THE RESPONSE OF ARTIFICIAL AGING TO SORPTION PROPERTIES OF BIOCHAR FOR POTENTIALLY TOXIC HEAVY METALS

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Abstract: This paper evaluates the effect of simulated conditions of artificial aging on sorption capacity of two types of biochar. These were produced by slow pyrolysis from different feedstock - beech wood chips (BC A) and garden green waste residues (BC B). Cadmium served as a model for potentially toxic metals. Twenty freeze-thaw cycles were used to simulate physical aging. The determination of biochar physico-chemical properties showed main changes in CEC and SA values of aged sorbents. The maximum sorption capacities of aged BC A sorbent were higher by about 26 % and aged BC B sorbent by about 20% compared to Q_{max} of non-aged biochar. Q_{max} of aged BC B peaked at 9.4 mg g^{-1} whereas BC A sorbed significantly less Cd. FT-IR analyses confirmed the changes in structural composition and content of functional groups on biochar surfaces. The artificial physical aging model was assessed as an efficient tool for investigation of natural weathering conditions.

Key words: biochar, artificial aging, sorption, cadmium

1. Introduction

Soil contamination with potentially toxic heavy metals (PTHM) usually Cd (cadmium), Cr (chromium), Cu (copper), Pb (lead), Ni (nickel) and Zn (zinc), is one of the main concerns in environmental protection due to their non-biodegradability and eco-toxicity, even at trace concentrations (O'CONNELL *et al*., 2008). Various technologies have been developed for removing metals from liquid wastes, such as extraction, coagulation, precipitation, reduction, separation with membrane systems, ion exchange and reverse osmosis (FRIŠTÁK *et al*., 2013; XIONG *et al*., 2015) and for immobilizing PTHM in soils, a process of adding metal-sorbing amendments is utilized (FRIESL *et al*., 2009). Sorption separation as a proven and practical treatment method leads to significant metal recovery and simple process realization. For heavy metal sorption removal from aqueous waste solutions a wide range of heterogeneous biological and non-biological materials can be used such as algae (KADUKOVÁ and HORVÁTHOVÁ, 2012), moss (PIPÍŠKA *et al*., 2010), dried sewage sludge (FRIŠTÁK *et al*., 2014a), synthetic zeolites (REMENÁROVÁ *et al*., 2014), natural zeolites (CHMIELEWSKA, 2013) or chitosan (MI *et al*., 2015). Biochar represents a solid by-product from biomass pyrolysis which is the thermal decomposition of organic materials at elevated temperatures (< 1000 °C) with little or no available oxygen. Theoretically, biochar could be produced from any carbon-rich biomass

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(LEHMANN and JOSEPH, 2009). This pyrolysis product has attracted attention mainly for its potential use as a soil amendment to improve soil quality (KARER *et al*., 2013; KLOSS *et al*., 2014). Biochar can be characterized by many important physico-chemical properties, mainly for rich porosity, high exchange capacity, water holding capacity, surface area, low bulk density, which play decisive roles in a wide range of agricultural or soil remediation applications. Sorption separation of toxic metals from aqueous or soil solutions provides a new field for biochar utilization as sorbent and in-situ stabilization tool. Generally, sorption capacities of sorbents can be modified by physic-chemical effects. Abiotic and/or biotic processes (so-called aging) affect the main characteristics and the strength of PTHM sorption. Biological, chemical and physical aging have been recognized to contribute to artificial aging (HALE *et al*., 2011). However, the studies to investigate the change in biochar sorption capacity under different temperature conditions over time of storage are scarce and limited.

Based on these scenarios, the main aim of this paper was to simulate the conditions of physical biochar aging and to assess the influence of different biochar feedstocks and aged sorbent characteristics on the Cd sorption capacity as a model of PTHM.

