Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Effect of steam activated biochar application to industrially contaminated soils on bioavailability of polycyclic aromatic hydrocarbons and ecotoxicity of soils

Michał Kołtowski [a], Isabel Hilber [b], Thomas D. Bucheli [b], Patryk Oleszczuk [a,*]

[a] Department of Environmental Chemistry, Maria Curie-Skłodowska University, 3 Maria Curie-Skłodowska Square, 20-031 Lublin, Poland
[b] Agroscope Institute for Sustainability Sciences ISS, Reckenholzstrasse 191, 8046 Zürich, Switzerland

## HIGHLIGHTS

- Biochar produced from willow, coconut and wheat straw were steam activated.
- Non- and activated biochars were added to three different soils.
- Bioavailable ($C_{free}$) and bioaccessible ($C_{bioacc}$) PAHs content was investigated.
- Biochar activation resulted in more pronounced reduction of $C_{free}$ and $C_{bioacc}$ PAHs.
- Activation of biochars decreased the toxicity of leachates from the soils.

## GRAPHICAL ABSTRACT


## ARTICLE INFO

*Article history:*
Received 22 March 2016
Received in revised form 11 May 2016
Accepted 17 May 2016
Available online xxxx

Editor: Sarmah Ajit

*Keywords:*
Bioaccessibility
Remediation
Soil amendment
Contamination
Biochar
Activation

## ABSTRACT

The aim of this study was to determine the effect of steam activation of biochars on the immobilization of freely dissolved ($C_{free}$) and bioaccessible fraction ($C_{bioacc}$) of PAHs in soils. Additionally, the toxicity to various organisms like *Vibrio fischeri*, *Lepidium sativum* and *Folsomia candida* was measured before and after the amendment of biochars to soils. Three biochars produced from willow, coconut and wheat straw were steam activated and added to three different soils with varying content and origin of PAHs (coke vs. bitumen). The soils with the addition of the biochars (activated and non-activated) were incubated for a period of 60 days. Steam activation of the biochars resulted in more pronounced reduction of both $C_{free}$ and $C_{bioacc}$. The range of the increase in effectiveness was from 10 to 84% for $C_{free}$ and from 50 to 99% for $C_{bioacc}$. In contrast, the effect of activation on the toxicity of the soils studied varied greatly and was specific to a particular test and soil type. Essentially, biochar activation did not result in a change of phytotoxicity, but it increased or decreased (depending on the parameter, type of biochar, contaminant source, and soil and soil type) the toxic effect to *F. candida*, and decreased the toxicity of leachates to *V. fischeri*.



* Corresponding author at: 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).

http://dx.doi.org/10.1016/j.scitotenv.2016.05.114
0048-9697/© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Soil contamination in industrial areas is a serious problem in many countries. Contaminated sites should be remediate, otherwise it may lead to negative consequences such as exclusion of soils from plant production. Due to the significant area of impact of different manufacturing plants, conventional remediation of such soils is not undertaken. Traditional remediation method of heavy contaminated soil is incineration. This method is fast, however technically difficult, mainly due to the transportation of contaminated soil and advanced infrastructure. It makes this method expensive and not feasible everywhere. Our preliminary calculations have shown that the cost of remediation using biochar is several times cheaper than using traditional methods. Contaminants present in a soil are not subject to any control and they often migrate in a natural way to the adjacent grounds, negatively affecting the environment. Polycyclic aromatic hydrocarbons (PAHs) are a common environmental hazard (Srogi, 2007). Due to their mutagenic and carcinogenic properties, they pose a threat to living organisms, including humans. The coking and bitumen industries are some of the sources of PAHs (Mastral and Callén, 2000). The soils in the surroundings of these types of plants are characterized by high levels of PAH contamination ranged even from 920 to 3330 mg/kg (Ahn et al., 2005; Wang et al., 2015). In situ techniques, whose action mechanism is based not on complete elimination of contaminants but on binding the bioavailable and mobile fraction of these contaminants, currently attract a great interest in the area of soil remediation (Ghosh et al., 2011; Kupryianchyk et al., 2015). It is assumed that this fraction determines the toxicity of contaminants. Adsorbents characterized by strong affinity for contaminants are used to immobilize them. Thereby, their mobility in the environment and the exposure to living organisms is reduced (Cornelissen et al., 2006; Gomez-Eyles et al., 2013; Zimmerman et al., 2004). The most popular material used for this purpose is activated carbon (AC) (Ghosh et al., 2011). The efficiency of AC has been successfully confirmed in sediments, where reduction of the bioavailable fraction of various organic contaminants (Cornelissen et al., 2008; Gomez-Eyles et al., 2013) and their bioaccumulation (Cornelissen et al., 2006; Zimmerman et al., 2004), as well as in soils (Jakob et al., 2012; Kupryianchyk et al., 2016) and sewage sludges was observed (Oleszczuk et al., 2012). Nevertheless AC is considered to be very expensive, thus there is still need to find a more cost-effective material.

