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Biochar application in the mercury ions adsorption from aqueous solutions

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Abstract: Biochar is the carbon-rich product produced by thermal decomposition of organic material in anaerobic conditions or under limited supply of oxygen. The removal of pollutants from water using biochar materials is a low cost, sustainable approach for providing pure water. The adsorption of mercury ions onto pyrolyzed chicken manure, sewage sludge and rye straw was studied and compared with the adsorption of mercury ions onto commercial activated carbons of various origins and grain size. The impact of pH, biochar adsorbents amount and phase contact time on the adsorption efficiency were investigated. Tested biochars were characterized by large, porous surface area and their adsorption potential was comparable with the activated carbons.

Keywords: sustainable development, biochar, activated carbon, water treatment, contaminants removal, adsorption

JEL codes: Q530, Q200

1. Introduction

Mercury is one of the most dangerous global environmental pollutions. This metal is toxic to all living organisms. It is not biodegradable and, therefore, it remains in the environment for a very long time, and as a result it bioaccumulates (mainly in the form of methylmercury) in animal and plant tissues and moves in the trophic chain to the human body. The absorption of this hazardous substance into the bloodstream, its distribution to the entire tissues and its bioaccumulation in the

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receptive sites result in many well-recognized adverse effects, such as potent neurotoxicity, blood vessel congestion and kidney damages (Tchounwou et al., 2003: 149).

A specific nature of this metal manifests itself in a great number of forms in which it occurs and high volatility resulting in the mobility in the environment. There are two ways of mercury emission to the environment: natural way connected with volcanic exhalations and anthropogenic way much more dangerous and connected with human economic activity, including mainly fossil fuel combustion processes. Mercury released to the environment remains there and moves in different forms between its elements, polluting the air, water, sediments, soil and accumulating in living organisms.

Mercury enters aquatic ecosystems together with rainfall and snowfall and as a result of leaching of mercury from soils, run-off of rainwater to water bodies and introduction of mercury into the water environment during water transport. Domestic and industrial wastewater from plants using mercury and its compounds in production processes is another rich source of this metal.

Due to the high toxicity of mercury and its compounds, its permissible content in the environment is governed by a number of legal documents. The regulatory functions in the scope of the environmental protection are performed by the Regulations of the Minister of Environment on the maximum permissible concentrations of mercury in surface water, groundwater and industrial waste while limits of concentration in drinking water are specified by the Regulation of the Minister of Health. Specific regulations together with mercury concentration limits contained therein are presented in table 1.

Table 1. Maximum permissible concentration of mercury in water

<table>
<tr><td rowspan="12">**Mercury and its compounds**</td><td colspan="5">**Permissible concentration for surface water [µg Hg/l]**</td><td>**Legal basis**</td></tr>
<tr><td colspan="2">Annual average concentration</td><td colspan="3">Maximum permissible concentration</td><td rowspan="2">(Regulation of the Minister of Environment, 2014a)</td></tr>
<tr><td colspan="2">**0.05**</td><td colspan="3">**0.07**</td></tr>
<tr><td colspan="5">**Permissible concentration for groundwater [H] [mg Hg/l]**</td><td rowspan="4">(Regulation of the Minister of Environment, 2016)</td></tr>
<tr><td colspan="5">*Water class*</td></tr>
<tr><td>I</td><td>II</td><td>III</td><td>IV</td><td>V</td></tr>
<tr><td>**0.001*)**</td><td>**0.001*)**</td><td>**0.001*)**</td><td>**0.005**</td><td>**>0.005**</td></tr>
<tr><td colspan="5">**Maximum limit values of pollutants in wastewater **) [mg Hg/l of wastewater]**</td><td rowspan="3">(Regulation of the Minister of Environment, 2014b)</td></tr>
<tr><td colspan="2">Daily average</td><td colspan="3">Monthly average</td></tr>
<tr><td colspan="2">**0.06 – 0.2**</td><td colspan="3">**0.03 – 0.05**</td></tr>
<tr><td colspan="5">**Basic chemical requirements that should be met by water intended for human consumption [µg Hg/l]**</td><td rowspan="2">(Regulation of the Minister of Health, 2015)</td></tr>
<tr><td colspan="5">**1**</td></tr>
</table>

H – Mercury is defined as a physicochemical element the limit values of which cannot be exceeded during the determination of groundwater quality classes at the measurement point.
*) – Lack of sufficient basis for diversification of limit values in certain quality classes; the class of the highest quality among classes containing the same limit value should be taken for assessment during the classification.
**) – According to the Regulation of the Minister of Environment of 18 November 2014 on the conditions that should be met during the disposal of waste into water or ground and on substances particularly harmful to the water environment, mercury and its compounds are included in the group of substances particularly harmful to the water environment, causing the pollution of water that should be eliminated (List 1 in the Annex No. 1).

