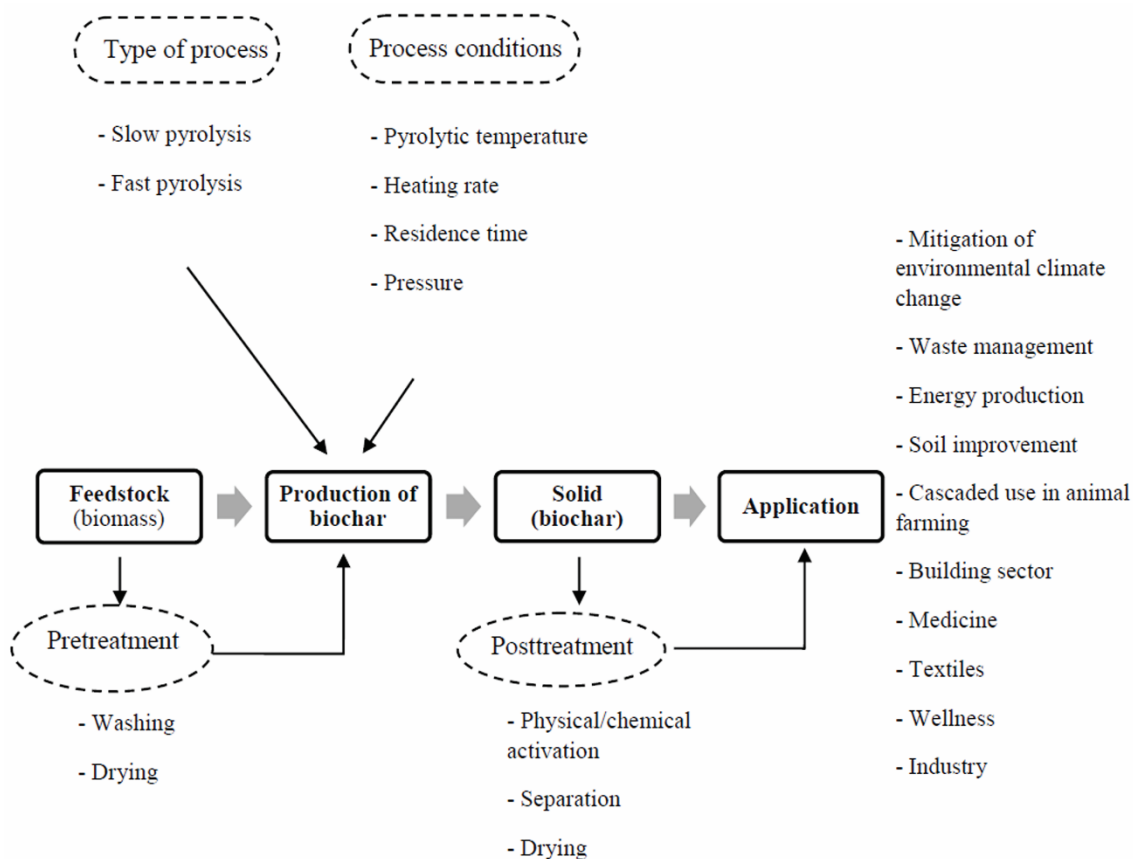
A possible reason for similarities in the properties of biochar from demolition wood, paper towel and newsprint and biochar from unprocessed wood is the fact that both feedstocks (processed and unprocessed) were originated from wood. In comparison, paper, cardboard biochars and biochars produced from leaves and grass had much higher ash content and lower amounts of fixed carbon; thus these biochars are suitable for being used as soil amendments.

Table 2. General classification of lignocellulosic biomass (Vassilev et al., 2010).

Biomass groups	Biomass sub-groups, varieties and species
1. Wood and woody biomass	Type of tree specie: coniferous or deciduous; Structure of wood: soft or hard; Form of biomass: stems, branches, foliage, bark, chips, lumps, pellets, briquettes, sawdust, sawmill and others from various wood species
2. Herbaceous and agri-cultural biomass	Grasses and flowers (alfalfa, bamboo, brassica, cane, cynara, miscanthus, switchgrass, timothy) Straws (barley, bean, flax, corn, mint, oat, rape, rice, rye, sesame, sunflower, wheat) Other residues (fruits, shells, husks, hulls, pits, pips, grains, seeds, coir, stalks, cobs, kernels, bagasse, fodder, pulps)
3. Contaminated biomass and industrial biomass wastes	Demolition wood, paper-pulp sludge, waste papers, paperboard waste, chipboard, fibreboard, plywood, wood pallets, boxes

