Bioresource Technology 263 (2018) 654–659

Contents lists available at ScienceDirect

Bioresource Technology

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

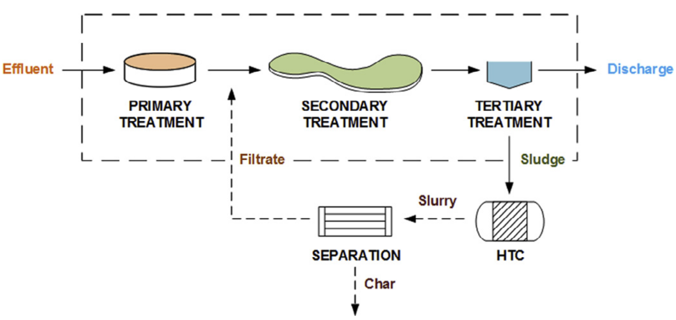
Short Communication

# Process water properties from hydrothermal carbonization of chemical sludge from a pulp and board mill

Mikko Mäkelä[a,b,*], Julia Forsberg[c], Christer Söderberg[d], Sylvia H. Larsson[b], Olli Dahl[a]

[a] Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems, PO Box 11000, 00076 Aalto, Finland
[b] Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, Division of Biomass Technology and Chemistry, Skogsmarksgränd, 90183 Umeå, Sweden
[c] RISE Processum AB, Hörneborgsvägen 10, 89122 Örnsköldsvik, Sweden
[d] Iggesund Paperboard AB, Iggesund Mill, Development Department, PO Box 15, 82580 Iggesund, Sweden

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Keywords:*
Biosolids
Experimental design
Hydrothermal treatment
Multiple linear regression
Principal component analysis
Wastewater treatment

## ABSTRACT

Hydrothermal carbonization (HTC) can be used to break down sludge structure and generate carbonaceous hydrochar suitable for solid fuel or value-added material applications. The separation of char and the reaction medium however generates a filtrate, which needs to treated before potential discharge. Thus, this work determined filtrate properties based on HTC temperature and sludge moisture content and estimated the discharge emissions and the potential increase in analyte loads to an industrial wastewater treatment plant based on derived regression models. Direct discharge of HTC filtrate would significantly increase effluent emissions at the mill, indicating the filtrate treatment is crucial for the future implementation of HTC at pulp and paper mills. Recycling the HTC filtrate to the wastewater plant would lead to only a nominal increase in effluent flow, but would increase the suspended solids, BOD, COD and total nitrogen loads by 0.1–0.8%, 3.8–5.3%, 2.7–3.1% and 42–67%, respectively, depending on HTC temperature.

## 1. Introduction

Sludge management represents a significant challenge for the forest industry. Sludge residues from wastewater treatment plants are currently the most important solid waste streams produced at pulp and paper mills. Wastewater treatment within the industry is generally performed through mechanical, biological or chemical methods which generate sludge residues with different properties. The low solids content and the physical form of sludge however makes their handling generally problematic. Primary sludge from mechanical clarification or biosludge from activated

* Corresponding author at: Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems, PO Box 11000, 00076 Aalto, Finland.
*E-mail addresses:* mikko.makela@aalto.fi, mikko.makela@slu.se (M. Mäkelä).

https://doi.org/10.1016/j.biortech.2018.05.044
Received 13 March 2018; Received in revised form 9 May 2018; Accepted 10 May 2018

sludge plants can in some installations be incinerated in the solid fuel or recovery boilers after mechanical dewatering or evaporation. Chemical sludge from the treatment of coating effluents, addition of chemicals or separate tertiary treatment is more difficult to dewater, pump or handle at treatment or final disposal sites (Hynninen et al., 2008). In Sweden, approximately 22,000 tons of dry chemical sludge was produced within pulp and paper mills in 2016. One third was incinerated while the rest was used in material applications such as landfill construction (Swedish Forest Industries Federation, 2017).

Hydrothermal carbonization (HTC) can be used to break down sludge structure and generate carbonaceous hydrochar more suitable for solid fuel or value-added material applications (Alatalo et al., 2013; Danso-Boateng et al., 2015a; Xu & Jiang, 2017). The use of subcritical water under elevated temperature and pressure does not require prior drying of sludge and improves respective drying properties and destroys potential sludge pathogens (Mäkelä et al., 2016; Peterson et al., 2008; Wang et al., 2014). Partial dissolution of organic compounds during HTC however requires further treatment of the subsequently separated filtrate or condensate before potential discharge. Laboratory hydrothermal experiments are generally performed with electrically heated autoclaves, as both external heating with auxiliary fuels or internal heating with steam is being used in continuous or batch-type industrial installations (Hitzl et al., 2015; Prawisudha et al., 2012). The use of steam can enable partial drying of the carbonized feed but will generate a condensate which will need to be further considered.

