ABSTRACT
Metal concentrations in soil and water have increased since the Industrial Revolution, which may have negative health and environmental effects. Metal pollution occurs, for instance, in municipal wastewater, industrial wastewater, and stormwater. Concentrations are often low, due to dilution. A common technology for metal removal is sorption. Char produced from pyrolysis of municipal sludge (SDC), has been pointed out as a potential low-cost sorbent. However, the scientific literature mainly focuses on experiments using artificial solutions at concentrations much higher than those found in said wastewaters (in a Swedish context).

The goal of this study was to investigate SDC use for the removal of metals, focusing on reuse of SDC in primary treatment (PT) of municipal wastewater and with some attention to other applications. The investigation was performed through experimental laboratory studies, modelling, and literature review/assessment.

The data obtained from the literature review indicated that sorption is suitable for enhancing removal of nickel (Ni), copper (Cu), cadmium (Cd), lead (Pb), and zinc (Zn) during PT. With respect to Ni and Cu, from ~7–50% and ~10–70%, respectively (no SDC), to ~65–98% and ~45–85%, respectively (with SDC). Experimental results showed that SDC could remove ~95% of Pb, Cd, Cu, Cr, Ni, Hg, and Ag from artificial solution, at concentrations similar to those in raw municipal wastewater. However, sorption of Cu and Ni was inhibited in real wastewater (a decrease from ~99 and 99%, respectively, to 68 and 40% respectively). The inhibition was linked to the presence of dissolved organic matter. Modelling, based on raw wastewater composition indicated that SDC addition in PT may enhance the removal of Cd and Cu (from ~39% to 79% and ~30% to 43%, respectively).

Experiments showed that the investigated SDC had a larger Pb sorption capacity, compared to activated carbon and wood-derived char. Experimental investigations and modelling (sorption isotherms) indicated that literature data did not give satisfactory estimations of the Pb sorption capacity onto SDC at concentrations considered, the available data was generally valid for much higher concentrations.

The experimentally determined Cd sorption capacity of SDC produced from primary sludge exceeded that of SDC produced from digested sludge. However, given the loss of biogas production the theoretical energy balance of primary sludge pyrolysis was negative. Finally, the local demand for Cd-sorbent in the Västerås region could potentially be covered by the SDC generated locally.
SLUDGE-DERIVED CHAR

UTILISATION AS A METAL SORBENT IN DILUTE WASTEWATERS

Ida Sylwan

2023

School of Business, Society and Engineering
SLUDGE-DERIVED CHAR
UTILISATION AS A METAL SORBENT IN DILUTE WASTEWATERS

Ida Sylwan

Akademisk avhandling

som för avläggande av teknologie doktorsexamen i energi- och miljöteknik vid Akademin för ekonomi, samhälle och teknik kommer att offentligen försvaras fredagen den 20 oktober 2023, 14.00 i Zeta, Mälardalens universitet, Västerås.

Fakultetsopponent: Konrad Koch, Technical University of Munich
Abstract

Metal concentrations in soil and water have increased since the Industrial Revolution, which may have negative health and environmental effects. Metal pollution occurs, for instance, in municipal wastewater, industrial wastewater, and stormwater. Concentrations are often low, due to dilution. A common technology for metal removal is sorption. Char produced from pyrolysis of municipal sludge (SDC), has been pointed out as a potential low-cost sorbent. However, the scientific literature mainly focuses on experiments using artificial solutions at concentrations much higher than those found in said wastewaters (in a Swedish context).

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Uppsala, Sweden, September 2023
Summary

The concentrations of metals in soil and water have been increasing since the Industrial Revolution. Some metals, such as copper, chromium, zinc, nickel, boron, iron, and molybdenum, are classified as essential nutrients; others, such as lead, mercury, cadmium, arsenic, and silver, have negative health effects. However, all these metals can be toxic at high doses. Metals are found in different types of wastewater such as industrial wastewater (from mining, tanning, dyeing, waste landfills, waste incineration, and car washes), as well as stormwater and household wastewater generated in urban areas. Lead and cadmium are two of the top priority metals due to their extremely adverse health effects, and the acceptable exposure to these through ingestion, according to the World Health Organization, is very low.