Adsorptive properties of lignocellulosic biochar (LB) could be further developed through physical, chemical and thermal modification techniques. Different types of LB could extend the application of biochar depending on the type of target adsorbate (anionic/cationic, polar/non-polar, organic/inorganic, hydrophilic/hydrophobic). In recent years, modification of LB could be made through various methods, e.g. acid/base treatment, carboxylation, amination, treatment with organic solvents, surfactant modifications, coating of LB, impregnation of mineral oxides, steam activation, gas purging and magnetization (Rajapaksha et al., 2016). Biochar can be used for adsorption of PTEs from water and soil (Ahmad et al., 2014; Tan et al., 2015; Mohan et al., 2014a; Zheng et al., 2015); therefore, the concept of modified biochar in environmental management to enhance the efficiency of PTEs adsorption should be developed, e.g. to match the properties of biochar to adsorb particular PTE (Ok et al., 2015). A detailed schematic description of production and application of modified LB is provided in Fig. 2.

In general, biochar can be modified at each stage of its production: while preparing the feedstock for pyrolysis one can choose different types of feedstock or pretreat the feedstock with acids, ammonia, salts and steam; during the pyrolysis process one can set different process conditions; after receiving the ready biochar product, one can apply activation.

**Fig. 2.** Scheme of biochar modification and application.

Depending on the type of modification, biochar could be distinguished into designed, engineered and smart: a) **designed** biochar is produced by selecting different feedstocks and choosing different pyrolysis conditions to form specific physical and chemical characteristics for particular applications, e.g. pellets of biochar, prepared from pyrolysed nutshells under 500 °C, can increase carbon sequestration in sandy soil (Novak et al., 2009, 2014); b) **engineered** biochar is enriched with chemical compounds, e.g. Al (Zhang et al., 2013), Mg (Yao et al., 2013), Fe and Ca (Agrafioti et al., 2014) etc.; c) **smart** biochar differs from engineered biochar by changing its properties under different stresses (temperature, pressure, pH etc), e.g. biochar activated with oxygen plasma is applied in life sciences, health care and engineering (Gupta et al., 2015).

The aim of this study was to provide a comprehensive review of recent research findings and theory developments on the existing modifications of biochar for adsorption of PTEs (i.e. inorganic compounds) from aqueous solutions. The specific objectives of this work are as follows: (a) to analyse the particularities of pyrolysis of lignocellulosic biomass, (b) determine the factors affecting adsorption of PTEs by biochar, (c) to evaluate the modification techniques for LB towards enhanced adsorption of PTEs.

Decomposition processes during LB production

Before modifying the biochar into a designed one, it is necessary to investigate the composition of different types of lignocellulosic feedstock and the peculiarities of the lignocellulosic biomass pyrolysis process. Types of lignocellulosic biomass with the average percentages of cellulose, hemicellulose and lignin are listed in Table 3.

Table 3. Types of lignocellulosic biomass and average chemical composition (adopted from Isikgor and Becer 2015).

Lignocellulosic biomass		Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood	Poplar	52.1	27.5	15.9
	Oak	40.4	35.9	24.1
Softwood	Pine	46	25.5	20
	Spruce	45.5	22.9	27.9
Agricultural waste	Wheat straw	37	26.5	14
	Barley hull	34	36	16.4
	Barley straw	39.5	28.5	8
	Rice husk	31	20.5	17.7
	Oat straw	33	23	12.5
	Corn cob	37.5	34	11
	Corn stalk	37.3	24.3	12.5
	Sugarcane trash	35	30	20
Grasses	Switchgrass	37.5	27.5	17.5

When the lignocellulosic biomass is pyrolysed, biochar is formed after the combustion of released gases and vapours (International Biochar Initiative, 2016). The pyrolysis parameters to consider include feedstock type selection (biomass type, particle size, biomass pretreatment), reaction conditions (pyrolysis temperature, pressure, heating rate, residence time), equipment configurations and other variables, i.e. addition of catalysts (Kan et al., 2016).

Differences in decomposition of the biomass components make biomass pyrolysis a complex process involving complex reaction mechanisms and rates, which also depend on the thermal conditions of the process and the design of the equipment. As the major components of the lignocellulosic biomass, such as cellulose (25-50%), hemicellulose (15-40%) and lignin (10-40%), interact with each other during pyrolysis, it is very difficult to predict biomass pyrolysis characteristics based on the thermal behaviour of the three separate compounds alone. For example, lignin-derived phenols and hydrocarbons are generated as a result of the interaction between hemicellulose and lignin. Interactions between lignin and cellulose hinder the polymerization of levoglucosan from cellulose, thus reducing biochar formation, while the interactions between cellulose and hemicellulose do not significantly influence the formation of pyrolysis products (Wang et al., 2011). In addition, lignocellulosic biomass contains some extractives (15%) and inorganic matter.

