Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water

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HIGHLIGHTS

- Lab-prepared biochar was better than commercially available one.
- Adsorption was correlated with O-containing functional groups on the biochar.
- Efficiency of metal removal was depended on initial pH of solution.
- Adsorption was affected by presence of chlorides and nitrates in the solution.

ARTICLE INFO

ABSTRACT

The goal of the presented work was the evaluation and comparison of two biochars (produced from *Sida hermaphrodita* – BCSH/laboratory produced and from wheatstraw – BCS/commercial available) to adsorb heavy metal ions (Cd(II), Cu(II) and Zn(II)) from water. Kinetics of the sorption as well as sorption isotherms, the influence of solution pH and interfering ions were investigated. Different physico-chemical properties of biochars had the great influence on adsorption capacity. The greater adsorption efficiency was observed for BCSH than for BCS in the case of all investigated metals. The adsorption efficiency of BCSH was correlated with higher content of carbon and oxygen, what is equal with higher content of polar-groups on the BCSH surface e.g., –COOH. Furthermore, the molar ratio of O/C as well as polarity index (which was higher for BCSH) was also important parameters.

1. Introduction

Increasing industrialization has exerted substantial pressure on the environment since the last century. The global emission of heavy metals, especially of Cd, Cu, and Zn, has become a serious problem because of the toxicity of these metals toward living organisms. In contrast to organic contaminants, the abovementioned heavy metals are nonbiodegradable and persist for a long time in ecosystems, especially in soils. Moreover, these substances tend to be accumulated by a variety of organisms, animals, and plants, and they are also toxic or carcinogenic when their concentrations exceed certain tolerance levels. The wide usage of heavy metals such as Cd, Cu, and Zn in various industries, e.g., in mining operations, fertilizer production, battery manufacture, and tanneries, is responsible for their direct or indirect discharge as wastewaters into the environment. This industrial discharge is the major cause of groundwater and soil contamination.

Because of the negative influences of these contaminants, their removal from wastewaters and soil has become a crucial issue, and a number of purifications methods have been applied. Conventional methods for the removal of heavy metal ions from wastewater or contaminated soil are based on ion exchange processes, chemical precipitation, separation through membranes, electrochemical techniques, and adsorption (Fu and Wang, 2011; Mohan et al., 2014). However, many of those methods are expensive because they require specialized reagents and apparatus, and they may also coproduce a large quantity of waste. Taking into account the above drawbacks, the removal of heavy metal ions from large volumes of polluted water or soil should be achieved using the immobilization route via adsorption onto low-cost materials (Mohan et al., 2014). Currently, a large variety of carbonaceous materials are used for the removal of heavy metal contaminants. Properties such as high surface area and large micropore and mesopore volumes make activated carbon (AC)

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the most commonly used material in adsorption processes. Nowadays, however, the costs of coal-based AC are increasing because of the depletion of commercial sources. Recently, because of the wide variety of low-cost sorbents and the potential financial rewards, adsorption has become the most frequently used method for the separation of metal ions from aqueous solutions. The most popular sorbents used are carbon-based materials and their complexes (Barczak et al., 2015; Gupta et al., 2015). These materials have great advantages such as a large sorption capacity, a developed internal pore structure, a large specific surface area, the presence of wide varieties of functional groups on the surface, and readily achieved modification. Therefore, researchers are searching for new low-cost adsorbents for the removal of heavy metal ions from wastewater.

Researchers have recently focused on biochar (BC) as a novel material for the removal of heavy metals (Cao et al., 2009; Frišták et al., 2015; Mohan et al., 2014; Qiu et al., 2008). Natural materials such as plant waste are widely available in large quantities and they also have great potential as low-cost and, most importantly, environmentally friendly adsorbents. The production of biomass-derived materials also has several positive effects on environmental conditions and climate protection (Roberts et al., 2010). Nowadays, substantial attention is being paid to the application of BCs not only from the agro-environmental perspective but also in the sorption processes to remove inorganic and organic contaminants (Ahmad et al., 2014; Mohan et al., 2014). Biomass-derived adsorbents have properties similar to those of AC; e.g., an extensive surface area, a high degree of porosity, and a surface carbon matrix. This similarity suggests that AC could be replaced with BCs.

In BC-based materials, the sorption of metal ions depends on the material's content of functional groups containing oxygen, including phenolic, carboxyl, and hydroxyl groups. These materials are used as low-cost sorbents of heavy metal ions and organic pollutants (Cao et al., 2009; Chen et al., 2011; Kołodyńska et al., 2012; Park et al., 2013; Wang et al., 2015; Xu et al., 2014).

