

Separation of heavy metals in municipal wastewater treatment – Cd sorption capacity of sludge-derived char

Project specifications

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Summary of results

Cadmium (Cd) sorption capacity of char derived from primary sludge (PSC) was found to be superior to that of char derived from digested sludge (DSC) (mix of primary and secondary sludge) under similar pyrolysis conditions. The maximum Cd sorption capacity found was 9.0 mg/g. Possible causes of the superiority of PSC were larger availability of oxygen containing surface functional groups in PSC (which may promote complexation and ion exchange), and larger pH which may promote precipitation of Cd. The sorption capacity of char derived from the respective sludge type correlated positively with SSA and pyrolysis temperature.

Pyrolysis conditions (temperature and time) will impact the yield and quality of sludge-derived char. Increased pyrolysis temperature led to decreased pyrolysis yield and surface area (SSA) while char ash content and pH increased. The yield and ash content were higher for DS compared to PS, which is explained by the higher original ash content in DS. Volatilization of Hg and Cd was seen with respect to both PS and DS, depleting the concentration of these metals in the chars produced.

Experimental results and calculations indicated that the drying and pyrolysis of dewatered sludge could be supported by the incineration of pyrolysis vapors. The results should be considered with caution since the extended time of pyrolysis was not explicitly considered in the calculations. Due to higher initial energy content in PS, a more positive net energy balance (possible extraction of excess heat from incineration of pyrolysis vapors) was found with respect to PS pyrolysis compared to DS pyrolysis.

Introduction

Municipal wastewater contains nutrients and organic matter that are of interest for agriculture, but the wastewater also contains unwanted micro-pollutants such as heavy metals and residues from pharmaceuticals and personal care products. These contaminants can cause environmental damage or health issues if spread to the environment through effluent discharge or sludge end use (European commission [EC], 2010). The current European legislation (EC, 1986) is aimed at promoting sludge use in agriculture to achieve nutrient reuse (Naturvårdsverket, 2013). In Sweden, the national certification Revaq, which is run by the Swedish Water and Wastewater Association, contains further requirements on the contents of contaminants in sludge and requires that municipal authorities work for continuous improvement of the sludge quality through reduction of heavy metal contents in raw wastewater (Svenskt Vatten, 2023-04-30). Sources of heavy metals in wastewater have been studied in several projects in Sweden and other Nordic countries during the last 15 years, for example the work by Sörme & Lagerkvist (2002). With decreased emissions from industrial activities during the last decades, households have been

found to contribute to a large portion of the metals found in municipal wastewater (Magnusson, 2003; Olofsson, 2012; Sörme & Lagerkvist, 2002). Reduced use of these metals in society could reduce metal concentrations in wastewater effluent and sludge. The focus of this work is to increase metal separation in municipal wastewater treatment plants.

There are a number of existing treatment technologies for removal of heavy metals. These include: precipitation (with hydroxides, sulfides, chelating precipitation chemicals), ion exchange (using synthetic or natural resins), adsorption (char materials, carbon nano tube adsorbents, cryo-gels, clays, agricultural wastes etc.), membrane filtration technologies (i.e. ultrafiltration, reverse osmosis, nanofiltration and electrodialysis), coagulation, flotation (after addition of a precipitant or surfactant), electrochemical treatment technologies (electrocoagulation, electroflotation, electrodeposition, electrodeionization) and photocatalysis (Barakat, 2011; Carolin et al., 2017; Fu & Wang, 2011). These treatment technologies have primarily been studied for treatment of industrial wastewater, which generally has much higher metal concentrations compared to municipal wastewater.

Adsorption and membrane separation are the most frequently studied methods for metal separation from water and wastewater. With the development of biosorbents produced from waste organic matter, adsorption is considered to be a potential low-cost process (Barakat, 2011; Fu & Wang, 2011). Benefits of adsorption processes, compared to many of the other treatment technologies studied, are low production of sludge and no chemical use (Inyang et al., 2016; Mohan et al., 2014; Niazi et al., 2016). Reported adsorption capacities for biochars produced from different organic wastes range from less than 1 mg metal/g biochar to more than 100 mg/g. Variations are large, depending on the biochar used (Inyang et al., 2016). In a study by Tao et al. (2015), adsorption of Pb to sludge-derived biochar was shown to be over 95 % at an adsorbent dosage of 2 g/L and metal concentration of 50 mg/L. Metal concentrations commonly found in municipal wastewater are generally in the range of ~10-100 µg/L, depending on metal. Large variations have also been observed between different geographical locations (Cantinho et al., 2016). At a dosage of 1 mg biochar/L, the metal adsorption capacity theoretically exceeds the metal contents in municipal wastewater.