During biomass pyrolysis, a large number of reactions occur, including dehydration, depolymerization, isomerization, aromatization, decarboxylation and charring (Kan et al., 2016). It is common knowledge that pyrolysis consists of three stages (White et al., 2011):

I – initial evaporation of free moisture,

II – primary decomposition,

III – secondary reactions (oil cracking and repolymerization).

Biomass decomposition generally occurs during the primary decomposition at 200–400°C and results in the formation of solid char, which is responsible for the largest degradation of biomass. The secondary reactions occur within the solid matrix followed by a rise in the temperature (Kan et al., 2016). The degradation pathways of the main biomass components have been investigated separately. Decomposition of hemicellulose, generally represented by xylan, takes place mainly at 250–350°C, followed by cellulose decomposition at 325–400°C, with levoglucosan as the main pyrolysis product. Lignin is the most stable component, which decomposes at higher temperatures of 300–550°C (Tan et al., 2015).

The biochar produced by lignocellulosic biomass pyrolysis is a valuable product that could be used as soil amendment, enhancing soil quality, increasing soil fertility and carbon sequestration (Isikgor and Becer, 2015). Rutherford et al. (2012)

demonstrated that the physical and chemical properties of biochar produced by pyrolysis of the lignin and cellulose components of plant biomass are dependent on formation temperature and duration of heating.

Mechanism of adsorption of potentially toxic elements by biochar

It is important to discuss the principal steps of adsorption because understanding of this helps to distinguish what characteristics of both adsorbate and adsorbent can be varied for enhanced adsorption. There are three steps in the adsorption of PTE by a porous adsorbent: (a) *film diffusion* – transport of the adsorbate to the external surface of the adsorbent; (b) *particle diffusion* – transport of the adsorbate within the pores of the adsorbent except for a small amount of adsorption that occurs on the external surface; (c) adsorption of the adsorbate on the exterior surface of the adsorbent. For steps *a* and *b* when external transport is lower or higher than internal transport, the rate is controlled by film and particle diffusion. When external transport is almost equal to internal transport, a liquid film with a concentration gradient surrounding the sorbent particles is formed. Usually, external transport is the rate-limiting step in systems with small particle size, insufficient mixing, dilute concentration of adsorbate and high affinity of adsorbate for adsorbent. For comparison, the intraparticle step limits the overall transfer for opposite systems (Mohan and Singh, 2002).

A liquid–solid adsorption involves liquid mass transfer, film diffusion, intraparticle diffusion and reaction. The adsorption is characterized by kinetic and equilibrium parameters. Sorption kinetics shows a strong dependence on the physical and chemical characteristics of the adsorbent, which also influences the sorption mechanism. Equilibrium divides species between the fluid phase and the sorbed phase, thus describing the relationship between the mass of sorbed adsorbate per mass of a sorbent and the equilibrium concentration of adsorbate in the aqueous solution.

Intraparticle diffusion studies at different temperatures show that the mechanism of adsorption is dependent mainly on diffusion. The method and level of activation of an adsorbent, particle size of adsorbent, concentration and physicochemical properties of adsorbate are the key factors affecting intraparticle diffusion (Wu et al., 2009). The intraparticle diffusion process is controlled by diffusion of ions within the adsorbent, e.g. the enhancement in adsorption capacity of Cr(VI) may be due to the increased rate of intraparticle diffusion of Cr(VI) ions into the pores of the biochar at higher temperatures (Karthikeyan et al., 2005). When the pore size of the adsorbent is larger than the diameter of the molecules of the adsorbate, then Knudsen diffusion begins to play a significant role (Xu et al., 2013).

The adsorption behaviour of biochar is well correlated with the properties of the PTE. For PTEs the possible adsorption mechanisms usually involve electrostatic attraction, ion exchange, physical adsorption, surface complexation and/or precipitation (Tan et al., 2015). The various mechanisms proposed for the adsorption of PTEs are summarized in Fig. 3.

