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Fate and behaviour of diclofenac during hydrothermal carbonization

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HIGHLIGHTS

- Diclofenac removal by HTC in inert experiments and spiked sewage sludge.
- Considerable diclofenac reduction in native sewage sludge during HTC.
- Characterization of six diclofenac transformation products.
- Proposal of an HTC degradation mechanism (for diclofenac).

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ABSTRACT

Hydrothermal carbonization (HTC) has become an esteemed method to convert sewage sludge into biochar. Besides dewatering and disinfection the process is suggested to reduce the micropollutant load, which would be beneficial for the use of biochar as fertilizer. This study was designed to examine reduction of micropollutants and formation of transformation products during HTC using the example of diclofenac. We investigated compounds' removal at HTC conditions in inert experiments and in real samples. Results showed that HTC temperature (>190 °C) and pressure (~15 bar) have the potential to fully degrade diclofenac in inert experiments and spiked sewage sludge (>99%) within 1 h. However, interfering effects hinder full removal in native samples resulting in 44% remaining diclofenac. Additionally, a combination of suspected-target and non-target analysis using LC-MS/MS and LC-HRMS resulted in the determination of six transformation products. These products have been reported in biochar from HTC for the first time, although other studies described them for other processes like advanced oxidation. Based on the detected transformation products, we proposed a degradation mechanism reflecting HTC reactions such as dehydroxylation and decarboxylation.

1. Introduction

Sewage sludge occurs as a product at waste water treatment plants (WWTP). Subsequently, the most favoured handling options are incineration or agricultural application In European countries the amount used as fertilizer varies between 0% (The Netherlands) and 90% (Luxembourg) (Goldenman and Middleton, 2008). In general, agricultural usage attains a low consumer acceptance because of its non-sterile character (Goldenman and Middleton, 2008). Consequently, upcoming regulations require disinfection steps (Bergs, 2013). Moreover, strict limitations regulate the exposure pollutants, because already a low constant input might induce negative effects such as the growth of resistant species in the presence of antibiotics (Bundesministerium, 1992; Eibisch, 2006). Despite this, the agricultural pathway is cheaper than sludge incineration (150€/t dry matter (DM) compared to about 250 €/t_{DM}) (Wiechmann et al., 2012). Beside the high incineration costs, nutrients like phosphorus remain in the ashes for disposal, which contradicts the concept of sustainable phosphorus management (Scholz, 2013).

In recent years, research has discovered approaches to improve sewage sludge handling. Pre-treatment procedures like wet air oxidation or thermal hydrolysis were tested in different scales (Libra et al., 2011; Hii et al., 2014). Hydrothermal carbonization

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(HTC) has turned out as a promising tool, which combines advantages for further utilization pathways. The process converts wet biomass to biochar at elevated temperature (180–300 °C) and pressure within a few hours (Libra et al., 2011). HTC has originally been applied to simulate natural coalification and has recently become interesting in the waste water sector, because HTC even works with low-energy biomass like sewage sludge due to the catalytic effect of water facilitating hydrolysis, ionic condensation and cleavage (Funke and Ziegler, 2010).

The biochar is beneficial to incinerate, because its specific heating content (12.03 MJ/L) exceeds sewage sludge values (3.17 MJ/L) (Buttmann, 2011). Alternatively, the disinfecting character of HTC promotes to apply biochar in agriculture and to recover valuable nutrients like nitrogen and phosphorus. Despite the promising features of biochar, conversion mechanisms during HTC are still unknown in detail. Libra et al. investigated the predominant reactions of model compounds during HTC (Libra et al., 2011). Cellulose and lignin mainly dehydrate and decarboxylate. Later, molecules recombine to aromatic and more complex structures again. However, reaction mechanisms of complex biomasses like sewage sludge including the fate of micro pollutants like pharmaceuticals and personal care products still remain unknown. Further studies have shown the potential of HTC to reduce selected pharmaceuticals in sewage sludge (vom Eyser et al., 2015). Nevertheless, mechanistic details appear like a black box. The incomplete knowledge about the process details makes it difficult to evaluate the biochar product. Although the occurrence of non-regulated micropollutants in biochar might not hinder its use as a fertilizer, they impact the product quality because high concentrations entail the risk of adverse effects in soil flora and fauna.

Therefore, this study was designed to get a deeper insight into the degradation characteristics of micropollutants during HTC. In fact, we investigated the behaviour of the representative micropollutant diclofenac during HTC in spiked sand, spiked sewage sludge and native sewage sludge to derive its degradation efficiency. Moreover, transformation products of diclofenac were investigated to elucidate the reaction mechanism. This approach should help evaluating the behaviour of the investigated and similar compounds during HTC of sewage sludge.