Source: Author's own elaboration based on: (Regulation of the Minister of Environment, 2014a; Regulation of the Minister of Environment, 2016; Regulation of the Minister of Environment, 2014b; Regulation of the Minister of Health, 2015).

Described above, the catastrophic effects of the mercury presence in the environment, potential fatal health consequences of mercury entering into the human bodies and connected with this restrictive legal regulations concerning the maximum concentrations of this element in the environment have contributed to report a number of studies on mercury removal from aqueous solutions. Many of the techniques used for this purpose include precipitation (Fulbright et al., 1997: 373; Blue et al., 2010:1326), coagulation (Henneberry et al., 2011:631; Nanseu-Njiki et al., 2009: 1430), cementation (Ku et al., 2002: 721; Anacleto and Carvalho, 1996: 385), ultrafiltration (Huang et al., 2015: 1; Han et al., 2014: 310), solvent extraction (Fábrega et al., 2016: 1; Reddy and Francis, 2001: 839), photocatalysis (Byrne and Mazyck, 2009: 915; Litter, 2009: 37), ion exchange (Oehmen et al., 2014: 65), adsorption (Santana et al., 2016: 293; Huang et al., 2016: 1) and various modifications and combinations of these methods (Byrne and Mazyck, 2009: 915; Chiarle et al., 2000: 2971).

The adsorption process is one of the simplest and the most effective technologies used to remove different forms of mercury from water and wastewater, especially in case of the treatment of water containing trace amounts of this element.

Activated carbons have been widely used adsorbent in the removal of mercuric ions from aqueous solutions. They have been proven to be effective adsorbents due to their developed internal pore structure, huge surface area and the presence of surface functional groups (Lu et al., 2012: 8247). Thermal and chemical treatment can modify the pore structure and the chemical nature of the activated carbon for the better mercury adsorption (Lu et al., 2014: 69). For example, sulfurized activated carbons (SACs) are modified sorbents with high affinity toward mercury. The equilibrium mercury adsorption capacity of activated carbon modified by dimethyl disulfide was very high, much more larger than typical values of adsorption capacity activated carbon without modification (Asasian and Kaghazchi, 2015: 2511).

Activated carbon is an adsorbent commonly used to remove heavy metals including mercury. However, due to high costs of production of activated carbon, the search for alternative, easily available and cheap adsorbents has become an essential issue. Sorption processes carried out with the use of natural resources or re-use of raw materials being potential waste are worth noting from the ecological and economical point of view. There are many studies which promote the use of waste-derived activated carbons or generally waste derived adsorbents (Agarwal et al., 2010: 1155; Kaghazchi et al., 2010:368).

Mixture of licorice residues and pistachio-nut shells activated by zinc chloride (Mix-ZC) using as an mercury adsorbent is described in the paper (Asasian et al., 2012: 283). It was established that Mix-ZC is an efficient adsorbent to remove mercury strongly from aqueous solution in less than 30 minutes. It was also determined that micro and mesopores are responsible for physical adsorption of mercury and the oxygen functional groups on the carbon play an important role in the process of chemisorption.

In recent years, many studies have been devoted to investigate the application of biochar for pollutants removal from aqueous solutions (Mohan et al., 2014: 191; Ahmad et al., 2014: 19).

