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Biochars and their derivatives for removal of various types of impurities from aqueous solutions

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ABSTRACT

Lately, there have been published numerous papers on application of biochar for removal of impurities from aqueous solutions. This is possible due to its favourable physicochemical properties such as large specific surface area, the presence of active functional groups and porous structure. Moreover, suitable conditions of the process (temperature, time of biomass stay in the reactor and heating rate) allow to control properties of the obtained biochar. Of significant importance is also the kind of raw material subjected to pyrolysis as towards it biochar has a homogeneous composition. In this paper, raw materials and methods used for biochar production, factors affecting its properties, application of biochar for removal of impurities from aqueous solutions taking into account magnetic molecules, chitosan and alginate modified biochar derivatives were compared.

Keywords: Biochar; Modification; Heavy metal ions; Application

1. Introduction

Biochar application goes back as far as the ancient time. By its addition into the soil, ancient Indian population inhabiting the Amazon region obtained the soil called *terra preta* which was characterized by extensive fertility compared with others not very fertile Amazon soils. Charcoal being its main component is a form of coal and burnt remains of plant and animal materials. Then, the charcoal obtained from the wastes was called biochar [1,2].

The research area connected with the biochar is quite new, complex and requires new theories to explain its environmental behaviour. Lately more and more papers have been published on the application of biochar as the material prepared from biomass. Fig. 1 presents the data obtained from the base Web of Science for the term 'biochar' (of 20.09.2017).

Interactions between mineral surfaces, metal ions and biochar particles are still insufficiently explored. These refinements are necessary to estimate the extent biochar which can be able to mitigate climate changes. Biochar is characterized by some advantages as regards soil management and climate change. The main advantageous factors associated with biochar application as soil amendment are good proportions of carbon in biochar after pyrolysis, appropriate net energy level emitted during the pyrolysis process, increasing the biochar carbon amount in soil, nitrous oxide emission as well as fertilizer requirements reduction as a growing effect of nutrient-holding capacity of biochar, crop growth increase, reduction of fossil fuel consumption. It is also well-known that biochar can adsorb 'green house gases' e.g., N_2O, CO_2 and CH_4 from the atmosphere, with a major potential to help slow global warming effect. Dissemination of research results on biochar provides new opportunities and challenges.

Biochar production is based on the widely used biomass, of primary importance of both bioenergy and biomass wastes. Raw materials for biochar production are numerous and diverse (Fig. 2).

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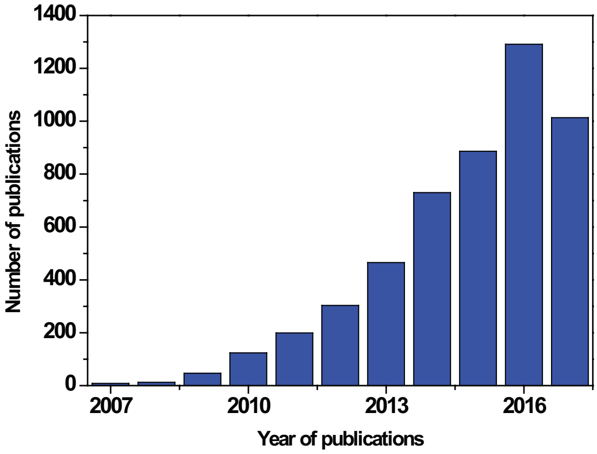


Fig. 1. The number of scientific papers (2007–2017) associated with the term 'biochar' according to the base Web of Science (of 20.09.2017).

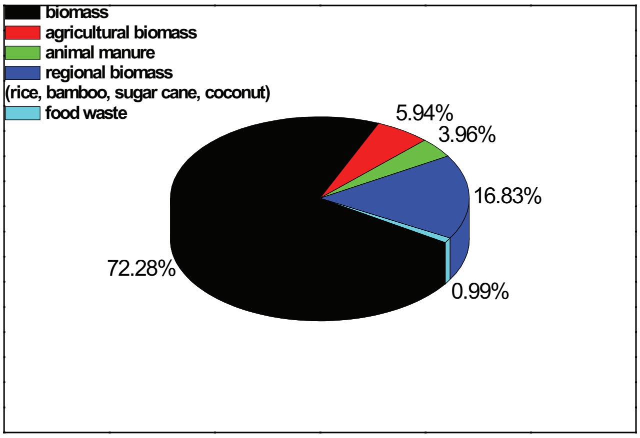


Fig. 2. Percentage of raw materials used to produce biochar in the world.

Broadly understood biomass accounts to 72.28% of the structure of processed raw materials. Another large group are the remains of plants such as wood [3,4], pine sawdust [5], cotton stems [6], orange peels [7], eucalyptus leaves [8] and agriculture origin biomass (5.94%) such as rape, sunflower, corncobs [9–11] and agriculture–food processing remains (0.99%) (e.g., postfermentation oat, rice husks [12,13], nut shells [14], coconut and hallow oil palm fruit [15]). Biochar is also obtained from solid manure [16] as well as from sewages [17,18] and industrial wastes [19]. Small contribution (4%) of animal biomass in the percentage share of raw materials probably results in limitation of technology connected with high moisture inhomogeneity of material and other physical properties of this fertilizer [20].

Choice of substrates for biochar production depends on factors such as physicochemical properties of substrates (e.g., water content, carbon content and molecule size), potential applications (e.g., production of energy and the additive improving soil properties), type of transformation process and its parameters. Classification of wet and dry biomass is based on the initial humidity. Newly collected biomass such as plant waste materials, sludge, algae, animal waste materials and others which generally have a large amount of humidity (wet biomass). The other type includes dry biomass covering agriculture residues and some species of trees which have low humidity during cutting down. Wet biomass can be dried to a smaller amount of humidity using some drying techniques. However, they are energy consuming and can reduce economic effectiveness of the system [20].