However, before the application of BCs as a soil amendment to stabilize and reduce the potential toxicity of heavy metal ions, these materials should be tested in model aqueous solutions. Therefore, the present work assesses the efficiency of two biomass-derived materials, which were obtained from Triticum straw and *Sida hermaphrodita* under different conditions, as sorbents for the removal of Cd(II), Cu(II), and Zn(II) ions from wastewater. Industrially and lab-produced BCs were compared. The influence of BC properties on the adsorption abilities was studied in detail, including the degree of carbonization, polarity, and presence of polar groups on the surface. Because the specific surface areas of BCs are nearly uniform, S_{BET} was not considered. The studied BCs, which do not differ significantly in S_{BET} but do exhibit different oxygen contents on their surfaces, were chosen based on the notion that the adsorption capacity for heavy metals is dependent on the amount of oxygen present on the surface and not on the surface area itself.

During the study, batch sorption experiments were conducted to investigate the influence of operating factors such as solution pH, contact time, initial concentration of studied heavy metal ions, and the presence of interfering ions in the solution on the adsorption capacity. XPS was used to identify the forms of metal ions bonded with the BC surface and to elucidate the mechanism of the studied process. The reusability of biomass-derived materials was also investigated.

The mechanisms of heavy metal removal with biochar might be attributed to electrostatic interaction, ionic exchange, chemical precipitation, and complexion with functional groups on BC surface according to recently published review papers (Tang et al., 2013; Zhang et al., 2013; Ahmad et al., 2014; Mohan et al., 2014). To date, only a few publications have focused on the aspects of adsorption other than kinetics, isotherms, and the influence of pH. Because of the possible future applications of the examined BCs in environmental samples, the current study also addressed other parameters such as the influence of interfering ions, in the form of nitrates and chlorides, which are characterized by high abundance in environmental samples, on the adsorption ability of BCs. Additionally, the present work presents a novel desorption study. BCs are known as low-cost adsorbents with regard to their production, but the possibility of using BCs for repeated adsorption steps should be also determined.

2. Methods

2.1. Adsorbents

The adsorption properties of two different biochars were studied, industrially (BCS) and lab-prepared (BCSH). The BCS produced from wheat straw was obtained from Mostostal Sp. z.o.o. (Wrocław, Poland). The limited-oxygen conditions (1–2%) and the temperature of pyrolysis range 650–700 °C (maximal combustion) were applied. The second biomass-derived material – BCSH was prepared from *S. hermaphrodita* in the furnace of own-construction at the temperature of 700 °C. The desirable temperature was kept constant for 4 h. Anaerobic conditions were obtained by the constant flow of nitrogen of 630 mL N_2/min controlled by the gas flow regulator (BETA-ERG, Poland).

The standard methods were used for studying the physico-chemical properties of biochars. The pH of each material was measured potentiometrically using 1 mol/L potassium chloride after 24 h in the liquid/solid ratio of 10. The TOC-VCSH (SHIMADZU) with Solid Sample Moduls (SSM-5000) was applied for the total organic carbon content (TOC) determination. The total nitrogen (N_t) was measured by using the Kjeldahl's procedure without the application of Dewarda's alloy (Cu–Al–Zn alloy-reducer of nitrates and nitrites). FT-IR/PAS spectrum of the biochar sample was recorded by means of the Bio-Rad Excalibur 3000 MX spectrometer equipped with photoacoustic detector MTEC300 (in the helium atmosphere in a detector) at RT over the 4000–400 cm^{-1} range at the resolution of 4 cm^{-1} and maximum source aperture. The spectrum was normalized by computing the ratio of a sample spectrum to the spectrum of a MTEC carbon black standard.

A stainless steel cup (diameter 10 mm) was filled with biochar sample (thickness < 6 mm). Interferograms of 1024 scans were averaged for the spectrum. The low-temperature (77.4 K) nitrogen adsorption–desorption isotherms were used for identify the structure of studied biochars. The data were obtained with Micromeritics ASAP 2405 N adsorption analyzer. In the base of the standard BET method the specific surface areas S_{BET} were calculated. The carbon, hydrogen and nitrogen content was determined with the CHN Elemental Analyzer (Carlo-Erba NA-1500) via high-temperature catalyzed combustion follow by infrared detection of resulting CO_2, H_2 and NO_2. The X-ray photoelectron spectroscopy was used for surface elemental composition characterization.

2.2. Chemicals

The initial standard stock solutions of Cd(II), Cu(II) and Zn(II) ions (each of 1000 mg/L) were prepared by dissolution of respectively $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ powder (POCH, Gliwice, Poland) in a redistilled water. The calibration curves of determined ions were established using the standard solutions of Cd(II), Cu(II) and Zn(II) prepared in 0.5 mol/L HNO_3 by dilution from stock solution each of 1000 mg/L (Merck,