Biochar can be defined as some fine-grained, porous solid rich in elemental carbon, obtained through oxygen-free thermal treatment of plant biomass and organic waste, as a result of which, apart from the solid product, a number of liquid and gaseous products of high calorific value are obtained depending on the conditions of the process (Korzyści środowiskowe i ekonomiczne…, 2014). As a result of the oxygen-free pyrolysis process, chemical properties of carbon contained in the biomass change, thanks to which the product that is more resistant to microbial degradation than the primeval material is obtained (Bis, 2012). Raw materials used for the production of biochar are, *inter alia*, agricultural waste, sewage sludge and animal faeces which after the high-temperature thermal treatment can be re-used. Such activities reduce the amount of waste deposited in landfills and, therefore, they comply with the sustainable development principle constituting a fundamental element of the environmental policy of EU member states, including Poland. Moreover, biochar demonstrates a highly developed surface of the internal structure of pores in comparison with the starting raw material, due to which it is a desirable adsorbent (Bis, 2012).

Due to the wide range of applications of biochar, it may be the answer to a number of currently existing problems in the scope of environmental protection, such as the management of biodegradable waste and sewage sludge, the improvement of soil properties, alternative methods of obtaining energy and the stabilization of climate changes through the sequestration of carbon in the soil (Malińska, 2012: 387). The Ithaka Institute from Switzerland indicates even 55 possible applications of biochar in various areas of life (Schmidt, 2012: 286).

The technologies of thermal processing of biomass, biowaste or sewage sludge into biochar as well as its potential use in the industry, power industry or agriculture attract growing attention. The unique properties of biochar make it particularly attractive from the point of view of the achievement of sustainable development goals according to which the needs of the present generation should be satisfied in such a way so as not to harm the environment and in such a way that the future generations could use the same natural environment as we do. The EU policy focusing on the implementation of the principles of sustainable development emphasises the need to reduce the exploitation of natural resources, to use technologies processing waste effectively and to develop new biodegradable and environmentally friendly products. Due to the wide range of applications of biochar, the ways of production, ensuring the reduction of waste generation, and its economic attractiveness, this product meets the expectations of the sustainable development policy.

In the recent years, due to the significant sorption potential of biochars, great attention has been given to the research on the use of biochar to remove pollutants from aqueous solutions. The researchers search for adsorption materials which are an alternative to currently used and expensive activated carbons and ion exchangers in processes of adsorption and removal of harmful pollutants, including mercury compounds, from industrial wastewater (Lloyd-Jones et al., 2004: 301; Asasian et al., 2012: 283; Kong et al., 2011: 12116). Low production costs and high binding capacity of pollutants are an important criterion for choosing this type of adsorbents.

Biochar can be a desirable adsorption material thanks to the large availability of raw materials necessary for the production, low production costs and favourable physiochemical surface properties. A lot of tests confirm high capacities of biochar to remove pollutants from aqueous solutions (Paranavithana et al., 2016: 1).

Moreover, biochar which is rich in ammonia, nitrates and phosphates is a perfect fertilizer characterized by slow release of minerals necessary to fertilize soils. Furthermore, biochar used in the adsorption process may contain a lot of nutrients valuable to soils and that is why, it is possible to re-use it as a fertilizer (Yao et al., 2011: 501; Yao et al., 2013: 1).

However, in spite of so many advantages and significant application potential of biochar, there are no regulations concerning its application in the Polish law. The development of standards for the assessment of the quality of biochar as a market product and its safe use is a necessary action that should be taken in order to develop biochar technologies. The Delinat Institute from Switzerland developed detailed guidelines and recommendations concerning the requirements of the production of biochar in the scope of raw materials used for the production of biochar, pyrolysis process and parameters that should be met by the obtained product. The fulfilment of the criteria contained in this elaboration entitles an entity to obtain the European Biochar Certificate (EBC) (European Biochar Certificate-Guidelines for a sustainable production of biochar, 2012).

The main aim of this study is determination of biochars adsorption potential towards mercury ions dissolved in the aqueous solutions and compare their adsorption capacities to activated carbons.

2. Materials and methods

Biochars tested for adsorption properties were produced, using testing installation of pyrolysis of biomass and biomass waste based on the German technology developed by WSK Anlage GmbH. The pyrolysis of three agricultural waste (chicken manure – BW1, sewage sludge – BW2, rye straw – BW3) was carried out at the temperature 500 °C, as a result of which biochars having various properties were obtained. The general chemical analysis of biochar samples was carried out. The elementary composition of samples (C, H, N, S) and the analysis of the TOC (Total Organic Carbon) content were determined using the high temperature combustion method by an elemental analyser. The heat of combustion was measured with the use of the calorimetric method. All parameters were determined based on the guidelines of the EBC (European Biochar Certificate-Guidelines for a sustainable production of biochar, 2012).