Biodegradable wastes such as those from agriculture and food processing, animal and agriculture ones as well as organic fraction of sewages should be managed by the methods different from storage in the dumping grounds. They can be materials for production of energy in different thermochemical processes during which biochar is also produced. Due to these processes reduction of wastes volume and mass and thus reduction of methane emission from dumping grounds take place [20,21].

In the production stage, the appropriate selection of raw materials and conditions of the biochar process enables the product to have favourable properties correlated with its subsequent uses [22]. A high-calorie biochar can be used in power generation which is an alternative to fossil fuels. Highly developed ash surface and low ash content can be used in agriculture for the production of fertilizers as it is stable in chemical composition and has a low susceptibility to degradation and microbial decomposition. The list of biochar-based applications and products are constantly growing. In addition, biochar is a material for the production of animal feed supplements and bedding, additives for lightweight building materials and in particular insulating materials and microfilters fillings. It is also applied as a component of paints, dyes, cosmetics and pharmaceuticals and as an additive to functional clothing where its role is to absorb odour and moisture. This is all about its uniqueness [23]. Promoted biotech applications should be linked to mitigation of climate change, rural economic development, agricultural soil productivity and water efficiency, reuse of biomass and pollution mitigation (Fig. 3).

The increasing attention is also observed in the growing numbers of biochar initiatives which support and promote the use of biochar, for example, The International Biochar Initiative (IBI), Terra – The Earth Renewal and Restoration Alliance (TERRA), the CarbonZero Project (CarbonZero), Biochar Carbon Sequestration (BCS), The Biochar Fund (BiocharFund), USBI (US Biochar Initiative), the Norwegian Geotechnical Institute (NGI) with the biochar initiatives in Zambia, Indonesia/Malaysia, Nepal, Tanzania and Brazil, Biochar for Sustainable Soils (B4SS), Implementation of biochar for sustainable agriculture in Poland (2014). The interest of biochar also results in the development of the industry related to its acquisition and use. Among the largest firms providing the combined heat and char systems, biochar pellet as well as combined power and char systems should be distinguished as follows:

- In North America: USA – ClearStak (NE), Ag Fuel Energy Systems (NE), ICM (KS), Aemerge (CA), Coaltec (IL), Genesis Industries (CA), BEK (CA), KARR group (CA), Pyrolyzer LLC (FL), ZeroPoint Clean Tech (NY), Ambient Energy LLC (WA), Avello Bioenergy (IA), Biochar

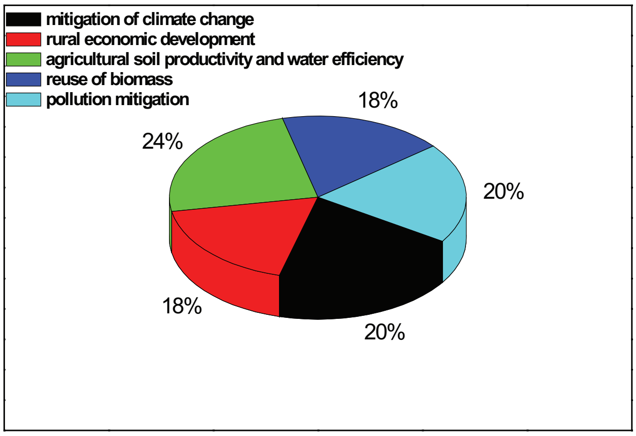


Fig. 3. Distinctive uses in the biochar area.

Solutions Inc (CO), Eprida (GA), Full Circle Biochar (CA), HM3 (OR), Interra Energy (CA); Canada – Ensyn Corp., ABRI-TECH Inc.
- In South America: Agri-Tech Producers, LLC (Columbia).
- In Europe: BioGreen Energy (France), Pyreg, BioMaCon, Carbon Terra, Regenis, Pyral AG (Germany), Advanced Gasification Technology (Italy), Ecoera (Sweden), Refgas (GB), 3REnvironmnetal Technology Group (Sweden, Hungary), Bio Carbo Energy, Piroliza, PSF Energia (Poland), Nettenergy (The Netherlands), Biouhel (Czechoslovakia).
- In Asia and Pacific Region – BioEnergy (Russia), Kansai Corporation, Super Stone Clean international (Japan), Pacific Pyrolysis, Black is Green (BiG), Piochar Project, Black Earth Products, Energy Farmers (Australia), Appropriate Rural Technology Institute, Pyrocrat (India) and others.

One of the largest-scale biochar producers is Coaltec Energy USA, Inc. It is the example of the firm producing biochar on the commercial scale by means of the gasification methods. It was founded in 2000 in the USA in the state of Illinois and due to the collaboration with different firms of this area it patented its own technology of biochar production. There biochar is prepared from manure and other fertilizers. Every year, Coaltec processes hundreds of thousands of tons of wastes. These are manure (of chickens, cows and turkeys), organic substances prepared from sewages, particularly used in agriculture, fuel originating waste, corn straw, coal and tyres. Their gasification is conducted in the temperature range of 1,033–1,255 K. Due to high temperature biochar from manure is free from pathogens, bacteria, growth hormones and drug remains. As a result there is formed biochar of the carbon content 20%–25% including the nutrient components such as nitrogen, phosphorus, potassium, calcium and magnesium (24%) [22]. Fig. 4 presents the gasification process in the Coaltec Energy firm.