Besides AC, biochar is a more and more used adsorbent to immobilize contaminants (Khan et al., 2015; Kupryianchyk et al., 2016; Oleszczuk et al., 2014). Biochar is a solid material obtained from the carbonization of biomass in an oxygen-limited environment. The research showed that biochar can effectively bind both heavy metals and organic contaminants (Ahmad et al., 2014; Beesley et al., 2014). Advantages of this type of material over AC include its lower production cost and its positive influence on the physical, chemical and biological properties of soils (Ok, 2016). Moreover, biochar may be also a source of nutrients (Lehmann, 2007), which are necessary for plants grow. Nevertheless, comparative studies revealed that the biochar is less effective in organic contaminants binding than AC (Jia and Gan, 2014; Kupryianchyk et al., 2016; Oleszczuk et al., 2012). This is mainly due to the worse surface properties of biochar, especially lower surface area (Kupryianchyk et al., 2016). Therefore, increasing the surface area of biochar as a result of activation can be a factor enhancing its effectiveness. In particular, activated biochar is usually produced via chemical or physical activation. Among these methods, steam activation enjoys great interest. The activation may affect other parameters of biochar concerning the surface chemistry. During the steam activation process decrease of the acidic and increase of phenolic functional groups occurs. Moreover, steam activation may affect other parameters like elemental composition or particle size distribution. Recent research has shown that steam-activated biochars can efficiently remove contaminants from water. For example, Ippolito et al. (2012) demonstrated the potential of steam-activated pecan shell biochar to sorb excess Cu ions from wastewaters. Shim et al. (2015) also used steam activation to improve sorption capacity of biochar to Cu ions. Rajapaksha et al. (2015) observed a 55% increase in sorption capacity of sulfamethazine on steam-activated biochar compared to the non-activated biochar. Steam activation of biochar may therefore be an efficient method for increasing its sorption capacity, thereby representing a cost-effective alternative to immobilize contaminants in waters or soils. However, in the literature there is a lack of studies on the use of activated biochar for this purpose. Moreover, our preliminary research concerning the comparison between different method of biochar activation (activation by microwaves, carbon dioxide and steam) showed the best results (the highest specific surface area, volume, etc.) for steam activated biochar.

Biochars can differ in their properties, hence it is important to determine the influence of activation on the sorption capacity of biochars to contaminants and on the toxicity of polluted soils that were amended with activated biochars. The most recent research (Shim et al., 2015) showed that activation may indicate the biochar toxicity, because of aromaticity increasing and decrease of polarity index. Our previous study (data not showed) showed that, depending on the soil type and contaminant source (coke vs. bitumen plants), the effectiveness of bioavailable PAHs binding by AC or biochar and the toxicity reduction can vary markedly (Kołtowski and Oleszczuk, 2016). However, there is still a lack of data that would provide comprehensive information in the context of the above considerations.

The aim of this study was to determine the effect of biochar activation on the effectiveness of immobilization of PAHs in soils with different properties and with a varying content and origin of PAHs (coke vs. bitumen plants). The study evaluated immobilization of freely dissolved ($C_{free}$) and bioaccessible ($C_{bioacc}$) PAHs. Furthermore, the effect of activated biochar on the toxicity of PAH polluted soils to different terrestrial organisms was studied.

## 2. Materials and methods

### 2.1. Soils and biochars

Three different soils (KOK, POPI and KB) and three types of biochar (produced from: 1) wheat straw (WS), 2) coconut (CS) and 3) willow (WI)) were selected. Soils KOK and KB were sampled from a coking plant area (Dąbrowa Górnicza, Poland) and soil POPI from the vicinity of a bitumen processing plant (Wólka Łańcuchowska, Poland). Biochar WS was provided by Fluid S.A. (Sędziszów, Poland) and biochars CS and WI were provided by Mostostal (Wrocław, Poland). All biochars were produced by pyrolysis of the biomass at a temperature from 350 °C (start of pyrolysis) to 650 °C (max. pyrolysis temperature) in an oxygen-poor atmosphere. The physico-chemical properties of soils and non-activated biochars were determined as described in the SI and presented in Table S1 and S2.

### 2.2. Activation of the biochars

Biochars were activated by the superheated steam, which was identified as a most effective activation in a previous study (data not showed). The biochars were activated in quartz fluidized bed reactor (heating rate: from 20 to 800 °C 10 °C/min in $N_2$ atmosphere with a flow rate of 100 mL/min for 78 min, isothermal heating at 800 °C in a superheated steam atmosphere at (steam was generated in evaporator at temperature 200 °C and flow rate of liquid water 0.6 ml/min ). Physicochemical properties of non-activated and activated biochars are presented in Table 1.

### 2.3. Experiment

Soils were milled with a ball mill (SM1 Retsch GmbH, Germany) and dried at 40 °C to constant weight. Dry soil aliquots (100 g) were transferred into 100 mL bottles (SIMAX, Czech Republic). Then, dried non-