

UPTAKE OF HEAVY METAL IONS IN AQUEOUS SOLUTION BY CHITOSAN MODIFIED BIOCHAR

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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, presence of active functional groups, porous structure. Moreover, suitable conditions of the process (temperature, time of biomass stay in the reactor, 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. The aim of this paper was to present 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.

Keywords: biochar, chitosan, modification, heavy metal ions

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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 to 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].

Biochar is a renewable solid fuel formed during the thermal conversion of plant and animal biomass, organic and other wastes resulting in formation, besides biochar itself, of liquid and gaseous products of high energetic value. The wastes, from which biochar can be obtained include: wood [3,4] and other plant remains: pine sawdust [5], cotton stems [6], orange peels [7], eucalyptus leaves [8], agriculture origin biomass (e.g. rape, sunflower, corn-cobs) [9–11], agriculture-food processing remains (e.g. postfermentation oat, rice husks [12,13], nut shells [14], coconut, hallow oil palm fruit [15]). Biochar is also obtained from stable manure [16] as well as from sewage [17,18] and industrial wastes [19].

Choice of substrates for biochar production depends on such factors as physicochemical properties of substrates (e.g. water content, carbon content, molecule size), potential applications (e.g. production of energy and the additive improving soil properties), pyrolysis 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 amounts 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].

1. Methods of obtaining biochar and its properties

1.1. Methods of biochar preparation

The main methods of biochar preparation are pyrolysis, gasification, torrefaction as well as hydrothermal carbonization. These methods differ in biomass stay in the reactor and temperature range of the heating process.

Biochar can be produced by means of thermochemical biomass decomposition process in the temperature range 523-1273 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 (bio-oil) and the others so called “not condensing” gases such as CO, CO₂, H₂ (synthesis gas). 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 573-1273 K is often applied for bio-oil 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 a dozen or so 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 1273 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, 22, 23].

Gasification is a process of partial biomass burning at a high temperature (873-1473 K) for a short period of time (10-20 s). Its basic product is a mixture of gases (CO, H₂ and CO₂) called also synthesis gas as well as biochar and bio-oil. 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 (PAH) which are toxic compounds formed in high temperature reactions. 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].

Hydrothermal carbonization (HTC) is a thermal process of transforming organic raw materials into a coal-rich product under milder conditions than other carbonization techniques. Hydrothermal carbonization is conducted in the temperature range 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 [26]. 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 [27]. 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 hydrothermal carbonization results in preparation of three main products: solid substance (called hydrochar), liquid substance (bio-oil mixed with water) and a small fraction of gases (mainly CO₂). Hydrochar is formed due to hydrothermal carbonization with the 40-70 % yield [28].

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. Generally, torrefaction is treated as an initial stage of pyrolysis. Taking into account physicochemical properties those of biomass are intermediate between the crude biomass and biochar [29, 30].

1.2. 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, 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 [31].

The studies carried out on the pistachio *Pistacia vera* shells by Lua et al. [32] 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 1073 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 [32].

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 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 to other materials [33]. Pyrolysis temperature has a significant effect on the yield of the prepared biochar. Uchimiya et al. [34] investigated properties of biochars obtained from cotton seeds in the function of pyrolysis temperature 473-1073 K. They observed 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 CO₂, CO, H₂ and CH₄. 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. 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. [35]. 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 [33]. 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 manure, poultry manure, digested dairy manure) and wastes (paper) and the smallest one for biochars produced from dendritic remains (hazelnut, oak, pine) [36].

Amounts of carbonates (HCO₃⁻+CO₃²⁻) contained in biochars are particularly essential for their agricultural application. For biochars obtained from corn straw at different pyrolysis temperatures the content of carbonates was different. As follows from the studies carried out by Rivka et al. [37], basicity caused by the presence of carbonates increased with the pyrolysis temperature increase. Higher contents were obtained for divalent cations.

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 to over two hours, the size of specific surface area drops which may be due to partial blockage of pores by amorphous products of decomposition [33]. 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 volatile organic compounds 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 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.

2. Application of biochars and its modifications

2.1. Application of biochars

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 [38]. However, essential application of biochar is a sorbent for removal of heavy metal ions [39, 40] and organic compounds [41, 42] from waters and wastewaters.

Due to the presence of surface functional carboxylic, hydroxyl and phenol groups containing oxygen, biochar can bind effectively impurities associated with the presence of heavy metal ions. Park et al. [39] studied the competitive sorption of Cd(II), Cr(III), Cu(II), Pb(II) and Zn(II) ions on biochar prepared from sesame. Based on the Langmuir isotherm model there were determined the maximal sorption capacity values [mg/g]: Pb (102) > Cd (86) > Cr (65) > Cu (55) > Zn (34) under the monometallic conditions and Pb (88) > Cu (40) > Cr (21) > Zn (7) > Cd (5) under the multi metallic conditions. Larger amounts of the sorption capacities were obtained for sorption of single ions compared to that of ions from mixtures. However, results from simultaneous sorption are indispensable for accurate estimation of biochar retention capability in the natural environment. Lead(II) sorption capacities were comparable for the mono- and multi metallic systems when Cu(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. Thus it can be stated that other sorbents can be replaced by biochar prepared from sesame as a cheap and abundant source of carbon which reduces costs of heavy metals adsorption.

As follows from the studies carried out by Ding et al. [40] 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 sugar cane. 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. [43]. Biochar prepared from sugar cane effectively removes Pb(II) ions from aqueous solutions.

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. The investigations carried out by Xu et al. [41] showed that such parameters 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.

Also nitrobenzene sorption using biochar prepared from lignin, cellulose and wood is an effective process. Arboreal biochar had a more developed microporous structure than biochar prepared from lignin which is a good sorbent for aromatic impurities and more advantageous compared to the other two biochars [42].

2.2. Biochar modifications.

Lately there has been observed increasing interest in the synthesis of biochars modified with magnetic molecules, chitosan, alginates and others [44–48]. Synthesis of their derivatives can improve physicochemical properties of biochar by combination of its advantages with other materials. 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. The magnetic particles such as Fe, Fe₂O₃ and Fe₃O₄ are introduced into the biochar structure by pyrolysis at high temperature or chemical co-precipitation, Magnetic biochar prepared by Fe coating of the biochar surface is characterized by large reactivity and affinity for heavy metal ions [44].

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 intra- and intermolecular hydrogen bonds in its lattice. It is characterized by biodegradability, nontoxicity, 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 [46]. 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 to 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 to 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) [45].

Efficiency of heavy metal ions removal by means of chitosan modified biochar is confirmed by the studies carried out by Zhou et al. [47]. The biochar samples were obtained from bamboo, sugar cane, 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 %.

Alginates are nontoxic and cheap natural materials widely used as gelation means for production of microcapsules and microspheres. Cui et al. [48] investigated the ability of phosphates removal by various modifications of biochar using: Mg, alginates, Mg-alginates, chitosan, Mg-chitosan. The highest sorption capacity compared with other sorbents was 23.57 mg/g in the case of magnesium and alginates modified biochar.

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, physisorption 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 environmentally and economically advantageous because of preparation from wastes.

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