2. Methods of obtaining biochar and its properties

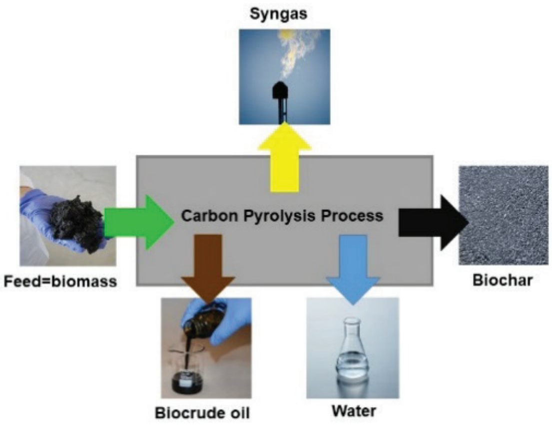
2.1. Methods of biochar preparation

Biochar is produced through the thermochemical transformation of biomass under oxygen or oxygen free conditions [23]. Main process parameters of biomass transformation methods provide more detailed information about technological, economical and climatic aspects as well as possibility of their application [24]. The main methods of biochar preparation are pyrolysis, gasification, torrefaction as well as hydrothermal carbonization (HTC). These methods differ in biomass stay in the reactor and temperature range of the heating process.

Fig. 4. Coaltec Energy gasification system at The Ohio Heifer Center.

Biochar can be produced by means of thermochemical biomass decomposition process in the temperature range of 523–1,273 K without oxygen access, so-called pyrolysis. This method is the most frequently applied for biochar preparation resulting in three main products coal-rich solid product (biochar), volatile substances which can condense to the liquid phase – pyrolysis liquid (also called pyrolysis oil, biooil, biocrude oil, biofuel oil, wood liquid or biocrude oil) and the others so-called ‘not condensing’ gases such as CO, CO_2 and H_2 (syngas) [25] (Scheme 1).

Pyrolysis can be generally divided into fast, indirect and slow depending on the time of biomass stay in the reactor and temperature range used for heating. Fast pyrolysis of very short time of raw materials stay in the reactor (<2 s) and heating in the temperature range of 573–1,273 K is often applied for biooil production because due to this process even up to 75% of the liquid product is obtained. Indirect pyrolysis is characterized by the time of reagents stay in the reactor from several seconds to a few minutes and the heating temperature is usually 773 K. Slow pyrolysis of the time of biomass stay in the reactor from a few minutes to a few hours and even days is generally preferred as the productivity of the obtained biochar is higher being about 35%. This process is most frequently conducted in a wide range of temperatures from 523 to 1,273 K. Temperature range, heating rate and time of reagents stay in the reactor affect significantly the percentage content of carbon and specific surface area of biochar. From the typical slow pyrolysis process three final products of similar yields are obtained [20,26,27].



Scheme 1. Biochar pyrolysis products.

Gasification is a process of partial biomass burning at a high temperature in the range from 873 to 1,473 K for a short period of time 10–20 s. Its basic product is a mixture of CO, H_2 and CO_2 also called synthesis gas as well as biochar and biooil. Different types of biomasses are suitable for biogas production and their gas yields vary within the content of carbohydrates, proteins and fats. The content of volatile solids is often used as an indicator for biogas production.

The gasification process proceeds similarly to that of pyrolysis. The only difference is furnishing the so-called gasifying agent as an additional substrate. This can be oxygen, air, hydrogen or carbon dioxide. However, biochar is not produced in the ideal gas generator as most organic substances transform into gases and ash. Yet, in practice this process results in a low yield of biochar (about 10%). The biochar produced from the gasification process contains a large amount of alkali metals and alkaline earth family (Ca(II), Mg(II), etc.) of silicon as well as polycyclic aromatic hydrocarbons which are toxic compounds formed in high temperature reactions [28,29]. Thus, application of biochar obtained due to the gasification process for soil fertilization can cause some problems. However, the recent field studies proved that introducing biochar from the gasification process into soil had advantageous effects for the soil where it was applied [24,25].

HTC is a thermal process of transforming organic raw materials into a coal-rich product under milder conditions than other carbonization techniques. HTC is conducted in the temperature range of 453–573 K. The process consists in immersion of biomass in water and heating in a closed system under pressure (2–6 MPa) for the period from a few minutes to a few hours [30]. During this process a minimal amount of carbon dioxide is released. For the first time the HTC process was proposed by Friedrich'a Berguis in 1913 for description of the natural carbonization process. The recent investigations using HTC have been rather focused on production of solid materials (hydrochar) which are effectively applied in industry and environment. Hydrochar differs from biochar with the conditions of preliminary treatment and production techniques. As a result, a substance of physicochemical properties different from those of biochar is formed [24]. As the HTC process is conducted in the presence of water, the large content of humidity in the raw material does not have any effect. This exceptional advantage of the HTC method excludes necessity of preliminary drying of wet biomass. As commonly known drying is a preliminary energy consuming and not economical process. In some cases it is also indispensable for dry pyrolysis and roasting. The HTC results in preparation of three main products solid substance (called hydrochar), liquid substance (biooil mixed with water) and a small fraction of gases (mainly CO_2). Hydrochar is formed due to HTC with the 40%–70% yield [31].

