Bioresource Technology 214 (2016) 225–233

Contents lists available at ScienceDirect

Bioresource Technology

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

Pyrolysis of waste materials: Characterization and prediction of sorption potential across a wide range of mineral contents and pyrolysis temperatures

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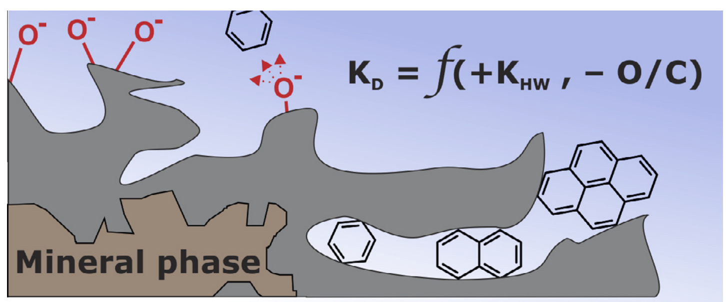
HIGHLIGHTS

- Changes in properties and sorption behavior were generally consistent among feedstock.
- There were clear changes in the contributions of partitioning and adsorption.
- Size exclusion of pyrene occurred for pyrolyzed plant-derived materials.
- Sorption to materials undergoing pyrolysis can be predicted based on K_{HW} and O/C.
- Describing the behavior of sewage sludge upon pyrolysis requires specific approaches.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form 16 April 2016
Accepted 18 April 2016
Available online 20 April 2016

Keywords:
Biochar
Pyrolysis
Biosolid
Manure
Dual mode model

ABSTRACT

Sewage sludge (50% mineral), manure (29%) and wood (<1%) were pyrolyzed at 200, 350 and 500 °C with the aim to study the characteristics and sorption potential of materials undergoing pyrolysis across a wide range of mineral contents. A commercial plant-derived biochar (41% mineral) was also considered. The materials were extensively characterized and tested for their sorption towards the model sorbates benzene, naphthalene and pyrene. Plant-derived materials, regardless of their mineral content, developed micropores causing size exclusion of pyrene. Changes in properties and sorption behavior upon pyrolysis were generally consistent for the manure and wood series. A single regression equation developed on our data (including the sorbate hydrophobicity and sorbent polarity) provided excellent prediction of previously reported changes in sorption upon pyrolysis across a wide range of mineral content (up to 500 °C). The sewage sludge series, however, followed a particular behavior, possibly due to very high mineral content (up to 67%).

1. Introduction

The pyrolysis of biomass wastes offers opportunities for efficient resource utilization and carbon sequestration. Pyrolysis may be particularly advantageous for the disposal and possible valorization of human or animal wastes (e.g. sewage sludge, animal manure) that potentially contain pathogens and/or organic contaminants (e.g. human, veterinary pharmaceuticals). The product of pyrolysis, often called "biochar", may be used as fertilizer in agriculture or as sorbent for water, soil or sediment remediation (Ahmad et al., 2014; Smith et al., 2009; Zielińska and Oleszczuk, 2015).

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http://dx.doi.org/10.1016/j.biortech.2016.04.091
0960-8524/

In view of the potential applications of pyrolyzed materials, it is crucial to understand how the physico-chemical properties and sorption behavior of a given feedstock evolves upon pyrolysis. A large body of literature has already demonstrated that pyrolysis can greatly enhance the sorption affinity and maximum capacity towards organic molecules. The vast majority of studies performed to date considered plant-derived feedstock and knowledge remains limited on biochars produced from animal/human wastes, which typically contain large amount of minerals. For instance, biochars derived from human/animal wastes represented less than 10% of the sorption data presented in recent reviews of the literature (Ahmad et al., 2014; Hale et al., 2016).

Up to now, the mineral content of pyrolyzed materials has hardly been considered with regards to its effects on sorption (Hale et al., 2016). Recent experiments carried out with sewage sludge containing large amounts of minerals (i.e. 56–79%), have shown that pyrolysis can increase the sorption potential of the material (Zielińska and Oleszczuk, 2015). Mineral phases have however also been shown to have a deleterious effect on the sorption of hydrophobic sorbates, mainly by blocking the accessibility to the porosity of the carbon matrix (Moreno-Castilla, 2004; Zhang et al., 2013; Zheng et al., 2013). The impact of mineral phases on sorption has been previously studied by conducting demineralization experiments. The interpretation of such experiments may be complicated due to the incomplete removal of mineral phases and possible effects of demineralization treatments on organic phases. For instance, about 7% ash remained after repetitive treatments of pyrolyzed pig manure with 1 M HCl and 1 M:1 M mixture of HCl:HF (Zhang et al., 2013) and it was shown that treatments with either HCl alone or HCl and HF, could significantly affect the surface chemistry and porosity of the materials (Lou et al., 2011). Overall, the impact that mineral phases have on the properties of pyrolyzed materials remain poorly understood, and this prevents a critical evaluation of feedstock materials typically rich in minerals (e.g. sewage sludge, manure) relative to others that were already extensively studied (e.g. wood). Recalling that mineral phases were suggested to impact the material porosity, investigations into the effects of minerals on sorption should carefully consider the impact that material porosity has on sorption behavior. Studies relating sorption to surface area and pore size distribution remain scarce, and the effects of feedstock and pyrolysis conditions on those relationships are lacking (Lattao et al., 2014). The aim of our research was to fill in some of these gaps in our knowledge, with the specific objectives to:

(1) Increase our understanding of the characteristics and sorption behavior of materials undergoing pyrolysis across a wide range of mineral contents,
(2) Evaluate pyrolyzed materials produced from human/sewage sludge (typically rich in minerals) relative to the more studied plant-derived materials (either rich or poor in minerals),
(3) Generate a large dataset of physico-chemical and sorption properties to support the development of pragmatic approaches to predict sorption behavior.

Three feedstock materials covering a range of mineral contents (i.e. sewage sludge, manure and wood) were considered, and the evolution of their physico-chemical and sorption characteristics was systematically analyzed upon pyrolysis at 200, 350 and 500 °C. A commercially available biochar derived from plant residues and with a relatively high mineral content was also included in the analysis. With the aim to investigate the impact that porosity has on sorption and possible size exclusion of large sorbates, sorption to the series of sorbents was measured for three model sorbates covering a range of molecular sizes (i.e. benzene, naphthalene and pyrene). The dataset generated in this study covers a much wider range of sorbate and sorbent properties than most datasets published to date, and allows interpretations at both mechanistic and pragmatic levels.

2. Materials and methods

2.1. Sorbents production

Three feedstock materials were selected to cover a range of mineral contents. Sewage sludge (47.57% mineral) was collected from an urban wastewater treatment plant (Breitenfurt bei Wien, Austria) and pig manure (29.03% mineral) was collected from a farm near Vienna (Austria). Wood shavings were obtained from a home improvement store (Bauhaus, Austria) to represent a feedstock material with a low mineral content (0.21% mineral). After drying at 50 °C and sieving down to 2 mm, the feedstock materials were pyrolyzed in lidded ceramic containers under oxygen-limited conditions in a muffle oven (Nabertherm L5/11P330). Temperature was raised up to 200 °C, 350 °C or 500 °C (25 °C/min), and maintained for 4 h. The furnace was then turned off and materials were allowed to cool down to room temperature. A commercial reference biochar (RefBC, 43.86% mineral) produced from a mixture of cellulose fibers and grain husks pyrolyzed at 600 °C, was obtained from Sonnenerde (Austria). All materials were homogenized and sieved down to 0.25 mm.

Overall, 13 materials (i.e. 3 feedstocks and 10 pyrolyzed materials) were extensively characterized and evaluated for their sorption behavior. All materials studied are hereafter referred to with acronyms starting with the type of feedstock material (SS for sewage sludge, PM for pig manure or WS for wood shavings), followed by the pyrolysis temperature (200 °C, 350 °C and 500 °C), when applicable.

2.2. Sorbents characterization

2.2.1. Bulk composition

Elemental composition was determined using an elemental analyzer (C%, H% and N%, Elementar Vario MACRO). Mineral content was measured by weighting samples before and after heating at 750 °C for 6 h (American Society for Testing and Materials, method D-1762-84). The oxygen content was estimated by mass balance: $O = 100 - (C + H + N + mineral)$ (all weight%). The total organic carbon content (OC%) was determined using a carbon analyzer equipped with a solid-state infrared detector (LECO RC-612). Analysis of the materials derived from WS was not possible due to their rapid combustion. The WS series contain <1% mineral, OC% was thus considered equal to C%.

2.2.2. Contaminants content

Total concentrations of heavy metals (i.e. Zn, Cu, Pb, Cr, Cd and Ni) and other elements (i.e. Ca, Mg, Na, K, Al, Fe, Mn, Si, Ti and P) were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (Perkin Elmer Optima 5300 DV), after microwave assisted acid digestion with nitric acid and hydrogen peroxide (Microwave 3000-Anton Paar, Hossain et al., 2011).

Concentrations of 16 polycyclic aromatic hydrocarbons (16 US-EPA PAHs) were determined in the materials pyrolyzed at 500 °C as well as RefBC. Many extraction methods have been previously proposed (Hilber et al., 2012). For instance, when using accelerated solvent extraction, Freddo et al. (2012) recommended dichloromethane, while in a study on soot, Jonker and Koelmans (2002) suggested that a 1:1 mixture of toluene/methanol achieved greater extraction efficiency for PAHs. Both approaches were evaluated in this study. Briefly, 2 g samples were spiked with deuterated internal standards and extracted by accelerated solvent extraction (ASE