2. Material and methods

2.1 Biochar production

Biochar samples were produced in slow pyrolysis process from two different feedstocks: beech wood chips (BC A) and garden green waste residues (BC B). Both materials had maximum dimensions 2 cm x 2 cm x 2 cm and had been pyrolyzed at a highest treatment temperature of 500°C and residence time 120 min in a rotary furnace (Fig.1). For ensuring inert and uniform heating conditions, nitrogen was used as flush gas. The biochars were ground and sieved to particles with size < 2 mm. Sorbents were pretreated by rinsing in deionised water with conductivity < 0.4 μS cm^{-1} to remove the ash impurities.

2.2 Biochar characterization

The active and potential pH values of BC A and BC B were measured after stirring the biochars with deionized water and 1.0 mol L^{-1} KCl (ratio 1:2.5) for 1 h and stabilization for 1 h (inoLab pH level 2P, Weilheim, Germany). The electrical conductivities (EC) of BC A and BC B were measured in a 1:10 deionised water extracts after 24 h mixing (inoLab pH level 2P, Weilheim, Germany). The cation exchange capacities (CEC) of biochars were determined by the $BaCl_2$ method described in our previous paper (FRIŠTÁK *et al*., 2013). Surface areas (SA) were estimated by the titration method with NaOH according to MELICHOVÁ and HROMADA (2013). The total C, N and H contents of biochars were measured by an elemental analyzer (CHNS-O EA 1108, Carlo Erba Instruments, Italy). Initial concentrations of Cd, Zn and Cu in biochar samples were determined after aqua regia digestion by ICP-MS (Perkin Elmer, Elan DRCe 9000). The intra-structures of BC A

and BC B sorbents and surface structure analysis were obtained by scanning electron microscopy (SEM) using electron microscope JEOL JSM7600F (Japan). The analyses was performed at voltage 30kV, vacuum pressure 9.0×10^{-3} Pa and magnification 250×.

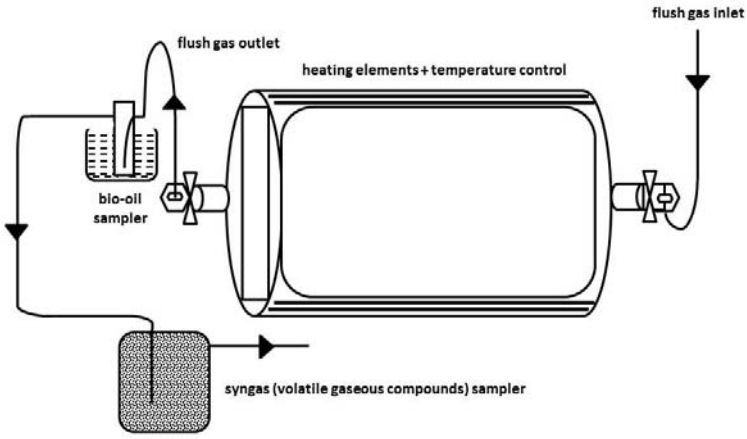

Fig. 1. Scheme of the pyrolysis reactor.

2.3 Artificial aging

For simulation of biochar artificial aging, a physical approach was used. For the sample series with freezing cycles, BC A and BC B were moved into a freezer at -18°C firstly. As a second stage, the biochar samples were then kept in an incubator at 25°C for thawing. Each of 20 freeze-thawing cycles consisted of 12 h freezing and 12 h thawing. After the last cycle, sorbents were dried at 50°C.