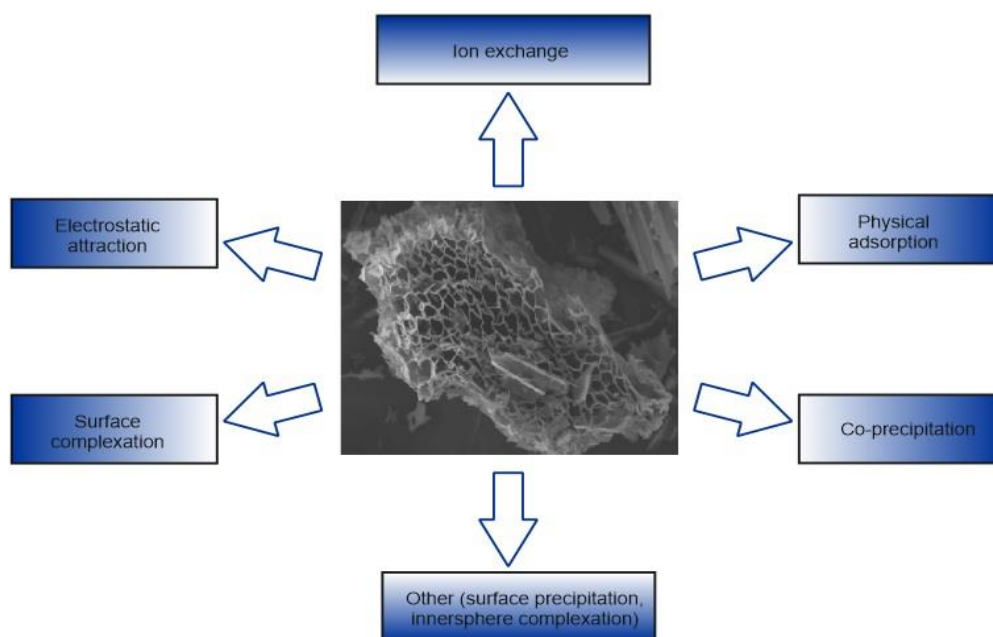


Fig. 3. Proposed mechanism for potentially toxic elements adsorption by biochar.

For application of the modified biochar in wastewater treatment, one should take into account the type of adsorbate (anionic or cationic). Removal of PTEs by means of LB is mainly controlled by the interaction between the metal ions in solution and the oxygen-containing functional groups (e.g. carboxylic ACOOH and hydroxylic AOH) on the surface of LB. Carboxyl groups slightly acidic in nature and in neutral or basic aqueous solutions carry an overall negative charge, which is capable of interacting with cations (Xue et al., 2012). Thus, unmodified LB is unsuitable for removing anionic contaminants because its surface is most likely to be negatively charged.

Dong et al. (2011) summarized the adsorption of Cr(VI) by sugar beet tailing biochar in three steps: first, the negatively charged Cr(VI) species were migrated to the positively charged surfaces of biochar (at low pH) with the help of electrostatic attraction; second, Cr(VI) was reduced to Cr(III) by the participation of hydrogen ions and the electron donors from biochar; third, part of

the Cr(III) reduced from Cr(VI) was released to the aqueous solution, and the other part of Cr(III) was complexed with the functional groups on biochar.

The surface area and porous structure of biochar can also have effects on the adsorption of heavy metals (Baltrėnaitė et al., 2015). Samsuri et al. (2014) showed that oil palm biochar, with lower surface area, exhibited a higher adsorption capacity for the PTEs than rice husk biochar, suggesting that surface area was less important than oxygen-containing functional groups.

Modification methods for lignocellulosic biochar towards enhanced adsorption of PTEs

How to prepare a 'designed' biochar?

Different factors such as biomass type and pyrolysis parameters (residence time, particle size, heating rate, temperature, surrounding gas) affect the decisive biochar parameters, such as surface properties (e.g., porosity and functionality) and ion-exchange capacity. Thus, by choosing suitable feedstock, proper parameters of pyrolysis and conditions of water treatment we can convert the biochar into 'designed'. For enhanced adsorption of PTEs the following parameters should be considered:

a) Biomass type

Different biomass types have various relative mass ratios of the organic and inorganic components. Pyrolysis of each component has unique thermochemical characteristics, and thus produces different products. Cellulose and hemicelluloses enhance the bio-oil production yield, while lignin leads to a larger proportion of solid char (Akhtar et al., 2012). According to the European Biochar Certificate, lignocellulosic feedstock is the most valuable raw material in terms of its accessibility and waste management reasons. Much higher yields of biochar can be obtained if inorganic impurities (e.g. sodium salts) are present in lignocellulosic feedstock (Baltrėnaitė et al., 2016a). In comparison with pine biochar, biochar produced from birch showed higher adsorption capacity for Cu, Zn, Pb, Cd owing to higher cation exchange capacity (Komkienė and Baltrėnaitė, 2015). Thus, wood and its waste are considered to be suitable raw material for biochar production in view of its low humidity and high lignin content. Besides, natural modifications of biochar are related to the biomass type, i.e. its mineral composition, lignin and water content, as will be discussed later.

b) Pyrolysis parameters

- Residence time. Increasing the vapor residence time helps the repolymerization of the biomass constituents by giving them sufficient time to react, resulting in bigger biochar yield. Residence time also promotes the development of macro- and microporous structure, i.e. longer residence time has been reported to enhance the pore size in the char (Tsai et al., 1997). Unlike fast pyrolysis, which has a residence time of 0.5–10 s, slow pyrolysis has a residence time of 300–550 s, being more favourable for adsorption of PTEs.