Several researchers (Chen et al., 2014; Zhang et al., 2013) have shown that the pyrolysis process is of importance for the sorption capacity of sludge-derived biochar. The aim of this work is to investigate properties of different sludge-derived biochars to find out how to pyrolyze the sludge to optimize the metal removal.

This report includes a written summary of selected results from the experimental work performed. The detailed results have been left out to avoid conflicts with regards to later scientific publishing. Full results are being included in a paper manuscript for submission to a scientific journal (later during 2023).

Methods

Purchase and installation of oven for production of sludge-derived char

In the initial phase of the project a tube furnace (later used for pyrolysis of sludge for production of char) was purchased, installed, and tested. The furnace was equipped with a nitrogen atmosphere to ensure inert conditions.

An overview of the furnace setup is given in Figure 1.

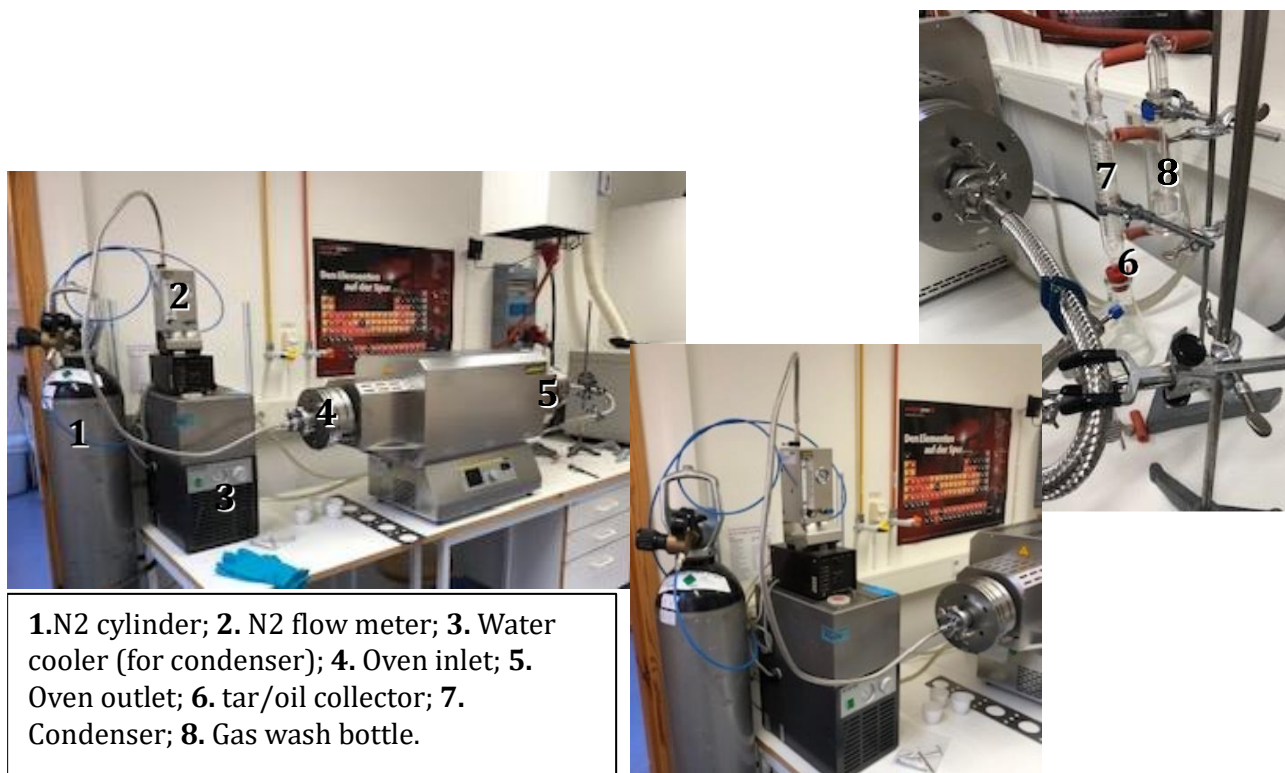


Figure 1. Overview of furnace setup.