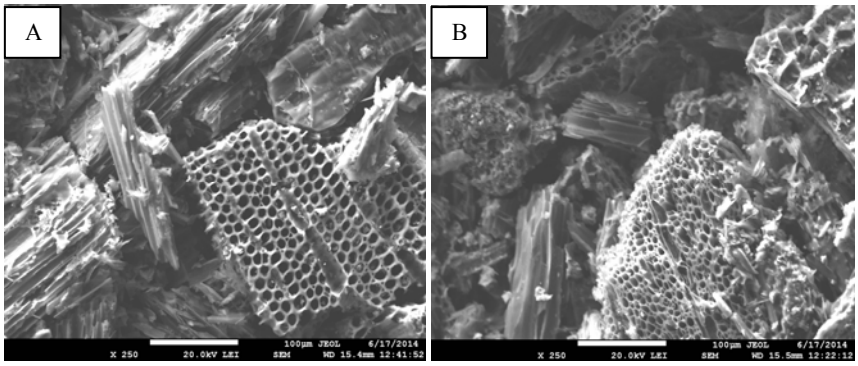

Fig. 2 SEM micrographs of BC A (A) and BC B (B) at magnitude 250 ×.

2.4 Sorption experiments

The sorption process of Cd from single component system was studied using a batch equilibration method according to the OECD guideline 106 (OECD, 2001),

modified by LAIR *et al*. (2006). 1 g of aged BC A or BC B sorbent was suspended in polypropylene centrifuge tubes filled with 20 ml of 0.01 mol L^{-1} $CaCl_2$ (pH = 5.65) and placed on a horizontal shaker for 24 h (200 rpm). The solution of $CaCl_2$ was used to ease phase separation and to keep ionic strength similar to natural soil solutions. Deionised water (<0.4 μS cm^{-1}), spiked with Cd as $CdCl_2$, was added to each tubes, resulting in a concentration range from 10 to 75 mg L^{-1} and pH 7.0±0.1. Biochar-solution ratio was 1:30. Solution pH changed from 5.65-5.50 with increasing concentration of metals. After agitation for 24 h, tubes were centrifuged (38 400 g, 15 min) and supernatant was filtered through a 0.45 μm pore size membrane filter (Schleicher and Schuell, Germany) to remove colloids from the solution. Filters were tested for retention of metals before use. Concentration of Cd in liquid phase was measured by atomic absorption spectrometry with flame atomization (FAAS, AA 400, Perkin Elmer, USA). All experiments were realized in triplicates.

Sorptions of cadmium were calculated according to Eq.1:

$$Q_{eq} = (C_0 - C_{eq}) \times V / m \quad (1)$$

where: Q_{eq} is the cadmium uptake (mg g^{-1}), C_0 is the initial liquid-phase concentrations of cadmium (mg L^{-1}), C_{eq} is the equilibrium liquid-phase concentrations of cadmium (mg L^{-1}), V is the volume (L) and m is the amount of biochar (g).

Obtained data were analysed by mathematical models with terms of Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR) isotherms (Table 1).

Table 1. Models of adsorption isotherms used to describe the sorption equilibrium of single metal system.

Adsorption model	Equation	Coefficients
Langmuir	$Q_{eq} = \frac{bQ_{\max}C_{eq}}{1+bC_{eq}}$	Q_{eq} – amount of sorbed metal at equilibrium b – isotherm coefficient characterizing affinity sorbent to metal ion in solution Q_{max} – maximum metal sorption capacity at saturated sorbent binding sites C_{eq} – metal equilibrium concentration in solution
Freundlich	$Q_{eq} = KC_{eq}^{(1/n)}$	Q_{eq} – amount of sorbed metal at equilibrium K,n – Freundlich empirical constants characterizing parameters of sorption process C_{eq} – metal equilibrium concentration in solution
DKR	$Q_{eq} = Q_m \exp\left[\frac{(RT\ln(1+\frac{1}{c_{eq}}))}{-2E^2}\right]$	Q_{eq} – amount of sorbed metal at equilibrium Q_m – monolayer maximum metal sorption capacity R – gas constant T – temperature C_{eq} – metal equilibrium concentration in solution E – sorption energy

Parameters of adsorption isotherms were calculated by non-linear regression analysis using the program MicroCal Origin 8.0 Professional (OriginLab Corporation, Northampton, USA). Mentioned program was applied also for Paired *t*-test of selected physico-chemical properties of unaged and aged biochar.

