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Effect of biochar activation by different methods on toxicity of soil contaminated by industrial activity

Michał Kołtowski[a], Barbara Charmas[b], Jadwiga Skubiszewska-Zięba[b], Patryk Oleszczuk[a,*]

[a] Department of Environmental Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland
[b] Department of Chromatographic Methods, Faculty of Chemistry, Maria Curie-Skłodowska University, Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland

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ABSTRACT

The objective of the study was to determine the effect of various methods of biochar activation on the ecotoxicity of soils with various properties and with various content and origin of contaminants. The biochar produced from willow (at 700 °C) was activated by 1) microwaves (in a microwave reactor under an atmosphere of water vapour), 2) carbon dioxide (in the quartz fluidized bed reactor) and 3) superheated steam (in the quartz fluidized bed reactor). Three different soils were collected from industrial areas. The soils were mixed with biochar and activated biochars at the dose of 5% and ecotoxicological parameters of mixture was evaluated using two solid phase test – Phytotoxkit F (*Lepidium sativum*) and Collembolan test (*Folsomia candida*) and one liquid phase test – Microtox® (*Vibrio fischeri*).

Biochar activation had both positive and negative impacts, depending on the activation method, kind of bioassay and kind of soil. Generally, biochar activated by microwaves increased the effectiveness of ecotoxicity reduction relative to non-activated biochars. Whereas, biochar activated with CO_2 most often cause a negative effect manifested by deterioration or as a lack of improvement in relation to non-activated biochar or to non-amended soil. It was also demonstrated that the increase of biochar specific surface area caused a significant reduction of toxicity of water leachates from the studied soils. Effectiveness of the reduction of leachate toxicity was weakened in the presence of dissolved organic carbon in the soil.

1. Introduction

Organic and inorganic contaminants such as polycyclic aromatic hydrocarbons (PAH) and heavy metals (e.g. As, Pb, Hg, Cd, Cr, Cu and Ni) present in the natural environment may be toxic and harmful to human health and to other living organisms (Harris et al., 2013; Jaishankar et al., 2014; Zhang et al., 2013). It is therefore necessary to struggle for the remediation of contaminated soils. Sometimes, however, due to technical problems and high costs, remediation is not possible. The lack of any efforts towards the remediation of contaminated soils can lead not only to a negative effect at the contaminated sites but also to the spread of contaminants onto areas that have not been contaminated before. It is, therefore, important to apply a universal and economically viable tool that would permit to effectively eliminate the potential risk. At present it is becoming more and more common to apply carbon adsorbents that immobilise contaminants in soils (Beesley et al., 2011; Brennan et al., 2014; Chai et al., 2012; Denyes et al., 2013; Gomez-Eyles et al., 2011). The effect of the application of adsorbents is not only a reduction of bioavailability of contaminants for living organisms, but also reduced spreading of contaminants in the environment. Another effect achieved through the limitation of bioavailability is a reduction of the toxicity of contaminants in relation to various organisms (Jośko et al., 2013; McLeod et al., 2007; Millward et al., 2005). Among the available carbon adsorbent, activated carbon (AC), characterised by large specific surface area and a high affinity to contaminants, is used on a large scale (Brändli et al., 2008; Hale et al., 2012; Hilber and Bucheli, 2010; Jakob et al., 2012; Oen et al., 2012). In recent years, an alternative for AC is biochar which is considerably cheaper (Ahmad et al., 2014) and more environment-friendly than AC. Biochar can be produced from biomass residue or other organic wastes whereas AC is mostly derived from charcoal, coal or synthetic polymers. Moreover, biochar can act as a fertilizer leading to improve the soil quality and be a source of nutrients to plants and other organisms (Shmidt, 2012). However, compared to AC, biochar is characterised by distinctly lower specific surface area (Amstaetter et al., 2012), which may significantly reduce its effectiveness in the immobilisation of organic contaminants, and indirectly also the reduction of toxicity. Nevertheless, Beesley et al. (2010) observed a reduction of phytotoxicity after the application of biochar in a soil contaminated with PAHs and heavy metals (As, Cd, Cu, Zn). Moreover,

* Corresponding to: Department of Environmental Chemistry, University of Maria Skłodowska-Curie, Pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland.
E-mail address: patryk.oleszczuk@poczta.umcs.lublin.pl (P. Oleszczuk).

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Table 1
Properties of original and activated biochars.

Biochar	C	H	N	O	Ash	H/C	O/C	(O+N)/C	S_{BET}	S_{mic}	V_p	V_{mic}
BC	69.94	2.08	1.13	19.13	7.72	0.36	0.21	0.22	11.4	4.5	0.006	0.002
BC-CO2	70.82	0.70	0.82	16.37	11.29	0.12	0.17	0.18	512.0	379.9	0.276	0.169
BC-H2O	56.86	0.59	0.37	21.68	20.50	0.12	0.29	0.29	840.6	509.3	0.577	0.225
BC-MW	73.92	0.95	0.66	8.72	15.76	0.15	0.09	0.10	443.2	258.6	0.242	0.114

C, H, N, O: elemental composition [%]; Ash: ash content [%]; H/C, O/C and (O+N)/C – molar ratios; S_{BET}: surface area [m^2/g]; S_{mic}: micropore area [m^2/g]; V_p: total pore volume [cm^3/g]; V_{mic}: micropores volume [cm^3/g].