Tested samples of biochar were compared with activated carbon, which was a commercially available granular activated carbon produced using the gas and steam method from different types of raw materials and having different graining:

- granular activated carbon containing grains of size 0.6-2.4 mm, produced from hard coal (WA1),
- granular activated carbon containing grains of size 0.75-2.0 mm, produced from hard coal (WA2),
- granular activated carbon containing grains of size 0.6-2.4 mm, produced from coconut shells (WA3).

Both types of materials, i.e. biochar and activated carbon, were tested to determine their adsorption capacities for mercury compounds presented in aqueous solutions.

The tests of adsorption of mercury from aqueous solutions were conducted for a batch of several samples. The basic solution of known mercury content (40 mg/L) was prepared by dissolving 54.35 mg of mercury (II) chloride in 1 litre of deionised water. Mercury chloride is one of the most available inorganic mercury compounds that are freely soluble in water environment. All tests were carried out at ambient temperature, using the static test method and a laboratory shaker working with the following speed 160 rpm. The experiment was conducted by adding 0.1; 0.3 and 0.5 g of the adsorption material to 100 mL of the previously prepared solution of mercury chloride.

In order to determine the influence of pH on adsorption capacities of adsorbents, a separate batch of samples was prepared; the solution of mercury chloride of a specific pH was added to weighted portions of adsorbents (0.5 g). The reaction of the solution was adjusted by adding 0.1M HCl and 0.1M NaOH. The impact of pH on adsorption efficiency was investigated in pH range of 1-12. The pH measurements were carry out after equilibrium time of adsorption was defined, i.e. 16 hours for biochars samples and 8 hours in case of activated carbons samples.

The batch of samples was shaken for 2 hours till the adsorption equilibrium was reached. The final concentration of mercury in these solutions was determined using the atomic absorption spectrometry method with the wavelength of 254 nm (LECO, AMA 254). In case the equilibrium studies, the mercury concentration was measured every hours till the adsorption equilibrium was reached. The samples were analysed twice; the presented results are the average of these two simultaneously conducted analyses. The degree of adsorption of mercury by the adsorbent was expressed by means of the adsorption efficiency calculated according to the following formula:

$$\%S = \frac{(C_0 - C_k)}{C_0} \cdot 100 \qquad [\%],$$

where:

C_0 – output concentration of mercury, mg/L,

C_k – concentration of mercury after the process of adsorption, mg/L.

The capacity of the adsorption was presented according to the following formula:

$$q_t = \frac{(C_0 - C_k)}{m} \cdot V \qquad [\text{mg/g}],$$

where:

V – volume of the mercury chloride solution, L (0.1 L),

m – mass of the adsorbent, g.

3. Results and discussion

Parameters of biochar tested with the use of the spectrometry method are presented in table 2. The hydrogen-total organic carbon ratio (H/TOC) is an important carbonization rate and it determines the stability of biochar. Its values change to a large extent and they depend on the type of the raw material and the conditions of the pyrolysis process (Schimmelpfennig and Glaser, 2012: 1001).

It is assumed that the H/TOC value exceeding 0.7 shows that the process was not conducted under pyrolytic conditions or signalises any irregularities of the pyrolysis (European Biochar Certificate-Guidelines for a sustainable production of biochar, 2012). Tested biochar has H/TOC ratios at the level of 0.06-0.12, which confirms that the process proceeded smoothly.

Table 2. Parameters of biochars

Property	Unit	BW1	BW2	BW3
Heat of combustion	kJ/kg	17631	17890	21869
Calorific value		16779	16882	21020
C	%	48.7	42.1	62.0
H		2.23	4.52	3.47
N		0.130	4.200	1.250
S		0.97	0.40	0.10
Cl		1.371	0.365	0.836
Total moisture		2.9	1.1	1.2
Analytical moisture		1.0	0.8	0.7
TOC		39.1	36.8	60.5
H/TOC		0.06	0.12	0.06
Ash content		34.7	43.8	18.7

Source: Author's own elaboration based on the research carried out by laboratory workers in ICiMB Division in Opole.