Treatment of wastewater can limit the spread of metals. One common technology for metal removal is sorption; the process by which a substance in solution is held to the surface of a solid material. The use of organic byproducts for producing metal sorbents has been pointed out as a possible low-cost technology for metal removal. Char generated from pyrolysis of municipal sewage sludge, “sludge-derived char”, could be an efficient sorbent for the removal of metals from water. However, previous studies have primarily been performed with artificial metal solutions and not real wastewater, which means that the competitive or blocking effect of other wastewater constituents is not considered. In this work, sludge-derived char as a sorbent in real wastewater has thus been examined at metal concentrations relevant to such wastewaters.

What is the suitability and expected performance of sorption technology for enhancing the removal of cadmium, chromium, copper, mercury, nickel, lead, and zinc during primary treatment of municipal wastewater? Enhanced metal removal could reduce metal concentrations in effluent wastewater and in sludge from subsequent treatment. The evaluation was performed through a literature review with respect to metal speciation and current removal in municipal wastewater. The results indicated that sorption could increase the removal of nickel, copper, cadmium, lead, and zinc during primary treatment. With respect to nickel, and copper, from ~7–50% and ~10–70% removal without sorbent to ~65–98% and ~45–85% removal with sorbent, respectively. With respect to lead, cadmium, and zinc an improvement of around 50% or more could be possible in some locations.
How does wastewater composition influence the metal sorption capacity of sludge-derived char? The sorption of metals to sludge-derived char was examined through laboratory experiments, focusing on the sorption of lead at low concentration (from 5 µg/L). The results showed that the determination of sorption capacity at low lead concentrations in solution requires experimental data at relevant concentrations because the sorption could not be reliably determined through commonly applied isotherm models based on higher concentrations (given the experimental data collected in this study). The results also showed that there is a risk that lead is released from sludge-derived char at low initial concentrations in solution. Thus, the metals initially contained in the sludge-derived char should be considered. The sorption capacity of sludge-derived char in real wastewater was examined with respect to lead, cadmium, copper, chromium, nickel, zinc, mercury, and silver. The sludge-derived char sorbed and removed less amounts of copper and nickel in wastewater (68% and 40%, respectively) compared to the sorption in artificial metal solution at similar metal concentrations (>99% and 99%, respectively).

With respect to lead, how does sludge-derived char perform in relation to other carbonised sorbents (i.e., sorbents which have gone through pyrolysis)? The sludge-derived char sorption capacity was experimentally investigated in relation to the sorption capacity of a commercial activated carbon and a wood-derived char. The results showed that the sludge-derived char had a larger sorption capacity for lead (maximum ~2 mg/g at pH 2) compared to activated carbon and wood-derived char (at least 10 times less sorption capacity at pH 2). The smallest initial concentration examined (5 µg/L) was an exception, where lead was released from the sludge-derived char.

Given the typical composition of municipal wastewater, how large metal removal could be expected when applying sludge-derived char as a sorbent during primary treatment of municipal wastewater? Metal removal in the primary treatment of municipal wastewater was modelled based on experimental data. Results indicated that sludge-derived char could increase the removal of cadmium and copper (from 39 and 30%, respectively, with no sludge-derived char to 79 and 43%, respectively, with sludge-derived char addition). Results also indicated that lead and zinc were bound to particulate matter in influent wastewater which limits the effect of sludge-derived char addition. Nickel was not sorbed efficiently and the possibility of increased removal was predicted as small.

With respect to the priority metal cadmium, how large is the sorption capacity of sludge-derived char compared to the local sorbent demand? Data with respect to cadmium contents in wastewaters (dilute industrial wastewaters and stormwater) in the local area around Västerås, Sweden, was assessed in relation to the cadmium sorption capacity of sludge-derived char. The results indicated that the amount of sludge-derived char which could be generated from the local wastewater treatment plant (and its sorption capacity) could cover the demands for local cadmium removal. A potential barrier for
the use of sludge-derived char is that the estimated char volumes required would be large compared to the volumes of ion exchange resins used in a current treatment plant.