2.5 FT-IR analysis

Spectral analysis of BC A and BC B in infrared region was used to determine binding characteristics, determination of functional groups of biochar and comparison of unaged and physically aged sorbent. The surface functional groups of BC A and BC B were detected by infrared spectroscope with Fourier transformation (FT-IR) (Nicolet NEXUS 470, Thermo Scientific, USA). The spectra were recorded from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1 Characterization of biochar-derived sorbents

Both biochar samples prepared from two different feedstocks contained more than 75% of carbon (Table 2), which is among the typical reported values of other biochars produces at these pyrolysis conditions (KLOSS *et al*., 2012). The C/N ratios of biochars were 200.75 for BC A and 122.74 for BC B. LEHMANN and JOSEPH (2009) identified the C/N ratio lower than 20 as a ratio of good soil amendment. Although it is still unclear whether the C/N ratio criterion is directly applicable to biochars which do not decompose at the same rate as other organic amendments, applications of biochars with higher C/N ratios may lead to lower N uptake and a delay in N turnover in soil (PROMMER *et al*., 2014). Comparison of physico-chemical properties of BC A and BC B showed the main differences in ash content, CEC and SA values. The initial concentration of Cd was lower than LOD of analytical measurement (<0.002 mg g^{-1}) for both biochar samples.

Table 2. Physico-chemical characteristics of unaged BC A and BC B.

	BC A	**BC B**
pH‡ (H_2O)	8.78 ± 0.12	9.03 ± 0.08
EC‡ (mS cm^{-1})	0.54 ± 0.02	1.67 ± 0.05
Ash content† (%)	15.20	19.30
Density† (kg L^{-1})	0.36	0.34
CEC‡ (mmol 100 ml^{-1})	9.83 ± 0.15	12.85 ± 0.12
SA‡ (m^2 g^{-1})	27.24 ± 0.30	31.54 ± 0.27
C† (%)	80.30	79.78
H† (%)	1.60	1.59
N† (%)	0.40	0.65
C/N ratio	200.75	122.74
Cd‡ (mg g^{-1})	<0.002*	<0.002*

* concentration lower than LOD of analytical equipment
† single determination
‡ determined in triplicate (mean ± SD)

Additionally, artificial aging caused the changes of basic physico-chemical properties (data not shown). The main differences in CEC and SA values were determined. Aged BC A provided an SSA of 28.21 ± 0.09 m^2 g^{-1} and BC B 33.09 ± 0.12 m^2 g^{-1}. In comparison with CEC of unaged biochars, aged BC A had 10.01 ± 0.05 mmol 100 ml^{-1} and BC B 13.91 ± 0.08 mmol 100 ml^{-1}. The CEC and SA values are important parameters for heavy metal sorption behaviour assessment (FRIŠTÁK *et al*., 2014b). Nonetheless, Paired *t*-test (α = 0.05) confirmed the small statistical significance of obtained data for aged and unaged biochar. LEHRSCH (1998) showed the main effect of freeze-thaw cycles on soil characteristics mainly in breakdown or formation of new aggregates. Equally, ZHAO *et al.* (2013) proposed a conceptual model of the mechanisms involved into freeze-thaw cycles of soil particles. However, a mechanism of this process remains unclear for biochar as a potential soil amendment.

3.2 Effect of artificial aging on Cd sorption process

The effect of Cd initial concentration to sorption capacity of artificially aged BC A and BC B was determined within the range of 10-75 mg L^{-1}. In general, the obtained data revealed that sorption capacity increased with increasing the initial Cd concentration in the reaction solution. For description of equilibrium relationships, Langmuir, Freundlich and DKR mathematical equations of adsorption models were used. Comparison of the coefficients of determination calculated by non-linear regression analyses showed that Langmuir model fitted the cadmium sorption data for BA A and BC B better than the Freundlich and DKR model (Table 3). Frequently, the Langmuir model better describes adsorption on homogeneous surfaces, while the Freundlich model is better for heterogeneous surfaces.