Torrefaction also defined as a mild pyrolysis is a process in which biomass is heated in the inert atmosphere maximum up to 573 K in the period from 30 min to a few hours. The efficiency of this process ranges from 40% to 80%. However, the product of biomass torrefaction cannot be called biochar as the obtained reagent possesses also volatile organic compounds (VOCs). Generally, torrefaction is treated as an initial stage of pyrolysis. Taking into account physicochemical properties of those biomass are intermediate between the crude biomass and biochar [32,33].

Slow pyrolysis and HTC are the most effective technologies of biomass transformation allowing to obtain solid products of good efficiency. These methods are characterized by high efficiency and a large variety of raw materials. The HTC method consumes less energy as it those do not require biomass drying as in the case of slow pyrolysis [34]. On the other hand Lehmann recommends 823 K as the optimal temperature for biochar production. This temperature enables preparation of biochar characterized by the presence of reactive surface group, high capability of cations exchange, high percentage content of carbon, large surface area and strongly developed porous structure. Biochar obtained at low temperatures is characterized by small adsorption capability, therefore, choice of methods and process conditions is essential. The yield of the obtained solid product depends largely on the kind of raw material subjected to heating and process conditions. Choice of suitable affects both physical and chemical properties [35].

2.2. Factors affecting biochar properties

Applying the above mentioned methods of biochar preparation is aimed at obtaining the material characterized by large specific surface area, suitably developed porous structure, the presence of functional groups, large content of carbon and low production costs [7]. The yield of the obtained biochar and its physicochemical properties depend on the type of substrate, temperature, heating rate and time of the biomass stay in the reactor [36].

Surface and porosity are main physical properties affecting capability of metal sorption on the biochar surface. During biomass pyrolysis micropores are formed due to the loss of water during drying [37]. Biochar pores size is changeable including nanopore (<0.9 nm), micropore (<2 nm), mesopore (2–50 nm) and macropore (>50 nm) according to the IUPAC classification International Union of Pure and Applied Chemistry (IUPAC) [38].

The studies carried out on the pistachio *Pistacia vera* shells by Lua et al. [39] showed that increase in the pyrolysis temperature from 523 to 773 K increases the surface area due to the release of volatile compounds from the pistachio shells which results in the increase of pores in biochar. Then, activation at higher temperatures causes formation of new pores which results in the increase of specific surface area. However, when the pyrolysis temperature rises from 773 to 1,073 K, the specific surface area diminishes gradually which can be due to distribution of some volatile fractions. Micropores surface, total pore volume and micropore volume show similar tendencies to the specific surface area after the pyrolysis temperature increase [39]. Microporous structure of biochar places an essential role in improvement of specific surface area and adsorption capacity. In agricultural applications large pores can favour permeability of soils, increase water content in soil and ensure space for growth and multiplication of microorganisms. Smaller pores can improve adsorption capability of biochar [40]. Large porosity is associated with large specific surface area and decides about biochar application as manure [41].

Analyzing the effect of temperature on the yield of obtained biochar, it should be taken into account that at the heating temperature over 393 K organic substances are thermally decomposed and loss of chemically bound humidity takes place. Each raw lignocellulose material is composed mainly of cellulose, hemicellulose and lignin with smaller fractions of inorganic materials (ashes), organic extracts and water. The fractions are characterized by peculiar behaviour of thermal distribution which depends mainly on treatment temperature. Hemicellulose decomposes in the temperature range of 473–533 K, cellulose 513–633 K and lignin 553–773 K. Comparing biochars prepared from hard and softwood, paper materials as well as mixed materials, it can be stated that hardwood had the largest yield (94%) at 573 K due to a large content of lignin and cellulose and then paper and mixed materials. Biochar derived from softwood was characterized by the smallest yield due to low content of lignin and cellulose compared with other materials [41]. Pyrolysis temperature has a significant effect on the yield of the prepared biochar. Uchimiya et al. [42] investigated properties of biochars obtained from cotton seeds in the function of pyrolysis temperature 473–1,073 K. They observed a sudden drop in the yield of biochars at a temperature below 673 K which is associated with a loss of volatile substances and gases such as CO_2, CO, H_2 and CH_4. However, at a temperature below 673 K biochar of high, stable yield was obtained.

The contents of carbon, volatile substances and ash in biochar are important from the point of view of its application. High content of volatile substances in the raw material subjected to heating can support favour development of porous structure and reactivity of the formed biochar. The size of pores determines accessibility of active sites on the sorbent surface [43]. In the case of pyrolysis conducted up to 973 K, the carbon content gradually increases but that of volatile substances decreases. Yet during heating at higher temperatures an opposite tendency is observed which is confirmed by the studies carried out by Enders et al. [44]. Furthermore, they found out that with the pyrolysis temperature increase, the carbon content increases whereas that of oxygen and hydrogen decreases independent of the kind of raw material used for biochar preparation. The H/C and O/C ratio is used in order to determine the degree of biochar aromatic character. High H/C ratio indicates low aromaticity of biochar. The results showed the decreasing tendency with the increasing pyrolysis temperature. Biochars produced at high temperatures over 773 K contain highly aromatic carbon compounds which are resistant to microbiological distribution ensuring their long semi-duration in soil thus making biochar application as the additive to improve soil fertility [41]. What is more, the kind of raw material subjected to pyrolysis affects the amount of ash. The largest proportion of ash was found in biochars obtained from animal manure (bull, poultry and digested dairy) and wastes (paper) and the smallest one for biochars produced from dendritic remains (hazelnut, oak and pine) [44].