The active pharmaceutical ingredient diclofenac served as the model compound, because it occurs ubiquitously. In Germany, about 90 t were consumed in 2008 (Meißner, 2008). Removal in WWTPs is low (Salgado et al., 2012). Diclofenac sorbs to different sewage sludges with coefficients (log K_d) of 1.2–2.7 L/kg (Ternes et al., 2004). Environmental studies reported 1–1.6 μg/L in WWTP effluents and up to 400 $\mu g/kg_{DM}$ in sewage sludge (Ternes et al., 2005; Radjenovic et al., 2009; Peysson and Vulliet, 2013). Toxic effects in fish can already occur at the level of 1 μg/L in the water body (Triebskorn et al., 2007) resulting in a predicted no effect concentration of 0.1 μg/L, which is therefore suggested as environmental quality standard ([39/2013/EU).

Analysis of diclofenac is hindered by ion suppression during LC-MS/MS measurement (Paull et al., 2008; Radjenovic et al., 2009). This might also appear during the analysis of coal-like products as they are known to hinder analysis by adsorbing organic substances (Ternes et al., 2002; Dickenson and Drewes, 2010). Therefore we evaluated the LC-MS method and considered model experiments as well as real samples.

2. Materials and methods

2.1. Chemicals

LC-MS grade water, acetonitrile and methanol were purchased from Th. Geyer GmbH & Co. KG (Renningen, Germany), diclofenac sodium and formic acid from Sigma-Aldrich (Taufkirchen, Germany) in the highest available purity. Ottawa extra pure 20–30 mesh sand (Fisher Scientific GmbH, Schwerte, Germany) served as inert filling material. We prepared stock solutions of 1 g/L diclofenac with water/acetonitrile (50/50, v/v). Calibration standards were prepared freshly for each experiment using the according amounts of stock solution and LC-MS water.

2.2. Sewage sludge characteristics

The WWTP Hollenstedt, located in the south-west of Hamburg (Germany), provided the sewage sludge. Sewage sludge parameters are shown in Table 1. Rural area mainly influences the composition of the waste water.

2.3. HTC experiments

Experiments were carried out by weighting 50 g sand or sewage sludge +17 mL water into a 200 mL laboratory scale limbo high pressure reactor system (Büchi Glas, Uster, Switzerland). In spiked experiments, 0.77 mL diclofenac stock solution (c = 1 g/L) was added to achieve an initial concentration of 15.4 mg/kg_{DM} in sand and 77 mg/kg_{DM} in sewage sludge, respectively. The reactor was closed and stirred at least 1 h at 500 rpm before adjusting the temperature to 190–210 °C for different runtimes. The bls 2.5 software (Büchi Glas, Uster, Switzerland) recorded reactor temperature, jacket temperature, heating and cooling power, stirring rate and pressure.

2.4. Sample extraction and preparation

After conducting the experiments with spiked sand the supernatant was separated from the sand. The supernatant was measured directly via standard addition while the sand residue was prepared like the sewage sludge and biochar. These samples were freeze-dried and extracted via pressurized liquid extraction (PLE) as described in detail by vom Eyser et al. (vom Eyser et al., 2015). In short: 11-mL cartridges were filled with aliquots of 1 g biomass and Ottawa sand served to fill up the cartridge. Samples were extracted in one 15 min cycle using methanol at 100 °C and 100 bar. The cartridges were flushed with 10% of the cell volume and purged with nitrogen for 150 s. Extracts were evaporated and dissolved in 5 mL LC-MS water. All extracts and filtrates were filtered with Chromafil RC 0.45 μm syringe filters (Macherey-Nagel, Düren, Germany) before LC-MS/MS measurement.

2.5. HPLC-MS/MS analysis

2.5.1. Quantification

HPLC-MS/MS analysis was carried out using a LC 20 HPLC system consisting of a CBM-20A communication bus module, a CTO-20AC column oven, a DGU-20A3 degasser, LC-20AD pumps and a

Table 1
Sewage sludge parameters from the waste water treatment plant Hollenstedt (Germany).

Dry matter	20%
pH	6.6
Organic substance	84%
Mineral substance	16%
Total nitrogen	78 kg/t_{DM}
Phosphorus	58 kg/t_{DM}
AOX	110 mg/kg_{DM}
Hydrocarbons	3770 mg/kg_{DM}