- Heating rate. The type of biomass pyrolysis, i.e., flash, fast, slow, vacuum, intermediate, hydrolysis, is defined by heating rate. Fast heating rates favour quick fragmentation of the biomass and yield, release of gases and production of less char, e.g. the heating rate of fast pyrolysis is 10–200 °C/s. For production of the solid carbonaceous biochar, slow pyrolysis is the most favourable process. In slow pyrolysis the biomass is pyrolysed with a heating rate of about 0.1 to 1 °C/s (Tripathi et al., 2016). Moreover, hydrochar, which is produced through hydrolysis at a heating rate of 10–300 °C/s, possesses fewer oxygen-containing functional groups than thermally produced biochar.

- Particle size. In order to improve pyrolysis performance, biomass should be milled or ground into smaller particles. Kan et al. (2016) referred to grinding as physical pretreatment of biomass. As biomass is generally a poor conductor of heat, the temperature influence across the small biomass particle will enhance the biomass pyrolysis mechanism (Shuping et al., 2010). Zheng et al. (2012) investigated the effect of particle size of biochar on immobilization of heavy metals in soil pore water. The biochar was crushed into coarse (0.5–2 mm) and fine (<0.18 mm) particles. Fine biochar showed a greater decrease in concentration of Cd and Zn than coarse biochar, but fine bran-char caused a 290% increase in concentration for As compared with the coarse fraction. There was no significant effect on the distribution of Pb between coarse and fine particles of the rice residue biochar. However, though most of the adsorption studies promote biochar particle sizes of less than 0.5 mm (Chen et al., 2011; Agrafioti et al., 2014), further investigations are needed.

- Temperature.

Pyrolysis temperature significantly influences the properties of biochar. With an increase in temperature the quantity of volatile and condensing compounds decreases. Development of porous structure is observed, the pH values and the specific surface area of biochar increase (Baltrėnaitė et al., 2016a), but a lower yield of the solid product is obtained. Also, they found a tendency that at the thermal stage of 300–450 °C the concentration of metals (Cu, Cr, Pb, Zn, Cd, Ni) in biochar increased by 1.3 times (irrespective of pine or birch wood type), while different tendencies were at temperatures of 450–700 °C depending on metal and wood type. Relatively high pyrolysis temperatures generally produce biochars that are effective in the sorption of organic PTEs because of increased specific surface area, microporosity and hydrophobicity; whereas the biochars obtained at low temperatures (less than 450 °C) are more suitable for removing inorganic/polar organic PTEs by oxygen-containing functional groups, electrostatic attraction and precipitation (Ahmad et al., 2014).

- Surrounding gas. Although biomass pyrolysis is usually carried out under inert atmosphere, other gases can be introduced as well to modify the pyrolysis process (e.g. steam can slightly oxidize the biomass and provide partial gasification). Gas activation makes the pores of biochar more heterogeneous, thus creating more activated sites. Steam-activated biochar from chicken litter, alfalfa stems, switchgrass and corn cob showed good removal of Cu²⁺ because of ion exchange (Lima et al., 2010). Xiong et al. (2013) found that ammonification (introduction of NH₃) could introduce N-containing groups onto the biochar and increase N content up to 3.91 wt.% in biochar, whereas CO₂ treatment plays a significant role in pore formation and improves the microporous structure of biochar, which is important for adsorption of PTEs. It was observed that the char obtained in the CO₂ environment had increased surface area and different chemical composition in comparison with the chars produced under

an inert atmosphere (Zhang et al., 2011). Physical modification methods are simple and cheaper, but less effective than chemical modification methods.

In addition to the above, conditions of water treatment (biochar dosage, solution pH, contact time) influence the efficiency of adsorption of inorganics. Chen et al. (2011) observed the highest metal sorption efficiencies for both hardwood and corn straw-derived biochar 1 g/L, while the increase in the concentration of biochar decreased the adsorption efficiencies owing to the increase in the total number of active sites. The optimum Cu (II) adsorption conditions were found to occur at 5–12 g/L of adsorbent dose (Pellera et al., 2012). Highly alkaline biochar could increase pH of treating water above the limits (according to international standards, pH of treated effluent water (including storm water run-off) should be within the limits of 6.5 – 8.5). The value of pH should be regulated according to the potential adsorbent, e.g. the highest adsorption of Ni(II) and Co(II) was observed at pH=7 (Kilik & Kirbiyik, 2013), for Cu (II) at pH=5-6 (Pellera et al., 2012). Large amounts of Ni(II) and Co(II) were removed within 150 min; after that the capacity of adsorption remained constant (Kilik & Kirbiyik 2013). Pellera et al. (2012) obtained similar results for Cu(II): the required time to reach equilibrium was 2 hours.

