Science of the Total Environment 537 (2015) 180–186

Contents lists available at ScienceDirect

Science of the Total Environment

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

Pharmaceutical load in sewage sludge and biochar produced by hydrothermal carbonization

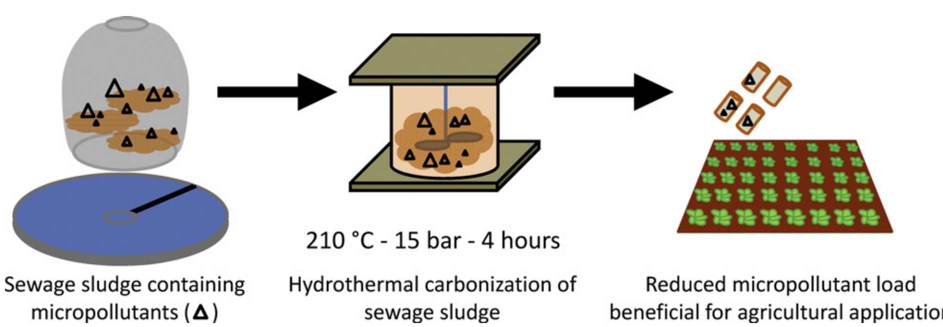
C. vom Eyser [a,b], K. Palmu [c], T.C. Schmidt [b,d], J. Tuerk [a,d,*]

[a] *Institut für Energie- und Umwelttechnik e. V., IUTA (Institute of Energy and Environmental Technology), Bliersheimer Str. 58–60, 47229 Duisburg, Germany*
[b] *Instrumental Analytical Chemistry, University of Duisburg-Essen, Universitätsstr. 5, 45141 Essen, Germany*
[c] *Hamburg University of Technology, Eißendorfer Str. 42, 21073 Hamburg, Germany*
[d] *Centre for Water and Environmental Research (ZWU), University of Duisburg-Essen, Universitätsstraße 2, 45141 Essen, Germany*

HIGHLIGHTS

- Production of biochar from sewage sludge using hydrothermal carbonization (HTC)
- Experiments with spiked sewage sludge to determine removal rates
- Removal rates of 39% to ≥97% for the investigated pharmaceuticals during HTC
- First study reporting remaining residuals of pharmaceuticals in biochar from HTC
- Concentrations of the four detected pharmaceuticals ranged from 9 to 510 μg/kg.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 June 2015
Received in revised form 4 August 2015
Accepted 4 August 2015
Available online 15 August 2015

Editor: D. Barcelo

Keywords:
HTC
Hydrochar
Micropollutants
Sewage sludge conversion
Waste treatment
Pyrazolones

ABSTRACT

We investigated the removal of twelve pharmaceuticals in sewage sludge by hydrothermal carbonization (HTC), which has emerged as a technology for improving the quality of organic waste materials producing a valuable biochar material.

In this study, the HTC converted sewage sludge samples to a biochar product within 4 h at a temperature of 210 °C and a resulting pressure of about 15 bar. Initial pharmaceutical load of the sewage sludge was investigated as well as the residual concentrations in biochar produced from spiked and eight native sewage sludge samples from three waste water treatment plants. Additionally, the solid contents of source material and product were compared, which showed a considerable increase of the solid content after filtration by HTC.

All pharmaceuticals except sulfamethoxazole, which remained below the limit of quantification, frequently occurred in the investigated sewage sludges in the μg/kg dry matter (DM) range. Diclofenac, carbamazepine, metoprolol and propranolol were detected in all sludge samples with a maximum concentration of 800 $\mu g/kg_{DM}$ for metoprolol. HTC was investigated regarding its contaminant removal efficiency using spiked sewage sludge. Pharmaceutical concentrations were reduced for seven compounds by 39% (metoprolol) to ≥ 97% (carbamazepine). In native biochar samples the four compounds

* Corresponding author at: Institut für Energie- und Umwelttechnik e. V., IUTA (Institute of Energy and Environmental Technology), Bliersheimer Str. 58–60, 47229 Duisburg, Germany.
E-mail addresses: vomEyser@iuta.de (C. vom Eyser), aww@tuhh.de (K. Palmu), torsten.schmidt@uni-due.de (T.C. Schmidt), tuerk@iuta.de (J. Tuerk).

http://dx.doi.org/10.1016/j.scitotenv.2015.08.021
0048-9697/© 2015 Elsevier B.V. All rights reserved.

phenazone, carbamazepine, metoprolol and propranolol were detected, which confirmed that the HTC process can reduce the load of micropollutants. In contrast to the other investigated compounds phenazone concentration increased, which was further addressed in thermal behaviour studies including three structurally similar potential precursors.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The proper handling of sewage sludge has gained attention in times of increasing energy costs and stricter legislative demands. In 2005, the German government banned sewage sludge deposition leaving the alternatives to incinerate the sludge or to apply it in agriculture. However, both choices face major drawbacks. On the one hand incineration is restricted to dried sewage sludge demanding lots of energy to separate the water. In addition, this alternative accepts the loss of nutrients like nitrogen and phosphorus. On the other hand agricultural application of sewage sludge is limited by regulations for heavy metals and pathogens and suffers from the low social acceptance (Wang et al., 2008). Although the nutrients nitrogen and phosphorus are recycled many contaminants may be released into the environment contributing to contamination of soils and adjacent water bodies (Kümmerer, 2008). In this context, pharmaceuticals are of particular concern because studies showed low effect concentrations and the evolution of multi-resistant pathogens (Kümmerer, 2008).