One of the challenges for the application of HTC is respective integration to existing industrial environments and the management of generated process water. Several research groups have thus determined the effects of process water utilization in various applications. Recycling the separated filtrate back to the reactor can increase char mass and energy yields with feedstocks where additional water for HTC is required (Catalkopru et al., 2017; Kambo et al., 2017). The decomposition of organic compounds during HTC generates organic acids, which lower liquid pH and can further catalyse hydrolysis and decarboxylation reactions upon recycling. The separated filtrate also contains hydrolysed sugars and can be used for methane production by anaerobic digestion (Danso-Boateng et al., 2015a; Erdogan et al., 2015; Villamil et al., 2017). Wirth et al. reported no significant differences between mesophilic and thermophilic digestion and suggested co-digestion of condensate due to increased phenol concentrations and comparatively lower gas production (Wirth & Reza, 2016; Wirth et al., 2015). Wet oxidation of separated filtrate for destruction of chlorinated aromatics not degraded by HTC, and use in acidification of animal slurries have also been reported (Keskinen et al., 2017; Riedel et al., 2015).

Pulp and paper mills represent a special case for the application of HTC as a wastewater treatment plant already exists on-site. The easiest way to treat the separated filtrate would thus be to recycle it back to wastewater treatment plant, generating a circulating carbon load between wastewater treatment and the HTC reactor. However, no research has been published on the effects of HTC conditions on filtrate properties that are important for industrial wastewater treatment. HTC conditions govern char and filtrate properties and affect potential filtrate recycling. The objective of this work was to determine filtrate properties based on HTC of chemical sludge from a pulp and board mill. Laboratory experiments were performed to systematically determine the effects of HTC conditions on filtrate properties based on multivariate and multiple linear regression models. The attained results are important for evaluating the potential of filtrate recycling to a wastewater treatment plant and the overall feasibility of sludge carbonization at pulp and paper mills.

## 2. Materials and methods

### 2.1. Sludge sampling and preparation

Chemical sludge was sampled from a Swedish pulp and board mill producing chemical pulp and paper board. The wastewater treatment plant at the mill included a large aerated settling pond to which all effluent streams were directed regardless of prior treatment. The effluent from the aerated lagoon was partially or entirely led to chemical treatment where aluminum sulphate was used as the main flocculating agent. After sampling, sludge samples with different moisture contents were prepared by dilution with deionized water to determine the effects of sludge moisture content on filtrate properties.

### 2.2. Sludge carbonization

The experiments were performed in a 0.28 L Büchi Limbo (Büchi AG) reactor fitted with a magnetic stirrer. Prepared sludge samples of 200 g were heated to 180–260 °C with a PID controlled electrical heating block after flushing with nitrogen. The approximate heating rate was 2.5–4.0 C $min^{-1}$ depending on target temperature. Reactor pressure was observed from a pressure gauge and was approximately equal to the saturated vapour pressure of water at respective temperatures. After an isothermal holding time of 1 h the reactor was cooled to 100 °C and placed in a cold-water bath. After cooling to 40 °C, the non-condensable gases were vented and the char and filtrate were separated by vacuum filtration through a Whatman 25 µm filter paper. The individual experiments were organized according to a central composite design in which carbonization temperature and sludge moisture content were varied on three different levels (Table 1). The final design was composed of 11 experiments including three repeated experiments in the design center.

### 2.3. Analyses

After solid and liquid separation, the filtrate pH values were measured with a Mettler-Toledo EL20 instrument (Mettler-Toledo LLC). The filtrate samples were then sent to an external laboratory certified by the national accreditation body SWEDAC. The total nitrogen and phosphorus contents were determined according to international standards SS-EN ISO 11905-1:1998 and SS-EN ISO 6878:2004, respectively. The seven-day biological oxygen demand (BOD) was determined according SS-EN 1899-1:1998 and the total organic carbon according to EN 1484:1997. The suspended solids in the filtrate were determined according to SS-EN 872:2005 based on filtration. For calculating the carbon and nitrogen yields in the filtrates, the CHN contents of the untreated sludge and dried chars were determined according to SS-EN 15407:2011 after the char samples were dried at 105 °C overnight and manually ground in a mortar. For determining sample properties on a dry-ash free (daf) basis, the respective ash contents were measured by loss on ignition at 550 °C according to SS-EN-14775. The above-mentioned filtrate analyses were chosen as they are commonly used within the pulp and paper industry to estimate effluent properties before and after wastewater treatment.

**Table 1**
The carbonization experiments.

| Experiment n:o | Reactor temperature (°C) | Moisture content (kg $H_2O$ $kg^{-1}$ db) | Dry solids (%) |
|---|---|---|---|
| 1 | 180 | 10.2 | 8.9 |
| 2 | 260 | 10.2 | 8.9 |
| 3 | 180 | 4.4 | 18.5 |
| 4 | 260 | 4.4 | 18.5 |
| 5 | 180 | 7.3 | 12.0 |
| 6 | 260 | 7.3 | 12.0 |
| 7 | 220 | 10.2 | 8.9 |
| 8 | 220 | 4.4 | 18.5 |
| 9 | 220 | 7.3 | 12.0 |
| 10 | 220 | 7.3 | 12.0 |
| 11 | 220 | 7.3 | 12.0 |

db = dry basis.