How to prepare 'engineered' biochar?

Practical application of conventional biochar needs further improvements, and therefore biochar should be modified to obtain new structures and surface properties. Recently the concept of engineered biochar has been developed, and novel biochar with improved physico-chemical properties has been used for PTEs removal. Modifications of the biochar for enhanced adsorption of contaminants are oriented towards increasing of specific surface area, content of oxygen-containing acidic functional groups, porosity development and changes in elemental composition.

Table 4. Various modifications of lignocellulosic biochar for adsorption of potentially toxic elements.

Modification agent	Biochar feedstock	Production temperature, °C	Adsorbate	Adsorption capacity, mg/g	Mechanism of adsorption	References
Activated with HCl, and coated with iron (FeCl ₃ ·6H ₂ O)	Wheat straw	450	NO ₃ ⁻ PO ₄ ³⁻	2.47 16.58	Electrostatic attraction	Li et al. (2014)
KOH	Switchgrass	300	Cu ²⁺ Cd ²⁺	31 34	Surface complexation	Regmi et al. (2012)
H ₂ SO ₄ +HNO ₃ , NH ₄ OH+Na ₂ S ₂ O ₄ +acetic acid (amination)	Saw dust	500	Cu ²⁺	17.01	Surface complexation, ion exchange, co-precipitation	Yang and Jiang (2014)
H ₂ O ₂	Peanut hull	300	Pb ²⁺ Cu ²⁺ Ni ²⁺ Cd ²⁺	16.45 1.22 0.07 0.21	Surface complexation, co-precipitation	Xue et al. (2012)
Fe	Risk husk	700	As ⁵⁺ As ³⁺	31.4 16	Surface complexation	Samsuri et al. (2013)
Chitosan	Bamboo	600	Pb ²⁺	14.3	Electrostatic attraction	Zhou et al. (2013)
MgO	Sugar beet tailings, sugarcane bagasse, cottonwoods, pine woods, peanut shells	600	PO ₄ ³⁻ NO ₃ ⁻	835 95	Surface complexation	Zhang et al. (2012)
AlOOH	Cottonwood	600	As ⁵⁺ PO ₄ ³⁻	17.41 135	Electrostatic attraction	Zhang et al. (2013)
Fe	Hickory chips	600	As ⁵⁺	2.16	Electrostatic attraction	Hu et al. (2015)
γ-Fe ₂ O ₃	Cottonwood	600	As ⁵⁺	0.003	Surface complexation	Zhang et al. (2013)
Fe ₂ (SO ₄) ₃ , FeSO ₄ and NaOH	Oak wood and bar	400–450	Cd ²⁺ Pb ²⁺	8.33 55.91	Metal precipitation	Mohan et al. (2014b)
Hematite	Pinewood	600	As ⁵⁺	0.429	Electrostatic attraction	Wang et al. (2015)

Biochar feedstock may be pretreated before pyrolysis through chemical pretreatment, which includes acid/base/metal salts treatment. The mechanism of biomass pyrolysis could be affected by inorganic minerals, especially the alkali (e.g. K, Na) and alkaline-earth (e.g. Mg, Ca) (Williams et al., 1994). The quality of biochars can be improved by reducing the ash content through water or acid (e.g. HNO₃, H₂SO₄) washing. Fristak et al. (2016) modified wood chips with Cu(OH)₂, FeSO₄, MgCl₂, KCl, Mg(OH)₂ and AlCl₃ (30% w/w) and observed the highest adsorption capacities for anions, i.e. sorption efficiency for As was the highest from AlCl₃-biochar (prepared at 400 °C), for P from Mg(OH)₂ (prepared at 400 °C). Agrafioti et al. (2014) immersed rice husk biomass in CaO and FeCl₃, and modified biochars showed high adsorption capacity for As (V) (>95%). Biochar prepared from Mg-accumulated tomato tissues showed 88.5% of P removal from water (Yao et al., 2013).

Available methods of biochar modification for enhanced adsorption of PTEs at the stage of modifying released biochar are summarized in Table 4 and could be divided into chemical modifications, impregnation of minerals and magnetic modifications (Rajapaksha et al., 2016).