Another important parameter for description of properties of biochar in aqueous solutions is the surface charge. The point of zero charge (pH_{PZC}) is the value of pH at which the surface of solution or solid in the aqueous solution has a zero charge which is associated with the zero charge of the sum of surface positive and negative charges. When solution pH is higher than pH_{PZC} the biochar surface exhibits a negative charge and binds metal cations but when a solution pH is smaller than pH_{PZC} the adsorbent binds metal anions [35]. It was proved that the change of pyrolysis temperature results in the change of biochar surface charge value. Tan et al. [45] found that the increasing of pyrolysis from 773 to 1,173 K increases the biochar pH_{PZC} value from 8.6 to 10.2. Similar observation where made by Yuan et al. [46] while investigating the biochar prepared from rape, corn, soya and nuts at 573, 773 and 973 K.

Amounts of carbonates (HCO_3^- and CO_3^{2-}) contained in biochars are particularly essential for their agricultural application. For biochars obtained from corn straw at different pyrolysis temperatures in the range of 573–873 K the content of carbonates was different. As follows from the studies carried out by Fidel et al. [47], basicity caused by the presence of carbonates increased with the pyrolysis temperature increase. Higher contents were obtained for CO_3^{2-}.

The stability of biochar is largely dependent on the type of used biomass feedstock. Different pyrolysis conditions (temperature and heating time) are essential for creating biochars with different degrees of stability. Being stable with respect to the chemical composition biochar is characterized by insignificant susceptibility to degradation and microbiological decomposition. The physical parameters responsible for numerous transformations and processes include porosity and specific surface area of biochar. They depend on the kind of substrate and heating parameters. The time of biomass stay in the reactor is of significant importance for the properties of created biochar. With the increasing time of biomass stay during pyrolysis, there is observed increase in the specific surface area, surface of micropores, volume of pores and micropores [32,33]. However, with the increase over 2 h, the size of specific surface area drops which may be due to partial blockage of pores by amorphous products of decomposition [41]. The main cause of differences in surface properties of biochar is oxidation of organic compounds formed in void spaces of its matrix. Yet, too high pyrolysis temperature and too large heating rate can destroy the biochar structure. Moreover, there can take place condensation of VOCs contained in the porous structure which in turn can result in clogging of pores and decreasing the total surface of biochar. Analysis of the biochar pictures made by the scanning electron microscope (SEM) revealed loss of fibrous structure of biochar prepared at high temperatures. Increase in the pyrolysis temperature resulted in the smooth surface which accounted for the decrease in the specific surface area with the temperature increase. Therefore, the choice of conditions of pyrolysis and other thermochemical processes is of significant importance.

3. Application of biochars and its modifications

3.1. Application of biochars for heavy metal ions removal

Biochar is an object of interest because of its wide application and benefits for the environment. Owing to its properties it is used as a renewable fuel in power industry which is an alternative to expensive mineral fuel [20] and as a raw material it improves properties of soil through the exchange of cations, increase of nutrient contents, rise in pH and water capacity of soil as well as carbon content [48]. However, essential application of biochar is a sorbent for removal of heavy metal ions and organic compounds from waters and wastewaters. The process of metal ions sorption on biochar can be influenced by a number of factors related to the nature of sorbent porosity, surface area, ash, volatile matter contents or types of functional groups; solution pH which affects protonation of metal ion binding sites and ionic state of the sorbate in the solution as well as sorbate type and its concentration. Metal ions sorption on biochar can occur either on the mineral components or the sites on the organic matter. The ratio of these two fractions influences the sorption efficiency. After pyrolysis inorganic compounds exist in biochar both as discrete mineral phases or part of the structure of the carbonaceous residue. With the increase of the pyrolysis temperature their concentration in biochar increases. It is also known that due to the presence of surface functional carboxylic, hydroxyl and phenol groups containing oxygen, biochar can bind effectively heavy metal ions such as lead(II), copper(II), arsenic(III), zinc(II), nickel(II), chromium(VI), antimony(III), mercury(II) and cadmium(II). They are dangerous for human and animal health and life due to carcinogenic activity and bioaccumulation capability [49]. Their removal from aqueous solution is of particular significance [50].

Metal ions sorption on biochar depends on the type of metal ion, raw material and conditions of biochar production. Park et al. [51] studied the competitive sorption of Cd(II), Cr(VI), Cu(II), Pb(II) and Zn(II) ions on biochar prepared from sesame. Based on the Langmuir isotherm model there determined the maximal sorption capacity values Pb (102 mg/g) > Cd (86 mg/g) > Cr (65 mg/g) > Cu (55 mg/g) > Zn (34 mg/g) under the monometallic conditions and Pb (88 mg/g) > Cu (40 mg/g) > Cr (21 mg/g) > Zn (7 mg/g) > Cd (5 mg/g) under the multimetallic conditions. Larger amounts of the sorption capacities were obtained for sorption of single ions compared with that of ions from mixtures. However, results from simultaneous sorption are indispensable for accurate estimation of biochar retention capability in the natural environment. Pb(II) sorption capacities were comparable for the monometallic and multimetallic systems when Cd(II) lost great adsorption capacity. The largest affinity of Pb(II) for biochar can result from formation of surface complexes between these ions and the active carboxyl and hydroxyl groups present on the biochar surface [51]. Cd(II) and Zn(II) ions have a larger radius thus a smaller ratio of charge and radius as well as lower ion potential than that of Cu(II) and Pb(II) ions. Therefore, Cu(II) and Pb(II) ions form surface complexes more readily with biochar functional groups so they are less mobile than Cd(II) and Zn(II) ions [52]. High capability of Cu(II) ions binding by biochar is confirmed by the investigations carried out by Lima et al. [53]. They compared eight different biochars originating from broiler litter, alfalfa steams, switchgrass, corncobs, corn stoves, guayule bagasse, guayule scrub and soybean straw with their active equivalents as regards capability of adsorbing copper(II), cadmium(II), nickel(II) and zinc(II) ions from water. Biochars there prepared due to fast pyrolysis and their effectiveness was compared with those subjected to steam activation and their activated sorbents were better at capturing metal ions. This is due to larger specific surface area of the activated biochars compared with inactivated ones as well as ready accessibility to their functional groups. All applied biochars were able to remove large quantities of four metal ions in the range from 55% to 85% for Cu(II), 22%–60% for Cd(II), 10%–50% for Ni(II) and 16%–49% for Zn(II) ions. Cu(II) ions showed the largest affinity for biochars compared with other metal ions which can be ascribed to their interactions with the biochar functional groups [53].