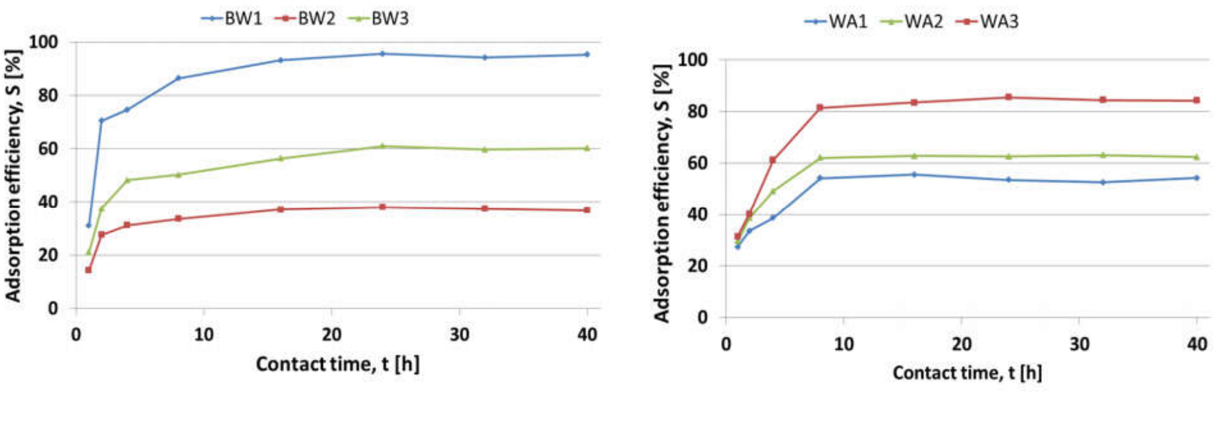
Biochars produced from chicken manure and sewage sludge are characterized by not too high value of the heat of combustion and calorific value with a significant fraction of the ash content. It is connected with a significant content of mineral substances in such raw materials which constitutes the so-called ballast. When using the product for power industry purposes, the increase in the mineral substance content decreases the calorific value, which contributes to the decrease in the effectiveness and thermal efficiency of furnaces and to the need to dispose of post-process residues in the form of large amounts of ash. In case of biochar obtained as a result of the pyrolysis of rye straw, the increase of calorific parameters can be observed with a significantly smaller fraction of ash in the product.

3.1. Effect of contact time

The time of contact of mercury compounds with the surface of the adsorbent significantly influences the efficiency of the adsorption process. In case of the use of both biochar adsorbents and activated carbon adsorbents, the amount of mercury adsorbed on the surface of adsorbents increased with time. The efficiency of adsorption on the surface of biochar reached the maximum value after sixteen hours of contact with the aqueous solution while the adsorption on activated carbon reached the maximum efficiency after eight hours of contact with the surface of the adsorbent.

A longer time of adsorbent surface contact with the adsorptive did not contribute to its further removal from the solution. It means that the amount of the substance desorbing from the adsorbent remained in the state of dynamic equilibrium with the amount of the absorbing substance. The amount of mercury ions adsorbed at the equilibrium time determined the value of the maximum capacity of the adsorbent under given conditions. In case of biochar used as adsorbents, these values amounted to 9.4, 3.1 and 6.2 mg/g of the adsorbent, accordingly for the biochar produced from chicken manure, sewage sludge and rye straw, and to 5.3-8.5 for activated carbon. The maximum adsorption capacity corresponding to 96% of the adsorption process efficiency was demonstrated by biochar produced from chicken manure. The increase in the adsorption efficiency with time is presented in figure 1.

Figure 1. Effect of contact time on the efficiency of the adsorption of mercury ions, a) biochar, b) activated carbon



Source: Author's own elaboration.