Treatment with acids produces positive sites on the surface of biochar, and protonation of surface hydroxyl groups causes an increase in electrostatic attraction. Oxidation increases oxygen-containing functional groups, particularly carboxyl groups, which causes enhanced Pb sorption ability in almost 20 times (22.82 mg/g in comparison with 0.88 mg/g) (Xue et al., 2012). A new concept of engineering the biochar with impregnation of mineral sorbents showed a significant increase in contaminant sorption. Magnetic modifications with metal oxides and metal hydroxides provide better sorption of anionic contaminants. Magnetic orange peel biochars had higher phosphate sorption efficiencies than their nonmagnetic analogs, indicating bound iron oxide aggregates assisted in phosphate removal (Chen et al., 2011). Zhang et al. (2013) pyrolysed cotton wood treated with FeCl₃ at 600 °C in a N₂ environment. γ-Fe₂O₃ particles were embedded in porous biochar matrix. Modified biochar possessed excellent ferromagnetic properties (saturation magnetization was 69.2 emu/g, which is close to pure γ-Fe₂O₃-materials of 76 emu/g) and high surface area and showed the maximum adsorption capacity of 3.147 mg/kg for As from water solution.

'Smart' properties of biochar in adsorption of potentially toxic elements

Smart biochar technology implies application of biochar in various smart materials, e.g. supercapacitors, smart building materials, batteries and sensors (Ok et al., 2015). Smart biochar could be called as 'stimuli-responsive' or 'environment-sensitive' biochar. Such biochar possesses properties capable to withstand controlled and reversible modifications in response to the external stimulation (e.g. temperature, pH, electrical and magnetic fields, mechanical stress, humidity rate, concentration of PTEs). And the responses can also be manifold: change in chemical (anionic/cationic surface charge, hydrophilic/hydrophobic surface, functional groups, electrical conductivity) or physical properties (shape, mechanical strength).

Properties of smart biochar for adsorption of PTEs are similar to those of activated carbon applied in health care, because biochar is a precursor of activated carbon (Azargohar and Dalai, 2006). Activated carbon is routinely used as very effective sorbent of different drugs and toxic substances. Bielicka et al. (2013) prepared activated carbon for delivering paracetamol: activated carbon (about 0.5 g) was added to 100 ml of 0.7 M paracetamol solution in ethanol at ambient temperature followed by heating at 453 and 473 K in the oven. De Guzburg et al. (2015) found that activated carbon-based product DAV132 could selectively adsorb drug compounds in the proximal colon without interfering with drug absorption in the proximal small intestine.

The smartness of biochar towards adsorption of PTEs could be presented with example of hydrogels. Hydrogels have been used extensively in the smart drug delivery systems, e.g. pH-, ion- and temperature-sensitive hydrogels can be used for specific body sites. For instance, ion-sensitive hydrogels show a sharp volume phase transition at a critical concentration of sodium chloride in aqueous solutions (Qui and Park, 2001).

Depending on the surface charge, cationic hydrogels can mask the taste of drugs and release drugs in the stomach by responding to gastric low pH. Anionic hydrogels respond to intestinal high pH, preventing gastric degradation of drug or assuring colon drug delivery (Yoshida et al., 2013). All the pH-sensitive hydrogels contain pendant acidic (e.g. carboxylic and sulfonic acids) or basic (e.g. ammonium salts) groups that either accept or release protons in response to changes in environmental pH. As the carboxyl groups become ionized at high pH, the resulting decomplexation leads to swelling of the hydrogels (Qui and Park, 2001). From this could be proposed, that pH-sensitive biochar could be obtained through modifications intended on changing the surface charge or increasing of carboxylic groups content.

As the temperature increases, most hydrogels increase their water-solubility. The inverse temperature-dependent hydrogels are made of polymer chains that either possess moderately hydrophobic groups (if too hydrophobic, the polymer chains would not dissolve in water at all) or contain a mixture of hydrophilic and hydrophobic segments. Depending on temperature, certain hydrogels swell at high temperature and shrink at low temperature. The swelling of those hydrogels is reversible, responding to stepwise temperature changes. Hydrogels that are responsive to both temperature and pH can be made by simply incorporating ionizable and hydrophobic functional groups to the same hydrogels (Qui and Park, 2001).

Porous structure of biochar favors achieving of smart properties. While studying the pH-sensitive porous and non-porous hydrogels for controlled release of amoxicillin, porous hydrogels (pore diameter 39.20 ± 2.66 μm) were found to exhibit superior pH-dependent swelling properties compared with non-porous hydrogels (Gupta et al., 2002). The degree of releasing coomassie brilliant blue drug was the highest at pH 10 for the pH-sensitive coconut-based AC-hydrogel composite due to the extensively developed pore structure of hydrogel and the hydrophilic surface nature of AC with BET surface area 1230 m²/g and the fraction of 67% micropore structure (Yun et al., 2009).