To which degree are cadmium sorption capacity and pyrolysis energy balance influenced by pyrolysis temperature and sludge composition? Pyrolysis of primary sludge and mixed digested sludge (primary sludge and sludge from subsequent biological treatment) was experimentally investigated. Though its surface area was smaller, char derived from primary sludge had larger sorption capacity for cadmium (9.1 mg/g; 30 m$^2$/g) compared to that derived from pyrolysis of mixed digested sludge (6.0 mg/g; 87 m$^2$/g). The cadmium sorption capacity and the energy balance were more favourable at higher pyrolysis temperatures. However, a literature review indicated that pyrolysis of sludge is more energy-demanding compared to use of dewatered sludge on agricultural land or sludge incineration.

In summary, the results indicated that sludge-derived char could be applied to increase the removal of cadmium and copper during primary treatment of municipal wastewater. The local demand for metal sorbent is crucial for the potential of sludge-derived char as a low-cost technology. Despite its lower surface area, sludge-derived char could be a more efficient lead sorbent compared to commercial activated carbon or wood-derived char. The composition of the sludge used is crucial for the cadmium sorption capacity of sludge-derived char. The energy balance of sludge pyrolysis is positive from a theoretical perspective, and more so at higher pyrolysis temperatures. However, it remains to be shown that this can be accomplished in a full-scale pyrolysis installation.

Rening av avloppsvatten kan begränsa spridningen av metaller. En vanlig teknik för metallavskiljning är sorption; den process där ett ämne i lösning hålls vid ytan av ett fast material. Användning av organiska restprodukter för att producera metallsorbenter har pekats ut som en möjlig lågkostnadsteknik för att avskilja metaller. Kol genererat via pyrolys av kommunalt avloppsslam, ”slamkol”, kan vara en effektiv sorbent för rening av metaller från vatten. Studier har dock främst utförts med konstgjorda metalllösningar, och inte med riktigt avloppsvatten, vilket betyder att hänsyn inte tas till konkurrens eller blockerande effekt av andra avloppsforreningar. I detta arbete har slamkol som sorbent i verkligt avloppsvatten därför undersöks, vid metallkoncentrationer som är relevanta för sådana avloppsvatten.

Hur påverkas metallinsorptionen av avloppsvattnets sammansättning? Sorption av metaller till slamkol undersöktes genom laboratorieförsök, med fokus på sorption av bly vid låga koncentrationer (från 5 µg/L). Resultaten visade att bestämning av sorptionskapaciteten vid låga initiala halter bly i lösning kräver experimentella data vid relevanta halter eftersom sorptionen inte kunde förutsättas på ett tillfredsställande sätt genom vanligen tillämpad isoterm-modellering baserat på högre halter (givet de experimentella data som genererades i detta arbete). Resultaten visade också att det finns risk att bly frigörs från slamkolet vid låg initial koncentration i lösningen. Därför bör hänsyn tas till de metaller som ursprungligen finns i slamkolet. Sorptionskapaciteten hos slamkol i verkligt avloppsvatten undersöktes med avseende på bly, kadmium, koppar, krom, nickel, zink, kvicksilver och silver. Slamkolet sorberade och avskilde mindre mängd koppar och nickel i avloppsvatten (68 respektive 40 %) jämfört med i metalllösning vid liknande metallkoncentration (>99 respektive 99 %).

Med avseende på bly, hur jämför sig slamkolets sorptionskapacitet med den hos andra karboniserade sorbenter (dvs. sorbenter som genomgått pyrolys)? Slamkolets sorptionskapacitet jämfört med sorptionskapaciteten hos ett kommersiellt aktivt kol samt ett träkol undersöks experimentellt. Resultaten visade att slamkolet hade högre kapacitet att ta upp bly (maximalt ~2 mg/g vid pH 2) jämfört med de andra sorbenterna (mer än 10 gånger lägre sorption vid pH 2). Den lägsta initiala koncentrationen som undersöks (5 µg/L) var ett undantag, där bly i stället frigjordes från slamkolet.