As follows from the studies carried out by Ding et al. [54] not only metal affinity affects sorption capacities but also sorbent preparation conditions. Their investigation included the effect of pyrolysis temperature 523–873 K on effectiveness of Pb(II) ions sorption on biochar prepared from sugarcane. In the case of the initial Pb(II) concentrations 20 and 105 mg/L, the percentage of ions adsorbed by biochar obtained at 523 K was 43% and 62%, respectively. Whereas for biochar obtained at 773 K its maximal sorption was 64% and 98% (for 20 and 105 mg/L, respectively). The studies of sorbent regeneration confirm that Pb(II) ions can be effectively eluted after sorption using hydrochloric acid. The experimental and model results of studies showed that sorption of lead ions on biochar was controlled by many mechanisms such as complexation, cations exchange, precipitation and diffusion of molecules which is also confirmed by the studies carried out by Lu et al. [55]. Biochar prepared from sugarcane effectively removes Pb(II) ions from aqueous solutions.

Shape of adsorption isotherm indicates the sorbate and sorbent interactions. The quick initial phase indicates the mechanism of physical sorption taking place before diffusion of ions in the biochar pores [56]. The Temkin isotherm model assumes that adsorption heat decreases linearly due to the effects connected with the adsorbate interactions. In this model chemical adsorption is assumed as electrostatic interactions. The obtained values of the determination coefficients ($R^2 > 0.814$) show that the electrostatic interactions of Cu(II) ions with the biochar prepared from the poultry manure are one of sorption mechanism [57]. The Dubinin–Radushkevich model is used for determination of adsorption mechanism on the heterogeneous surface based on the obtained value of activation energy (E_a) which is in the range of 1–8 kJ/mol the adsorption process is of physical character. The adsorption process proceeds through the ion exchange when E_a is in the range of 8–16 kJ/mol. When E_a is in the range of 16–40 kJ/mol, this process consists in chemisorption [17]. According to the literature data the carboxylic –COOH, hydroxylic –OH and phenolic –ROH groups are generally considered to be responsible for coordination of metal ions on the biochar surface [57]. In order to establish the sorption mechanism Xiao et al. [56] used the elementary analysis of Ca(II), Mg(II) and Pb(II) contents before and after sorption. They found that the concentration of Mg(II) and Ca(II) in biochars was lower after sorption which indicates the ion exchange. The measurements made by the X-ray diffraction method proved that biochar prepared from the pyrolysis at 873 K showed insignificant changes after sorption. This proves small contribution of precipitation mechanism to Pb(II) ions sorption [56]. As follows from the above presented papers the mechanisms of heavy metal ions are electrostatic interactions, ion exchange, physical adsorption, complexation or precipitation processes [35].

3.2. Application of biochars organic compounds removal

Many organic compounds are stable or can be transformed into other products which are resistant to conventional water treatment processes and long-term consumption of such contaminated water results in adverse health effects [58]. Sorption of organic impurities from water on biochar is possible as it is characterized by a large specific surface area and the presence of micropores. In addition, biochar surface is characterized by polarization and aromatic character. Typical organic pollutants present in drinking water sources include VOCs, disinfection by-products (DBP), pesticides, herbicides and insecticides used in agriculture, pharmaceuticals and dyes [58].

An example of a VOC is nitrobenzene. Nitrobenzene sorption using biochar prepared from lignin, cellulose and wood at 673 and 873 K is an effective process. Biochar from wood had a more developed microporous structure than biochar prepared from lignin which is a good sorbent for aromatic impurities and more advantageous compared with the other two biochars [59].

Nitrosoamines are organic chemicals, amine derivatives, belonging to DBP. Nitrosodimethylamine (NDMA) belongs to this group and attracts a greatest interest, particularly in the process of wastewater treatment. Of significant importance is its content in drinking water because NDMA is a highly mutagenic compound [60]. Chen et al. [60] used biochar derived from bamboo, rice and wood pyrolysis to remove NDMA from aqueous solutions. They observed that the solution pH had no significant effect on the efficiency of NDMA removal from aqueous solutions. The largest removal efficiency of NDMA (61.7%) was obtained from bamboo-derived biochar [60].

Pesticides, herbicides and insecticides include carbaryl, atrazine and catechol. Carbaryl (1-naphthyl methylcarbamate) belongs to the carbamate group and is mainly used as an insecticide. Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) is a herbicide which belongs to the triazine class. Zhang et al. [61] studied the sorption of carbaryl and atrazine on biochar obtained from animal manure which was characterized by a high ash content. Pesticides were found to be hydrolyzed more quickly in the presence of biochars obtained by pyrolysis at 973 K compared with 623 K. The yield was 71.8% for carbaryl and 27.9% for atrazine. Additionally, it was found that pH is the basic parameter controlling hydrolysis. Elevated pH resulted in accelerated hydrolysis [61].