Due to elastic nature, hydrogels are able to return to their memorized reference configuration even after being deformed for a long time. It is known that another smart materials as Cu-based and ferrous shape memory alloys are deformed in the low temperature phase, and recover its original shape by the reverse transformation upon heating to a critical temperature (Otsuka and Wayman, 1999). Consequently, could biochar achieve memorized reference configuration by adding Cu or Fe compounds into biochar structure?

The concept of smart biochar in water treatment should be developed through the achieving of smart properties in biochar.

Natural ways of modification

As the adsorption capacity of biochar is influenced by natural composition of feedstock, some natural ways for biochar modification exist, such as syngenetic compounds in feedstock for biochar production (Jones and Quilliam, 2014). They provide an effect on adsorption and include C, O, N, H, water, trace elements, lignin content, morphology and pore structure.

Syngenetic elements in feedstock are novel aspects in biochar modification studies, as they are generated by biogenetic processes during plant growing (photosynthesis, diffusion, pino-, endo- and exocytose, hydrolysis, etc.). In decreasing order of abundance, the elements in biomass are commonly C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn and Ti (Vassilev et al., 2010). For example, C, O, H, N content in wood can influence the C, O, H, N content in biochar. While H/C indicates the aromatization of biochar, O/C indicates the degree of surface hydrophilicity and polarity. The decreasing in the O/C and/or N/C ratios can indicate the increasing in the hydrophobicity and the reduction of polar groups, therefore, decrease of adsorption of PTEs (Suguihiro et al., 2013).

Concentration of minerals in plants varies as follows: leaves > small branches > large branches > stems (Kozłowski, 1997). The bark has higher contents of ash (2.5-5%), Al and Si than wood (<2%). As trace elements composition of lignocellulosic feedstock can influence the properties of biochar produced, Xu et al. (2013) found that PO_4^{3-} and CO_3^{2-} served as additional adsorption sites, contributing to the dairy manure biochar's high adsorption capacity for Cu, Zn and Cd. Baltrėnaitė et al. (2016a) established that for effective application in biofiltration systems, selected biochar should contain inorganic nutrients in sufficient quantity (nitrogen 0.4%, phosphorus 0.15%, potassium 0.15%). Can similar ratios in elemental composition contribute to adsorption of PTEs by biochar?

In 300 B.C. Theophrastus wrote that a good charcoal source is wood, which contains a large amount of water after drying. Experiments show that biochar that holds higher amount of water after drying suppress greenhouse gases production. Small branches and foliage of trees, short-rotation woods, have the greatest contents of moisture in comparison with stems, barks and large branches of trees (Vassilev et al., 2010). Could air dried moisture content be more critical than even surface chemistry for adsorption of PTEs?

It was noted that removal efficiencies of Pb and Cd by oak bark biochar are comparable to that of commercial activated carbon (Mohan et al., 2007). Lignin-adsorbent proved 90% of removing Cr(III) from real wastewater (Wu et al., 2008). Maybe high lignin content in feedstock can enhance adsorption of PTEs by biochar, as far as?

Even though most studies focus on investigating biochar properties and designing biochar for specific purposes (Novak et al., 2009, 2014), 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 (Zheng et al., 2015; Baltrėnaitė et al., 2016b) and surface water run-off (Mancinelli et al., 2015).

Conclusions

Various biochar modification techniques in terms of enhanced adsorption of inorganic PTEs are oriented towards changing the biochar surface properties: increasing specific surface area, microporosity volume, content of oxygen-containing functional groups.

Depending on the modification procedure, modified biochar is classified into designed, engineered and smart biochar. In order to modify biochar into a designed one, a lignocellulosic feedstock should be crushed to particle size less than 0.5 mm and pyrolyzed under 300–450 °C with CO_2 purging. To prepare an engineered biochar, lignocellulosic feedstock or biochar should be treated with metal salts/acids/bases. The way of treatment is chosen depending on the potential adsorbate, e.g. magnetic modifications are suitable for anions (NO_3^- , PO_4^{3-}), while bases and acids for cations (Cu^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+}).

Natural ways of biochar modification should be developed through investigation of influence of intrinsic properties of feedstock (C, O, N, H, water, trace elements, lignin content, morphology and pore structure) on the adsorptive properties of biochar. Smart biochar for adsorption of PTEs should be developed through achieving of smart properties by biochar (pH-, temperature and ion-responsive behaviour) through chemical modifications, e.g. Cu and Fe-composites.

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Author disclosure statement

No competing financial interests exist.

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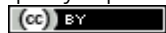
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