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The conversion of sewage sludge into biochar reduces polycyclic aromatic hydrocarbon content and ecotoxicity but increases trace metal content

*Anna Zielińska, Patryk Oleszczuk**

Department of Environmental Chemistry, Faculty of Chemistry, 3 Maria Curie-Skłodowska Square, 20-031 Lublin, Poland

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ABSTRACT

The presence of contaminants considerably restricts the application of sewage sludge for the fertilisation and reclamation of soils. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment and vary widely in sewage sludge depending on the input of industrial effluents. The objective of the study was the investigation whether the pyrolysis affect (reduces or adds) the total quantity of PAHs in sewage sludge-derived biochars and whether the pyrolysis changes the PAHs spectrum in terms of relative contributions of more hazardous components. Additionally, the trace metal content was determined before and after pyrolysis as well as the ecotoxicological parameters test towards plant (*Lepidium sativum*), bacteria (*Vibrio fischeri*) and crustacean (*Daphnia magna*). Sewage sludges conversion to biochar significantly reduced the content of PAHs (from 8- to 25-fold depending on pyrolysis temperature and kind of sludge). The exception was the content of naphthalene. Naphthalene was predominant in sewage sludge-derived biochars. However the concentration of the most hazardous 5- and 6-rings PAHs in sewage sludge-derived biochars was much lower compared to sewage sludge. The pyrolysis of sewage sludges caused also a significant reduction of their toxicity towards the test organisms. Only in the case of crustacean it was observed that the extracts from some biochars, obtained at higher temperatures (600 °C and 700 °C) were more toxic to *D. magna* than extracts from sewage sludge. In turn, after pyrolysis an increase was noted for trace metals content (Pb, Cd, Zn, Cu, Ni and Cr).

1. Introduction

Industrialisation and urbanisation increase the volume of sewage sludge produced by wastewater treatment plants. Sewage sludge is a valuable source of phosphorus, nitrogen, microelements and organic matter which have a favourable effect on the properties of soil and thus also on the level of yields. However, the presence of contaminants in sewage sludge, such as highly toxic organic compounds (polycyclic aromatic hydrocarbons), potentially toxic elements (trace metals) and pathogenic microorganisms, significantly

* *Corresponding author*. Department of Environmental Chemistry, University of Maria Skłodowska-Curie, pl. M. Curie-Skłodowskiej 3, 20-031 Lublin, Poland. Tel.: +48 81 5375515; fax: +48 81 5375565.
E-mail address: patryk.oleszczuk@poczta.umcs.lublin.pl (P. Oleszczuk).
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restricts its application for soil fertilisation or for the reclamation of degraded soils. Sewage sludge conversion to biochar may be a chance for minimisation of negative effects related with the agricultural utilisation of sewage sludges. For example, sewage sludge conversion to biochar may reduce the leaching of trace metals [1], increase the enzymatic activity of soils [2], and also reduce the bioaccumulation of trace metals [1,3] and PAHs [1,3–6]. Due to its large sorption capacity, biochar has an ability of binding trace metals and organic contaminants, thus immobilising them and reducing their bioavailability for a long time [7]. In that manner it reduces the potential toxicity of the contaminants with relation to various groups of organisms.

It needs also to be emphasised that, in spite of its so positive effects with relation to soil, biochar also has its drawbacks. One should mention here its content of trace metals whose presence is related with their content in the initial material. Other common contaminants of biochars are PAHs which are formed in the process of biochar production [8]. There is also a whole array of other compounds in biochars, that can be toxic to living organisms [9–11]. This is of particular importance in the conditions of biochar utilisation in agriculture.

Nevertheless, the conversion of sewage sludges to biochars is becoming an increasingly common method of their utilisation [4–6,12–15]. Therefore it is important – due to the presence of the above-mentioned contaminants in sewage sludges – to determine how that conversion will affect their content in the biochar produced.