Experimental work

Collection and processing of sludge substrates:

- Primary (PS) and digested (DS) sludges were collected at Käppala WWTP, Lidingö, Sweden, DS was collected after dewatering, from centrifuge. PS was manually dewatered in the lab. Drying of both sludges was performed in the lab. Sludges as collected and after drying were analysed with respect to metal content, moisture content, ash content, elemental composition, calorific value, and surface area.

Pyrolysis:

- The dried sludges were shredded and sieved to <8 mm, and pyrolysis was performed in the afore mentioned tube furnace.
- Sludge samples were placed in ceramic cups inside the furnace tube. Pyrolysis was performed at temperature interval 400-800°C, and residence time 70-120 minutes. Three different residence time-temperature combinations were investigated: 400°C-70 min; 800°C-70 min; and 600°C-120 min. Chars produced were denoted PSC (primary sludge char) and DSC (digested sludge char) respectively.
- Char was collected the following morning. After pyrolysis the chars were ground and sieved (<0.250 mm).

Characterization of sludge-derived char

- Sludge-derived char was characterized with respect to metal content, pH, surface area, calorific value (higher heating value), elemental composition, ash content, and surface functional groups (through Fourier transform infrared spectroscopy). Metal content was analysed by an external lab, while other parameters were analysed in-house.

Metal sorption investigation:

- The chars were tested with respect to Cd sorption capacity, through batch sorption tests to investigate the maximum Cd sorption capacity.

Assessment of Cd sorbent production and economic viability in relation to local need for sorbent

To assess the viability of producing a Cd sorbent from sludge, the local need for Cd sorbent and the associated economic benefit were assessed in relation to the sorption capacity of the char generated. Results with respect to this topic are preliminary at this stage, and not included in this report.

Furthermore, the energy balance of pyrolysis for char production was assessed.

Results and discussion

Characteristics of sludge-derived char and its influence on char Cd sorption capacity

As could be expected, the pyrolysis yield for the respective sludges decreased with increasing pyrolysis temperature (and increased carbonization), while char ash content and pH increased. The yield and ash content were higher for DS compared to PS, which is explained by the higher original ash content in DS.

The SSA increased with increasing pyrolysis temperature. The most pronounced increase occurred between 600 and 800°C. Increased pyrolysis temperature and residence time are generally beneficial for the development of pore structure (and SSA), however, pore enlargement due to volatile losses in the range 550-650°C may limit the SSA development (Xu et al., 2018).

The calorific value of PSC was similar to that of dried PS. With respect to DSC, the calorific value decreased with increasing pyrolysis temperature, in proportion to the decreasing yield. The energy content of dried sludge and char was comparable to that found in previous studies (Kim and Parker, 2008).

Cd sorption capacity for the respective sludge types (PS and DS), correlated positively with SSA and pyrolysis temperature. However, PSC generally had larger sorption capacity than DSC, though the SSA was smaller. A possible explanation is the contribution of oxygen containing surface functional groups in PSC which had larger O content. The maximum Cd sorption capacity found was 9.0 mg/g (for PSC - 800°C, 70 min) and is of similar magnitude as according to previously published studies with respect to unmodified sludge-derived char (23 mg/g (800°C, 20 min) and 1.7 mg/g (350°C, 15 min); Chen et al. (2014) and Wongrod et al. (2018) respectively).

Considering the metal contents in dried sludge and chars, Cd and Hg were volatilized during pyrolysis; Hg from 400°C, and Cd at 800°C (at these temperatures, Cd and Hg concentrations in char were below the concentrations in dried sludge substrate). The other metals investigated all increase in concentration when comparing char to dried sludge substrate. However, based on mass balance calculation (details not given here), all metals (with exception of Ni in DS-derived chars) were partly transferred to pyrolysis vapors at 800°C, and some were transferred at 400°C. DS and DSC (with exception of Hg concentrations in DSC), had higher metal concentrations compared to PS and PSC.