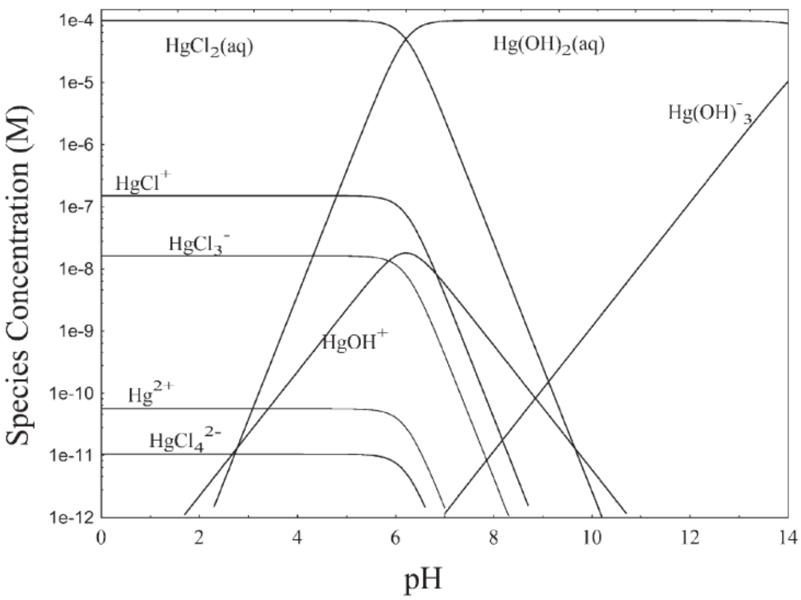
3.2. Effect of pH

The pH value plays an important role in the adsorption process. It influences the value of the surface charge of the adsorbent as well as speciation forms of metals in the solution. The speciation diagram of $1 \cdot 10^{-4}$ M of mercury chloride is presented in figure 3.

As it appears from the speciation diagram of $1 \cdot 10^{-4}$ M $HgCl_2$ solution, mercury occurs almost in 100% in the form of $HgCl_2$(aq) within the pH range between 1 and 5. In case of a higher pH value, mercury ion adsorption capacities were determined through the test of a batch of samples under different pH conditions (1-12).

The adsorption of Hg(II) from aqueous solutions with the use of activated carbon and biochar depends on the pH of the solutions and increases as the pH of the solution decreases.

Figure 2. Speciation diagram for 1·10-4M $HgCl_2$ in aqueous solution

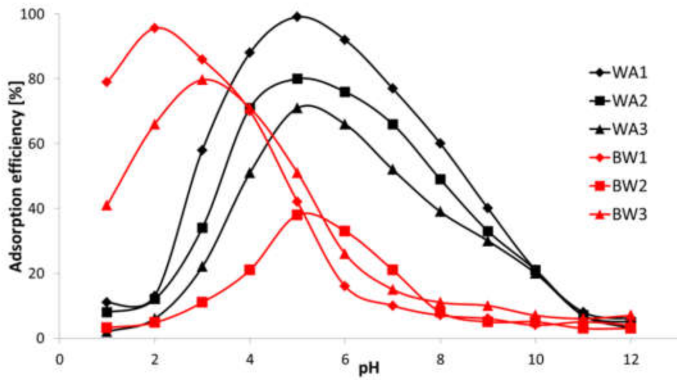


Source: (Lloyd-Jones et al., 2004: 301).

However, the contaminant removal efficiency depends on the type of the adsorbent. The adsorption of mercury on the basis of activated carbon demonstrated the highest efficiency at the pH value close to neutral (Figure 3). All of the analysed activated carbons demonstrated higher mercury ion adsorption capacity at pH=5. The activated carbon WA1 adsorbed the largest amount of mercury ions. The adsorption process did not proceed effectively in a very acidic pH due to the significant content of H_3O^+ ions in the solution which competed with Hg^{2+} cations for the place in active centres, which resulted in the decrease of the available adsorption surface.

However, in case of biochar, the highest mercury ion adsorption efficiency (96%) was obtained for biochar produced from chicken manure (BW1) at pH=2. The acidic medium also favoured the adsorption of mercury on the surface of biochar produced from straw (BW3). Sewage sludge-based biochar in turn demonstrated slightly higher adsorption capacities at pH 5. The decrease in the adsorption in the neutral and alkaline medium can mean that $HgCl_2$(aq) is the preferred form of mercury in the adsorption process; pursuant to the data presented in figure 2, it dominates in the solution up to the value of pH=5.