Mondal et al. [62] investigated the effectiveness of ibuprofen removal from contaminated water by biochar obtained from *Parthenium hysterophorus* which after the carbonization stage was impregnated with sodium hydroxide solution. Ibuprofen ([2-(4-isobutylphenyl)propionic acid]) is a non-steroidal anti-inflammatory drug applied for colds. Its physicochemical properties indicate a high mobility in the aquatic environment, so it is present in wastewater along with its metabolites [63]. It was observed that the maximal capture of ibuprofen at 2 g/L of adsorbent dose was under following conditions: pH 2.0, stirring speed 160 rpm and temperature 293 K at the initial ibuprofen concentration 20 mg/L [62].

Studies on the removal of dyes congo red [64] and methylene blue [65] using biochars from aqueous solutions showed that biochars have the ability to remove the above dyes by about 85.0%. Additionally, the investigations carried out by Xu et al. [66] showed that parameters such as pH and ionic strength can also affect methyl violet increase insignificantly with the pH increase up to the pH values from 7.7 to 8.7 where a rapid increase in the sorption capacity was observed. This is caused by the increase of electrostatic attraction between the dye and biochar surface with the increasing pH value as a result of dissociation of the phenol groups biochar thus increasing the negative charge on its surface.

Taking into account specific physicochemical properties such as surface area, surface charge and chemical functionality, biochar can sorb organic pollutants successfully. These effects also depend on the structural and chemical properties of sorbates [58]. Based on the results obtained by Zhang et al. [67] the sorption mechanism is also dependent on the biochar preparation conditions. Adsorption is the dominant mechanism for the removal of VOCs in the case of biochars produced at higher pyrolysis temperatures. They have higher surface area and lower non-carbonic organic content, whereas the division was the main mechanism for lower carbon biochars with higher non-carbonic organic content and smaller area. In general, the sorption of organic pollutants can take place through pore filling mechanisms, diffusion and division, hydrophobic interactions, aromatic-π and cation-π interactions, electrostatic interactions and hydrogen bonding as well as their simultaneous occurrence [60,61].

3.3. Biochar modifications

Lately there has been observed increasing interest in the synthesis of biochars modified with hydrogel, magnetic molecules, chitosan, alginates and others. Synthesis of their derivatives can improve physicochemical properties of biochar by combination of its advantages with other materials. The research carried out by Karakoyun et al. [68] proves that biochar inside the hydrogel matrix, that is, friendly for the environment, is an effective sorbent to remove organic contaminants from wastewaters. Sorption capacity for phenol adsorption on the hydrogel-biochar composites was 28.06 mg/g at pH 10.

The addition of iron into the biochar structure enables preparation of nanocomposites which, due to their magnetic properties, can be more readily separated from the solution after sorption using the external magnetic field as biochar is difficult to separate after sorption [69]. The magnetic particles such as Fe, Fe_2O_3 and Fe_3O_4 are introduced into the biochar structure by pyrolysis at high temperature or chemical coprecipitation. Magnetic biochar prepared by Fe coating of the biochar surface is characterized by large reactivity and affinity for heavy metal ions [70]. Devi and Saroha [71] prepared biochar as a result of the pyrolysis of sewage sludge at 973 K and then modified it by applying zerovalent iron particles for its surface modification. Reduction to Fe(0) was achieved by mixing $FeSO_4$ with a solution of $NaBH_4$. The resulting sorbent was doped with nickel and used to remove pentachlorophenol. The studies show that the removal efficiency of pentachlorophenol is the highest for the Ni-zerovalent iron magnetic biochar composites and being about 100% compared with that of other sorbents. It is for zerovalent iron about 30%, for Ni-zerovalent iron about 37%, for biochar about 70% and for zerovalent iron magnetic biochar about 95% [71]. Magnetic biochars prepared by reducing iron sulphate with sodium borohydride were used to remove heavy metal ions in the studies carried out by Kołodyńska et al. [72]. The obtained modifications differed in the proportions used for the synthesis of reagents. The sorbent identified as MBC2 exhibited a higher affinity for the test ions, with the highest yields of lead(II) ions [72].

Chitosan is a polysaccharide formed during chitin deacetylation. It is one of the most common biopolymers in nature. The ordered structure of chitosan is due to the presence of intramolecular and intermolecular hydrogen bonds in its lattice. It is characterized by biodegradability, non-toxicity, availability and low price. Moreover, due to suitable sorption capability it is used for removal of heavy metals and inorganic impurities from waters and wastewaters. Ability to capture impurities results from the presence of functional amine and hydroxyl groups. Modification of chitosan modified biochar combines advantages of both at low production costs [73]. The presence of chitosan coating on the biochar surface promoted the effectiveness of Pb(II) ions removal from 23.9% up to 59.6% and that of Cr(VI) from 0% to 27.8% compared with the unmodified biochar. This may be due to the presence of amine groups which chelate metal cations in aqueous solutions. Additionally, the presence of Fe promotes removal of Pb(II) ions up to 93%. However, removal of Cr(VI) ions increased with the increasing amount of iron compared with biochar and chitosan. The obtained results indicate that molecules of chitosan and iron on the biochar surface improve sorption of Pb(II) and Cr(VI) [74].