Table 3. Langmuir (L), Freundlich (F) and Dubinin-Kaganer-Radushkevich (D) equilibrium parameters (± SD) for Cd sorption by aged BC A and BC B obtained by non-linear regression analysis.

Sorbent	Model	Q_{max} [mg g^{-1}]	b [L mg^{-1}]	K [L g^{-1}]	$1/n$	Q_m [mg g^{-1}]	β [mol^2 J^{-2}]	R^2
BC A	L	2.51 ± 0.12	0.08 ± 0.015	-	-	-	-	0.993
	F	-	-	0.28 ± 0.012	0.64 ± 0.017	-	-	0.979
	D	-	-	-	-	1.39 ± 0.02	$-9.58*10^{-7}$	0.867
BC B	L	9.43 ± 0.32	0.16 ± 0.019	-	-	-	-	0.996
	F	-	-	0.68 ± 0.042	0.92 ± 0.044	-	-	0.979
	D	-	-	-	-	2.19 ±0.06	$-4.72*10^{-7}$	0.866

Langmuir parameters demonstrated that the effect of freeze-thaw cycles caused increases of sorption capacity for both BC A and BC B. Values Q_{max} of BC A and BC

B were higher by about 26 % and 20% compared to Q_{max} of non-aged biochar (Table 4). HALE *et al*. (2011) showed the crucial effect of freeze-thaw cycles on structure and also sorption properties of biochar. Authors highlighted the correlation between increased SA and CEC values of aged biochar samples. In the report of YAO *et al*. (2010) a detailed simulation of geochemical weathering of biochar samples using physico-chemical methods was described. In our study, increasing sorption capacity of both aged biochar-based sorbents can be caused by several processes. Freezing alters biochar properties through various mechanisms, and has direct or indirect chemical and biological consequences as well. Freeze-thaw process significantly influences the amount and chemical forms of biochar water-extractable components and also possible reaction sites for cadmium sorption. Additionally, WANG *et al.* (2007) confirmed the crucial effect of temperature conditions on sorption and desorption of phosphorus by wetland soil and highlighted the role of altered micropores structures. Biochar as a porous material provides a huge volume of micro- and mezopores, both involved in sorption processes (FRIŠTÁK *et al.,* 2015). Freeze-thaw process can contribute to formation or damaging of these structures and thus changing the total porosity of biochar-based sorbents in terms of different water bonding and effect of liquid-solid phase.

Table 4. Comparison of maximum sorption capacities (Q_{max} ± SD) of BC A and BC B for Cd before and after artificial aging process obtained from Langmuir adsorption isotherm.

Sorbent	Q_{max} [mg g^{-1}]	
	unaged	*aged*
BC A	1.99 ± 0.19	2.51 ± 0.12
BC B	7.80 ± 0.70	9.43 ± 0.32

As illustrated in Fig. 3 and 4, FT-IR spectra of unaged BC A and BC B indicated carboxyl and hydroxyl groups were present in abundance. Similar broad peaks in FT-IR spectra were found in the study of ŠTEFUŠOVÁ *et al*. (2012) for rapeseed and wheat straw-derived biochar. These functional groups can serve as proton donors and hence the deprotonated hydroxyl and carboxyl groups can be involved in coordination of free Cd ions (LU *et al*., 2012). Artificial aging caused mainly the changes in absorption intensity at σ 3418 cm^{-1} (BC A) and σ 3415 cm^{-1} (BC B) that are responsible for stretching vibration of –OH functional groups of water, alcohols and phenols. The absorption bands at σ 1559 cm^{-1} and 1445 cm^{-1} for BC A and σ 1581 cm^{-1} and 1437 cm^{-1} for BC B after freeze-thaw cycles were changed by shifts and extensions of peak areas. The highlighted differences could be induced by the freeze-thaw processes during the artificial aging induced that caused the main changes in biochar consistency and structure.