Recently, the technology of hydrothermal carbonization (HTC) has been established as an improved sewage sludge handling method. HTC generates biochar from wet biomass at elevated temperature and pressure (Libra et al., 2011). Bergius introduced the process in 1913 to simulate natural diagenesis of coal (Bergius, 1913). HTC is feasible for biomass with poor fuel properties like sewage sludge and entails benefits in subsequent processing (Funke and Ziegler, 2010). In fact, HTC increases the specific heat content of sewage sludge, which is valuable for mono-incineration (Kang et al., 2012). Alternatively, governmental efforts support the recycling of nutrients, which favors the application of biochar in agriculture. The loss of functional groups increases the hydrophobic character of the biochar enhancing its dewaterability, which reduces drying and transport costs. Escala et al. (2013) estimated thermal and electric energy savings using the HTC instead of conventional drying methods for sewage sludge on a laboratory scale. In their experiments about 60% of thermal energy and 65% of electric energy was saved. Additionally, the high carbon efficiency of the process minimizes greenhouse gas emissions and contributes to a positive carbon footprint (Lal, 2009).

However, little is known about the behaviour and whereabouts of micropollutants during the HTC of sewage sludge yet. For model substances, a reaction-process dependency regarding the micropollutant behaviour has been shown (Funke and Ziegler, 2010). Weiner et al. (2013) reported that selected micropollutants degrade at HTC conditions in water and sucrose solution. However, these results have not been transferred to sewage sludge yet. Recently, we (vom Eyser et al., 2015) developed a method to determine pharmaceuticals in sewage sludge and biochar.

Based on the described method we investigated the fate of 12 representative pharmaceuticals during the HTC comparing two HTC reactors and sewage sludges from three German waste water treatment plants including repeated sampling campaigns. Analyses comprised diclofenac, ibuprofen, phenazone, carbamazepine, sulfamethoxazole, clarithromycin, roxithromycin, erythromycin, bezafibrate, fenofibric acid, metoprolol, and propranolol. Furthermore, the three pyrazolones propyphenazone, 4-aminoantipyrine and 4-methylaminoantipyrine were investigated in additional experiments.

2. Materials and methods

2.1. Chemicals

Diclofenac, ibuprofen, phenazone, propyphenazone, 4-aminoantipyrine (4-AA), 4-methylaminoantipyrine (MAA), carbamazepine, sulfamethoxazole, bezafibrate, fenofibric acid, metoprolol, propranolol, clarithromycin, roxithromycin and erythromycin were purchased from Sigma-Aldrich (Taufkirchen, Germany) in highest available purity. Table 1 list the physico-chemicals characteristics of the investigated pharmaceuticals. Th. Geyer GmbH & Co. KG (Renningen, Germany) delivered LC–MS water, acetonitrile and methanol. Fisher Scientific GmbH (Schwerte, Germany) supplied the extra pure mesh sand from Ottawa. Stock solutions were prepared in water/acetonitrile (50/50, v/v). Storage at 4 °C did not exceed three months. Standards were prepared for every experiment by diluting the stock solutions with LC–MS water.

2.2. Sewage sludges

LINEG, Ruhrverband and Hamburg Wasser enabled sewage sludge sampling at the waste water treatment plants (WWTP) Rheinhausen, Rahmedetal and Hollenstedt. The samples consisted of centrifuged secondary sludge. Hollenstedt (9500 population equivalent, PE) located southwest of Hamburg treats waste water from a mainly rural area. In contrast, mixed rural, urban and industrial influences are present in Rahmedetal (64,000 PE) in North Rhine-Westphalia. The catchment area of Rheinhausen (220,000 PE) located in the western Ruhr catchment shows mainly urban and industrial impacts. The WWTP represent classical profiles of different catchment influences. Additional sewage sludge parameters are given in the supplementary material (S 1). Samples were taken after the final drying step in five sampling campaigns distributed over two years. Five samples originated from Hollenstedt, two from Rheinhausen and one from Rahmedetal.

2.3. Biochar produced by HTC of sewage sludge

HTC was conducted in high pressure systems (Büchi Glas Uster, Switzerland) with reactor volumes of 0.2 L and 5 L. The sewage sludge was adjusted to 20% dry matter (DM) using water. Then, the mixture was filled into the reactor. The system was closed and heated to 210 °C while a stirrer continuously mixed the content at 500 rpm. After keeping the final temperature for 4 h, the reactor was cooled down to room temperature. The product from HTC of sewage sludge is called biochar or hydrochar. Bls 2.5 software (Büchi Glas Uster, Switzerland) controlled and recorded the experimental parameters reactor temperature, jacket temperature, heating power, stirring rate and pressure. Afterwards, the produced biochar was stored at 4 °C until analysis.

2.4. Experimental design

First, the HTC process was evaluated considering its dewaterability dependent on the runtime with sewage sludge from the WWTP Hollenstedt. In fact, sewage sludge and biochar were compared regarding their solid content after filtering the samples with a 1-μm glass fibre filter (Macherey-Nagel, Düren, Germany). The solid fraction resulted from $\frac{m_d}{m_w} \times 100$ with the dried mass m_d and the wet mass m_w.

Download English Version:

https://daneshyari.com/en/article/6325459

Download Persian Version:

https://daneshyari.com/article/6325459

Daneshyari.com