Givet typisk sammansättning hos kommunalt avloppsvatten, hur stor metallavskiljning kan förväntas vid användning av slamkol som sorbent vid primärrenning av kommunalt avloppsvatten? Metallavskiljningen vid primärrenning av kommunalt avloppsvatten modellerades baserat på experimentella data. Resultaten indikerade att slamkol kan öka avskiljningen av kadmium och koppar (från 39 respektive 30 % utan slamkol, till 79 respektive 43 %, med tillsats av slamkol). Resultaten indikerade även att bly och zink till stor del är bundna till partikulärt material i inkommande avloppsvatten vilket begränsar effekten av slamkoltillsats. Nickel sorberades inte effektivt och potentialen till ökad avskiljning förutspåddes vara låg.

Med avseende på den prioriterade metallen kadmium, hur stor är sorptionskapaciteten hos slamkol jämfört med den lokala efterfrågan på sorbent? Data med avseende på kadmiuminnehåll i avloppsvatten (utspädda industriavloppsvatten och dagvatten) lokalt kring Västerås värderades i relation till kadmiumsorptionskapaciteten hos slamkol. Resultaten indikerade att mängden slamkol som kan genereras vid det lokala avloppssamhället (och dess sorptionskapacitet) skulle kunna täcka behovet av kadmiumrening lokalt. Ett möjligt hinder för användning av slamkol är att de uppskattade volymerna slamkol som skulle krävas var stora jämfört med volymerna jonbytarmassa som används vid en befintlig reningsanläggning.
I vilken mån påverkas slamkolets sorptionskapacitet samt energibalansen för pyrolys av den temperatur som tillämpas för pyrolys och av sammansättningen hos det slam som används? Pyrolys av primärsram respektive rötat blandslam (primärsram och slam från efterföljande rening) undersöktes experimentellt. Trots att ytarean hos slamkolet var lägre hade slamkol från primärsram högre sorptionskapacitet (9,1 mg/g; 30 m$^2$/g) än slamkol från pyrolys av rötat blandslam (6,0 mg/g; 87 m$^2$/g). Såväl kapaciteten att ta upp kadmium och energibalansen för slampyrolys var mer fördelaktig vid högre pyrolystemperatur. En litteraturöversikt indikerade dock att pyrolys av slam är mer energikrävande jämfört med användning av slam på jordbruksmark eller slamförbränning.

List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


IV. Sylwan, I., Bergna, D., Runtti, H., Johansson Westholm, L., Thorin, E. *Primary and digested sludge-derived char as a Cd sorbent - feasibility of local utilisation*. Submitted manuscript.


Reprints were made with permission from the respective publishers. The author made the following contributions to the respective papers:

I. Conceptualisation, collection of literature data, and writing the paper with input from the co-author and Eva Nordlander.

II. Conceptualisation with input from Eva Thorin, Jesus Zambrano, and Lena Johansson Westholm. Performing the main experimental
work together with Hanna Runtti. Performing calculations and isotherm fitting together with Jesus Zambrano. Writing the paper with input from the co-authors.

III. Conceptualisation with input from the co-author and Eva Nordlander. Performing the main experimental work and writing the paper with input from the co-author and Lena Johansson Westholm.