A crucial role in this process was played by the water bonded capillary forces between biochar particles. After freeze-thaw cycles the structures for water bonding could be damaged. After the sorption of Cd by aged biochar , shifts and changes of absorption bands of C=O and C=C vibrations at wave numbers 1579 and 1445 cm^{-1} for BC A and 1581 and 1437 cm^{-1} for BC B were detected. For C-H bending at σ 1042 cm^{-1} (BC A)

and σ 1038 cm^{-1} (for BC B) only small changes in the spectra after cadmium sorption process were found.

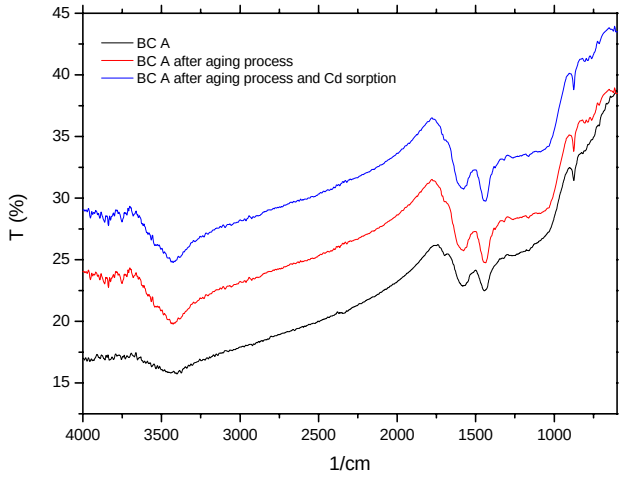

Fig. 3. Representative FT-IR spectra of unaged BC A and aged BC A before and after cadmium sorption process.

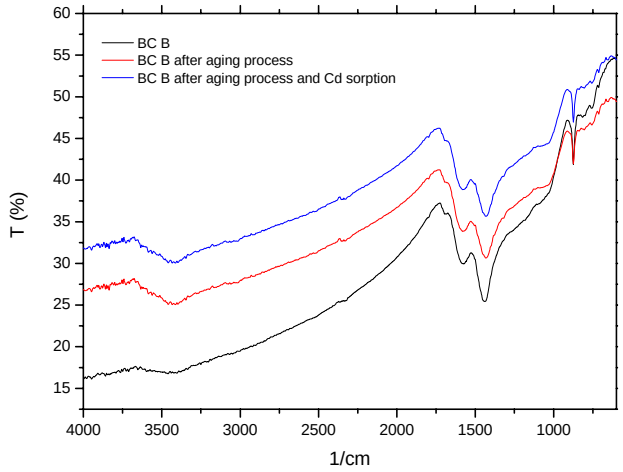

Fig. 4. Representative FT-IR spectra of unaged BC B and aged BC B before and after cadmium sorption process.

4. Conclusions

This paper illuminates the utilization of biochar as an efficient sorbent for cadmium removal from liquid waste and waste waters. Mainly, the positive effect of artificial aging by freeze-thaw cycles on sorption capacity of these biochar-based sorbents was confirmed. The maximum sorption capacities of aged BC A sorbent were

higher about 26 % and aged BC B sorbent about 20% compared to Q_{max} of non-aged biochar. The changes of temperature could lead to the structural changes (porosity) of biochar-based sorbent in terms of changes in water bonding and effect of water liquid-solid phase on biochar. However, the differences in sorption capacity of the two biochars were much larger (BC B sorbed more than three times as efficiently as BC A), demonstrating the importance of biochar feedstock material for the sorption capacity of biochar. Apparently, biochar artificial aging by freeze-thaw cycles presents a promising new model for studying weathering effects assessment which should be further investigated and compared with real-world conditions of biochar aging in a soil matrix.

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