in a study by Park et al. (2011) an addition of chicken manure biochar to a soil contaminated with heavy metals caused an increase of plant biomass and reduced heavy metals accumulation in Indian mustard. Hale et al. (2013) noted an increase of *F. candida* reproduction and decrease of *V. fischeri* bioluminescence inhibition after corn stover biochar amendment to soil. In recent years, however, a trend is observed aimed at increasing the effectiveness of biochar as a result of its activation with various methods (Han et al., 2015; Jung and Kim, 2014; Park et al., 2013; Rajapaksha et al., 2015; Vithanage et al., 2014). As can be seen from recent research (Shim et al., 2015), biochar activation may lead to an increase of its acute toxicity (in this study *Daphnia magna* was the tested organism) probably due to the increased aromaticity upon steam activation. So far, the existing studies are concerned with AC, while there is a lack of ecotoxicological data concerning the effect of application of biochar, activated with various methods, for the reduction of toxicity of soils containing industrial contaminants. In addition, studies concerning AC also indicate that it may have a negative effect on organisms. For example, an addition of AC to soil may contribute to: (1) a decrease of availability of nutrients in soil, that may be adsorbed in AC pores; (2) an inhibition of mobility of organisms through AC accumulation on their bodies, thus inhibiting the development of muscles; (3) an inhibition of nutrient intake by certain organisms, as they cannot digest assimilated particles of AC and (4) a decrease of water availability (Hale et al., 2013; Jakob et al., 2012; Jośko et al., 2013). In relation with the above, it is also important to estimate the toxicity of biochar after the activation. So far no research of this type has been conducted.

The objective of the study presented herein was to determine the effect of various methods of biochar activation (with the use of microwaves, carbon dioxide and overheated steam) on the ecotoxicity of soils with various properties and with various content and origin of contaminants.

2. Material and methods

2.1. Soils

Three different soils were collected from industrial areas. Two soils (KOK and KB) soils were sampled from the Upper Silesian Basin in southern Poland. Soil KOK was sampled from area of cooking plant (Dąbrowa Górnicza, Poland) around 10 m distance from cooking plant battery and KB soil was sampled from the same coking plant as KOK soil at an industrial waste deposit. Third soil (POPI) was sampled near a bitumen plant in the Lublin Province - east of Poland (Wólka Łańcuchowska, Poland).

The 10 subsamples (0–20 cm depth) were collected from different places in case of all of the investigated soils and thoroughly mixed. Before the sorbent amendment experiment, the soils were milled, dried at 40 °C till constant weight and sieved (2 mm). The physico-chemical properties of investigated soils are presented in supporting information (Table S1). The different soils were selected to evaluate their toxicity after biochar or activated biochar application depending on the source of soil contamination. Moreover, each soil is characterised by different properties which can also affect differently on toxicity of biochar and activated biochar.

2.2. Biochar characterization and modification

Non-activated biochar was produced by slow pyrolysis from willow (*Salix viminalis*) at a maximum temperature of 700 °C and at low oxygen content (> 2%). Biochar was characterised by 69.9%, 2.1% and 1.1% of C, H, N content respectively. The O/C, H/C and (O+N)/C molar ratio were at a level of 0.21, 0.36 and 0.22, respectively.

Biochar was activated using 1) microwaves (MW), 2) carbon dioxide (CO_2) and 3) superheated steam (H_2O). Biochars obtained after activation were named BC-MW (MW activation), BC-CO_2 (CO_2 activation) and BC-H_2O (H_2O activation). The microwaves activated biochar was activated in a high pressure microwave reactor (NANO 2000, Plazmatronika, Poland) under an atmosphere of saturated steam (heating time – 30 min, temperature - 200 °C, power of reactor – 100% (300 W), pressure – from 42.5 to 45.6 bar; cooling time – 10 min). The activation of biochar by a carbon dioxide was carried out in quartz fluidized bed reactor (heating rate - 10 °C/min to 800 °C in a CO_2 atmosphere with carbon dioxide flow rate at 100 ml/min for 78 min; isothermal heating at 800 °C in a CO_2 atmosphere at a flow rate of carbon dioxide 100 ml/min for 1 h). Superheated steam activation was also carried out in quartz fluidized bed reactor (heating rate - 10 °C/min to 800 °C in N_2 atmosphere with nitrogen flow rate at 100 ml/min for 78 min; isothermal heating at 800 °C in a superheated steam atmosphere for 1 h - steam was generated in evaporator at temperature 200 °C and flow rate of liquid water 0.6 ml/min; cooling to room temperature in N_2 atmosphere with flow rate 100 ml/min). The characteristic of non-activated and activated biochars is presented in Table 1.

2.3. Sorbent amendment experiment

The soil was homogenized by rolled end over end (Rotax 6.8. VELP, Poland) for 24 h before the biochars amendment. A 100*g* of soil were transferred into a 100 ml bottle (SIMAX, Czech Republic). Then, non-activated or activated biochars were added in dry state to each bottle at the dose of 5.0% (w/w). The dose of biochars was chosen based on our previous study (Kołtowski et al., 2016) as a most effective in C_{free} PAHs immobilisation in contaminated soils. Pure soil samples, without biochar, were used as a control soils. The Milli-Q water (Spring 15 VF/UF, Hydrolab, Poland) was added to each bottle to rehydrate the treatments. The soils and biochar-soil mixtures were rolled end over end at 10 rpm for two months in the dark and at a room temperature of 21 ± 1 °C. After mixing, the control soils (without biochar), non-activated biochar with soil and activated biochars with soil, were ecotoxicologically evaluated.

2.4. Bioassays

To determine the toxicity, a battery of three bioassays was used: two solid phase test, with plant – *Lepidium sativum* (Phytotoxkit F) and collembolan - *Folsomia candida* (Collembolan test) and one liquid phase test with marine bacteria *Vibrio fischeri* (Microtox). Phytotoxkit