Efficiency of heavy metal ions removal by means of chitosan modified biochar is confirmed by the studies carried out by Zhou et al. [75]. The biochar samples were obtained from bamboo, sugarcane, wood and peanuts. All studied sorbents exhibited ability to remove Pb(II), Cu(II) and Cd(II) from aqueous solutions. Generally, most biochars modified with chitosan (except for that from peanuts) removed larger amounts of heavy metals. Chitosan was the most effective in the sorption of heavy metal ions for biochar prepared from bamboo. The Pb(II) sorption percentage increased from 20% to 50%, for Cd(II) from 10% to 45% and for Cu(II) from 18% to 55% [75].

Our research compares the removal efficiency of heavy metal ions from the mixture for the different ratios of biochar (BC) to chitosan (CS) masses (e.g., BC:CS = 1:1, 2:1, 4:1 and 8:1; Fig. 5).

Based on the above results it can be stated that the range of heavy metal ions affinity is as follows: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Co(II) and the highest amounts of adsorbed ions were observed for the ratio of BC:CS 8:1 masses.

The SEM images presented in Fig. 6 show the morphologies of the used biochar–chitosan samples. The low BET surface area of the BC–CS samples is due to the small pore structure material which occurs in the case of high ash content materials. No distinct structural differences for the BC–CS samples before and after sorption processes were observed. They are of a heterogeneous appearance due to the nature of the feedstock used in the pyrolysis process.

Alginates are non-toxic and cheap natural materials widely used as gelation means for production of microcapsules and microspheres. Cui et al. [76] investigated the ability of phosphates removal by various modifications of biochar using Mg(II), alginates, Mg(II)–alginates, chitosan and Mg(II)–chitosan. The highest sorption capacity compared with other sorbents was 23.57 mg/g in the case of magnesium and alginates modified biochar.

4. Conclusions

Biochar can be successfully applied for removal of organic and inorganic impurities from aqueous solutions. As follows from the literature various raw materials and methods are used for its production. Physicochemical properties and capability of absorbing impurities of biochars were dependent on the process conditions. Based on the analysis of adsorption mechanisms, it was found out that different kinds of interactions including ion exchange, electrostatic attraction, physiosorption and chemisorption as well as complexation and precipitation are responsible for removal of impurities from water. The studies confirmed possibility of application of biochars and their derivatives with satisfactory productivity. Furthermore, their application is

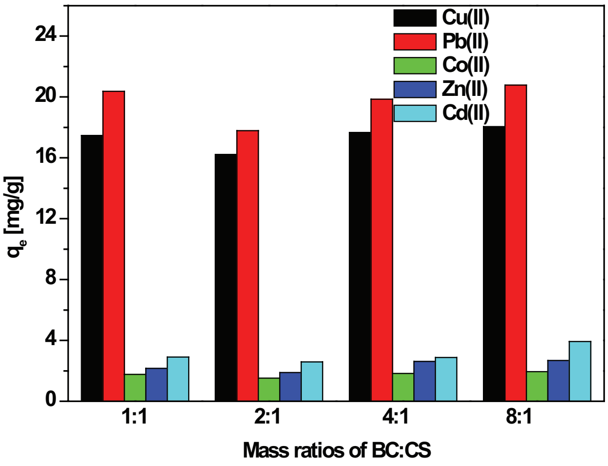


Fig. 5. Comparison of equilibrium capacities for simultaneous sorption of heavy metal ions for different ratios of BC to CS masses.

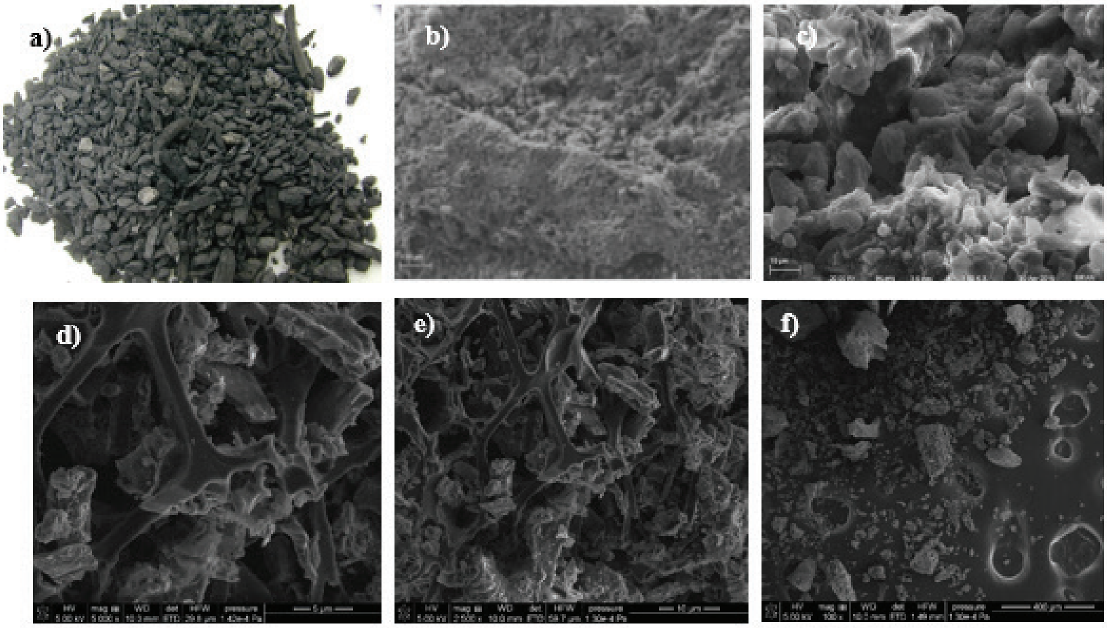


Fig. 6. Images of BC with different magnifications.

environmentally and economically advantageous because of preparation from wastes.

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