**Is** **hydrothermal carbonization (HTC) sustainable ? - Pollutants in liquid HTC residues**

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Burning or even composting bio-waste or sewage sludge produces CO2 and partly nutrients are taken out of the biogeochemical cycles. Burning is widely used for contaminated bio-waste. One alternative to burn biomass could be a transformation into char in a process called hydrothermal carbonization (HTC) that works at moderate pressure and temperatures in wet surroundings [1], [2]. The transformation of the organic compounds into char allows CO2 sequestration. It has been speculated that this method could be used to detoxify biomass or sludge as any organic pollutants could be chemically transformed, while the products still contain nutrients like nitrogen and phosphorus. Beside the char, an organically highly loaded process water is produced by the hydrothermal carbonization.

Recently, patterns of volatile organic compounds were detected by gas chromatography [3]. It was shown that in some HTC process waters benzenes, phenols, furans, and ketones occur which prevents their use as fertilizer.

The main goal of this research was to evaluate the hydrothermal carbonization by the characterization of its process water. In the current work different HTC process waters were analyzed. In order to cover a reasonable spectrum of process products, the input materials and HTC process parameters were varied: sewage sludge, coffee grounds, and clean wheat straw, wood chips and cotton wool to find out about their effects. The focus was on semi-volatile compounds as well as on phenols. Phenols (phenol, o-cresol, m-cresol, p-cresol, 2,6-dimethylphenol, 2-ethylphenol, 2,5-dimethylphenol, 2,4-dimethylphenol, 3-ethylphenol, 2,3/3,5-dimethylphenol-4-ethylphenol, 3-4-dimethylphenol, 2,4,6-trimethylphenol, 2,3,5-triphenol and 3,4,5 -triphenol) were chosen because of their toxicity. They occurred in concentrations of 30 mg/L to 300 mg/L, depending on the food stock and the specific compound. Additional common waste water sum parameters like total organic carbon (TOC), dissolved organic carbon (DOC) and chemical oxygen demand (COD) were determined. DOC was for all samples higher than 50 g C/L, for samples of sewage sludge or coffee grounds even higher than 100 g C/L. The chemical oxygen demand (COD) was at least 1/3 of the DOC value. This indicates a mean oxidation stage, which is in good accordance with typical natural products. The samples from carbonized sewage sludge as well as carbonized coffee grounds showed better biodegradability than samples of carbonized straw, wood chips or cotton wool. This may be explained by attributes of the starting materials. All HTC process waters, except the one of carbonized sewage sludge, showed high loads of aldehydes and ketones. Furans were seen most intensively in samples from cotton wool and sewage sludge. Heterocyclic compounds were particularly noted in samples of carbonized straw and sewage sludge. Also, samples of carbonized sewage sludge showed high loads of sulphur compounds and p-cresol. Phenol as well as ortho-, metha- and para-methylphenol was present in all samples with highest concentrations in carbonized coffee ground. The assumption that phenols originate from lignin was disproved, as samples of lignin-free input material also contained phenols. The discharge of phenols into the environment should be avoided due to their toxicity Generally the influence of the input material on the contaminant pattern was clearly visible.

Well matching are, the preferential formation of sulphur-containing heterocyclic compounds, from carbonized sewage sludge with higher sulphur loads, the occurance of furan from carbonized glucose cotton wool, and the of phenols from poly phenolic coffee grounds. Additionally it could be shown that some compounds and structural features are persistent within the HTC process which is in good agreement with the recent study of Weiner [4]. They will be released to the environment, if process water is used for fertilization. Therefore we suggest to further analyze process waters for persistant anthropogenic trace substances to prevent their discharge to the environment by HTC process waters.

1. Libra, J.A., et al., Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. Biofuels, 2011. 2(1): p. 71-106.

2. Titirici, M.-M. and M. Antonietti, Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. Chemical Society Reviews, 2010. 39(1): p. 103-116.

3. Becker, R., et al., Hydrothermally carbonized plant materials: Patterns of volatile organic compounds detected by gas chromatography. Bioresource Technology, 2013. 130(0): p. 621-628.

4. Weiner, B., et al., Potential of the hydrothermal carbonization process for the degradation of organic pollutants. Chemosphere, 2013. 92(6): p. 674-680.