Figure 3. Effect of pH on the amount of mercury compounds adsorbed on the surface of adsorbent

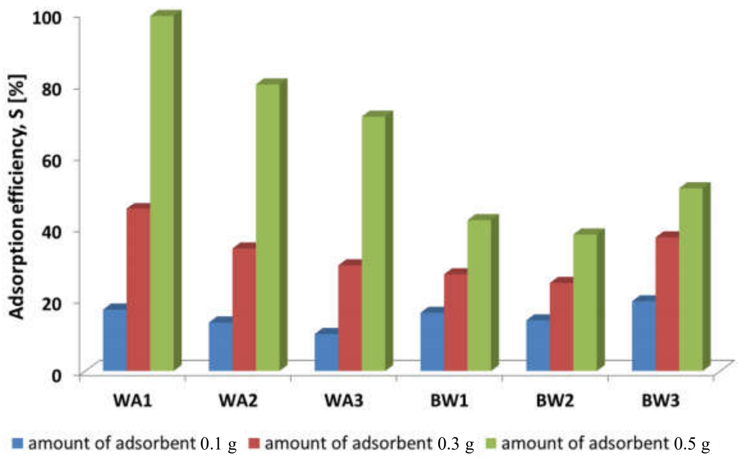


Source: Author's own elaboration.

3.3. Effect of the adsorbent amounts

In case of the use of biochar and activated carbon as adsorbents, the adsorption efficiency increased with the increase in the amount of the adsorbent. The adsorption efficiency values fluctuated between 10.3 and 19.4% for the amount of the adsorbent equal to 0.1g/100 ml of the solution, between 24.5 and 45.2% in case of the amount of the adsorbent equal to 0.3g/100 ml of the solution and between 38 and 99% in case of using adsorbent weighted portion equal to 0.5g/100 ml of the solution (Figure 4).

Figure 4. Adsorption efficiency depending on the amount of the adsorbent



Source: Author's own elaboration.

4. Conclusion

Biochar shows a significant adsorption potential towards mercury compounds in aqueous solutions, comparable with adsorption capacities of activated carbon. The adsorption efficiency of biochar mostly depends on the type of the biochar used, the raw material used for its production and on the conditions in which the adsorption of mercury compounds occur. The pH of the aqueous solution, the amount of biochar used as an adsorbent and the contact time of biochar with the removed adsorptive are crucial for the adsorption process.

The best values of mercury adsorption on biochars were obtained for 16 hours of contact with contaminated solution, while the equilibrium contact time with the surface of activated carbons was only 8 hours. The best mercury removal degree values were obtained in an acidic or light acidic environment. The pH values characteristic for the best adsorption efficiency were specific for every biochar, i.e. 2 for the BW1, 5 for the BW2 and 3 for the BW3. For comparison, all of the analysed activated carbons exhibit higher mercury adsorption capacity at pH=5.

Activated carbons are well-known adsorbents, suitable for the removal of heavy metals, including mercury. However, high cost of this materials is still ab important problem, which could be solved by using waste-derived adsorbents to diminish the cost of their production.

Due to the porous structure of biochar, the availability of raw materials for its production and the possibility of re-using generated biodegradable waste, the use of biochar as an adsorbent is a favourable, economic and ecological solution complying with the principles of sustainable development.

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Zastosowanie biowęgla w procesie adsorpcji jonów rtęci z roztworów wodnych

Streszczenie

Biowęgiel zdefiniować można jako bogaty w węgiel produkt otrzymany poprzez termiczny rozkład materii organicznej w warunkach beztlenowych lub z nieznacznym udziałem tlenu. Usuwanie zanieczyszczeń z wody z zastosowaniem biowęgla stanowi opłacalne ekonomiczne, zgodne z założeniami zrównoważonego rozwoju rozwiązanie. W pracy analizowano stopień adsorpcji jonów rtęci na pirolizowanych odpadach organicznych pochodzących z kurzeńca, osadu ściekowego oraz słomy żytniej. Wyniki badań zestawiono z potencjałem adsorpcyjnym węgli aktywnych o różnym pochodzeniu i uziarnieniu. Określono wpływ pH, ilości dodawanych adsorbentów oraz czasu kontaktu adsorbenta z adsorptywem na wydajność procesu adsorpcji. Badane biowęgle charakteryzowały się dużą powierzchnią właściwą, a ich potencjał adsorpcyjny był porównywalny z potencjałem węgli aktywnych.

***Słowa kluczowe**:* zrównoważony rozwój, biowęgiel, węgiel aktywny, oczyszczanie wody, usuwanie zanieczyszczeń, adsorpcja.