Taking into account the fact that biochars are applied mainly in agriculture, it is important to determine also their toxicity towards various groups of organisms. Contaminants content alone, determined by chemical analysis is not a sufficient tool for the estimation of the risk involved in their application as a potential fertilizer [10]. Ecotoxicological tests may prove to be useful for that purpose, though they should not be treated as an alternative for chemical analyses. Research supplementation with biological assays may, however, expand the knowledge on the potential threats. Moreover, the application of biological tests permits the analysis of possible interactions between various contaminants, that constitute the most important proof of the existence or absence of a toxic effect on organisms.

The objective of the study was the estimation of the effect of the process of pyrolysis of sewage sludges on the content of PAHs and trace metals (Pb, Cd, Zn, Cu, Ni and Cr), and also on the toxicity of the biochars produced. The study was conducted with the use of sewage sludges with diverse properties and content of contaminants. Detailed analysis of the results will permit for the optimisation of the process of sewage sludges pyrolysis in terms of their content of contaminants and their safe utilisation as fertiliser materials.

2. Materials and methods

2.1. Biochar preparation

Four sewage sludges (SS) were obtained from municipal (mechanical–biological) wastewater treatment plants (WWTPs) located in different parts of Poland: Koszalin (KN, 54°11′25″N 16°10′54″E), Kalisz (KZ, 51°45′45″N 18°05′23″E), Chełm (CM, 51°07′56″N 23°28′40″E) and Suwałki (SI, 54°06′04″N 22°55′57″E). In the supporting information (Table S1) the characteristic of wastewater treatment plants is presented. The sewage sludges were collected during summer 2012, at the end point, after the sewage sludge digestion process. A few representative subsamples were taken for the present experiments. The comparable amounts of sewage sludge from ten randomly selected sites of landfill were collected using a plastic shovel. Ten subsamples were carefully mixed on the foil and transported to the laboratory. After drying (about 25 °C for few weeks) in the dark, samples were ground and passed through a 2 mm sieve. Such pre-prepared samples (about 75 g–150 g) were pyrolysed in the furnace of own construction (Fig. S1). The water mass fractions of sewage sludges before pyrolysis were 4.9% (SSKN), 4.3% (SSKZ), 4.6% (SSCM) and 4.4% (SSSI).

Biochars (BC) were prepared at 500 °C, 600 °C or 700 °C. The pyrolysis heating rate was employed at 25 K min^{-1} and nitrogen gas was injected at a rate 630 cm^3 min^{-1} (at stp 298 K, 101.2 kPa) to ensure an oxygen-free atmosphere. The temperature of pyrolysis was held for 5 h (slow pyrolysis). The properties of sewage sludges and sewage sludge-derived biochars are presented elsewhere [16] and in supporting information (Tables S2 and S3).

2.2. Determination of trace metals and polycyclic aromatic hydrocarbons

For heavy metal determination each sewage sludge and biochar sample was mineralised in a PROLABO microwave oven (Microdigest 3.6, France). An analysis for the content of Pb, Cd, Zn, Cu, Ni and Cr was carried out using emission spectrometry on the Leeman Labs (PS 950) apparatus with ICP induction in argon.

For polycyclic aromatic hydrocarbon determination dry sewage sludge and biochar samples were extracted with toluene using accelerated solvent extractor (ASE 200) from Dionex GmbH (Idstein, Germany) according to the method developed by Hilber et al. [17]. The extracts were evaporated and cleaned-up according to the method described by Brändli et al. [18]. A qualitative and quantitative analysis of PAHs was carried out on Thermo Scientific Trace 1300 Gas Chromatograph equipped with a Restek Rxi-5 ms Column (length 30 m, 0.25 mm id and 0.25 μm film thickness). Detailed information about trace metal and PAH analysis is presented in supporting information.

2.3. Sewage sludge and biochar toxicity

Sewage sludge and biochar toxicity was assessed with solid phase test – Phytotoxkit F Test [19] with *Lepidium sativum* (plant) and two leachates tests – Microtox® [20] and Daphtoxkit F [21] with *Vibrio fischeri* (bacteria) and *Daphnia magna* (crustacean), respectively. Tests were performed according to the standard operational procedure manuals.

Leachates from sewage sludge or biochar samples were obtained according to the EN 12457–2 protocol [22]. Detailed