FTIR analysis confirmed the decomposition and aromatization occurring during pyrolysis. Dried PS contained O-H bonds, found in alcohols or carboxylic acids, and C-N-C bonds (broad trough around 3350 and small trough at ~1550 cm⁻¹ respectively) (Kim et al. 2012; Hossain et al., 2011; Lu et al., 2012). FTIR spectra indicated that these bonds decomposed during pyrolysis. No O-H peak was seen for DS, which may be due to the (previous) decomposition of sludge occurring

during digestion. The aromatization process was also indicated by destruction of alkene C-H bonds in both PS and DS (through the disappearance of small distinct troughs at ~ 2920 and ~ 2855 cm^{-1}) (Zhang et al., 2013). The troughs at ~ 1600 cm^{-1} may indicate stretching of aliphatic or aromatic C=C and C=O bonds (Lu et al., 2012; Kim et al. 2012). These peaks could slightly shift or decrease due to increased aromaticity which was seen as pyrolysis temperature increased. In the fingerprint region (<1450 cm^{-1}), carbon-carbon (C-C) and carbon-oxygen (C-O) bonds absorb IR at a wide range of wavenumbers (Clark, 2020) and may contribute to a combined peak at ~ 1000 cm^{-1} . Comparing the FTIR spectra of PS, DS, and the respective chars, it appears that PS as a starting material has a richer functional group composition compared to DS, which is in line with the observed sorption capacities and oxygen content of the chars. The surface functional groups could thus contribute to balancing the lacking SSA of PSC compared to DSC.

Energy balance of pyrolysis

Experimental data and calculations indicate that energy in pyrolysis vapors is sufficient to support sludge pyrolysis. With increased pyrolysis temperature, the energy balance is shifted so that the surplus energy increases, mainly due to the increased generation of pyrolysis vapors which generates more energy compared to the increase of energy required for heating the pyrolysis process. PS pyrolysis has a more positive energy balance compared to DS pyrolysis, due to ~ 39 % larger initial calorific value. Similar results were found by Kim and Parker (2008), who found PS to have 35 % larger energy content than DS, per kg dry sludge. Buonocore et al. (2015) found a similar energy use for drying of sludge (~ 2000 kJ/kg dewatered sludge, or 937 MJ/472 kg dry sludge, dewatered from 75 to 10 % moisture content). Uncertainty exists with respect to net excess energy because energy required to maintain the temperature during residence time was not considered. A previous study based on modelling indicated that, due to energy losses, the energy in pyrolysis vapors (syngas and oil) covered ~ 80 % of the energy needed for drying (73 to 10 % moisture) and pyrolysis of digested sludge at 500°C (Salman et al., 2019).

Conclusions

The sorption capacity of sludge-derived char increased with increasing pyrolysis temperature, which was in line with increased surface area and pH. However, based on the comparison of PSC and DSC, the surface area has less significance for Cd sorption compared to the abundance of surface functional groups and pH of the chars. The results point to the favorable properties of PSC/ PS pyrolysis compared to DSC/ DS pyrolysis:

- The Cd sorption capacity of PSC exceeded that of DSC, even though PSC had smaller surface area. The probable explanation is the richer composition of surface functional groups in PS as a starting material (and higher oxygen content of PSC). The surface functional groups could thus contribute to balancing the lacking SSA of PSC compared to DSC.
- The net energy balance of pyrolysis was more positive with respect to PS pyrolysis than DS pyrolysis. Excess of heat/pyrolysis vapours is favoured by increased pyrolysis temperature (800°C compared to 400°C).

Dissemination

A manuscript is currently being finalized for publication in a scientific journal within the coming months. The publication will also be included in the doctoral thesis of Ida Sylwan (to be finalized during 2023).

Economic report

The project budget from ÅForsk was 300 000 SEK. The total project costs are 297 911.62 SEK. Specification of the costs are given in Table 1.

Table 1. Specification of project costs.

Type	Description	Cost (SEK)	Anticipated cost (SEK)*
Oven for pyrolysis including shipping fees and taxes	Oven in which pyrolysis can be performed in a controlled manner with respect to temperature and time, in an oxygen free atmosphere.	98 400,00	
Oven spare parts	Spare tube for tube furnace.	35 425,84	35 425,84
External analysis of char/water	External analysis with respect to metals in char and water (the majority of char analysis was performed in-house).		26 875,00
Materials, reagents and equipment for internal analysis	Sample containers, filter papers, acids for pH adjustment and preservation of samples, metal salts, etc.	16 464,60	
Salary costs	Technician, supervision, and part of experimental work**.	58 801,09	
Travel costs in association with experimental work	Collection of sludge.	1 519,25	
Publishing fee	The deliverable from the project is an article in an open access journal.		25 000,00

*Invoices expected later during 2023 (after delivery of this project report).

**The salary cost for Ida Sylwan has mainly been taken from another project.

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