IV. Conceptualisation, performing the main experimental work, and writing the paper with input from the co-authors.

V. Conceptualisation, collection of literature data, and writing the paper with input from the co-authors.

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# Nomenclature

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<tr>
<td>AC</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>AD</td>
<td>Anaerobic digestion</td>
</tr>
<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>DM</td>
<td>Dry matter (mass of sample remaining after drying at 105°C)</td>
</tr>
<tr>
<td>DOM</td>
<td>Dissolved organic matter</td>
</tr>
<tr>
<td>DS</td>
<td>Digested sludge (from municipal wastewater treatment)</td>
</tr>
<tr>
<td>DSC</td>
<td>Char produced from digested sludge</td>
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<tr>
<td>EQS</td>
<td>Environmental quality standard</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic retention time</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>P</td>
<td>Phosphorus</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>Phosphate</td>
</tr>
<tr>
<td>PS</td>
<td>Primary sludge (from municipal wastewater treatment)</td>
</tr>
<tr>
<td>PSC</td>
<td>Char produced from primary sludge</td>
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<tr>
<td>SEM-EDS</td>
<td>Scanning electron microscopy-energy dispersive X-ray spectroscopy</td>
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<tr>
<td>SDC</td>
<td>Sludge-derived char (produced through pyrolysis of municipal sludge)</td>
</tr>
<tr>
<td>SSA</td>
<td>Surface area</td>
</tr>
<tr>
<td>TIC</td>
<td>Total inorganic carbon</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>WDC</td>
<td>Wood-derived char</td>
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<td>WWTP</td>
<td>Wastewater treatment plant</td>
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</table>
1. Introduction

Metal contamination is a concern due to elevated metal concentrations in the natural environment as a result of anthropogenic activities (Vareda et al., 2019). Metals of concern include biologically essential elements such as copper (Cu), chromium (Cr), zinc (Zn), nickel (Ni), boron (B), iron (Fe), and molybdenum (Mo), as well as elements that are non-essential and toxic, such as lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), and silver (Ag) (Vardhan et al., 2019). In Europe, excess concentrations of essential and toxic metals constitute the main type of pollution in soil and groundwater (Vareda et al., 2019). A major source is atmospheric deposition originating from the incineration of fossil fuels and wastes (Thevenon et al., 2011). Metal pollution also occurs in wastewaters, which may contribute significantly to the local metal load on recipients (Sörme & Lagerkvist, 2002).

The World Health Organization has identified ten top priority chemicals of public health concern, including the metals Cd, Pb, As, and Hg (WHO, 2020). The release of these metals to water (release of treated wastewater) and to soil (through sludge reuse) is regulated by limit values and freshwater standards (EC, 1986, 2008; US EPA, 2023, 2023b). The regulation also includes the metals Cr, Cu, Ni, and Zn. Metal toxicity may arise even at low metal concentrations, causing disease to the gastrointestinal, renal, and cardiovascular systems, etc., including conditions such as cancer, liver and kidney disease, melanchohy, and osteoporosis. Metal contamination may also affect plant metabolism and growth (Vardhan et al., 2019). Low concentrations in soil and water bodies may lead to bioaccumulation, which causes ecotoxicological effects (Häder et al., 2020). Metal accumulation in the food chain can affect human health adversely (Tóth et al., 2016).

Metal removal from wastewater can be achieved using various technologies, e.g., chemical precipitation, ion-exchange, sorption, coagulation-flocculation, electrodialysis, membrane filtration, photocatalysis, and electro-chemical treatment (Barakat, 2011; Carolin et al., 2017; Fu & Wang, 2011). Metals are found in wastewater from industrial activities (mining, tanning, dyeing, waste landfills, waste incineration, and car washes) as well as in runoff in cities, also referred to as stormwater, and in municipal wastewater. Due to dilution these wastewaters often contain low metal concentrations. In this work, dilute wastewaters were defined as those containing metal (sorbate) concentrations in the µg/L range (<1 mg/L).
Sludge is generated as a by-product of municipal wastewater treatment. The typical treatment process generates at least two types of sludge, primary sludge (PS) (from primary settling) and secondary sludge (from biological treatment) (Salgot & Folch, 2018). The two sludge types are typically mixed and anaerobically digested to form digested sludge (DS). The main disposal paths of digested (and dewatered) sludge in Europe is through agricultural use and incineration (Domini et al., 2022). However, there is currently a growing interest from the wastewater industry with respect to thermal treatment of sludge, including pyrolysis (Winchell et al., 2022).

Pyrolysis of sludge generates sludge-derived char (SDC). The use of SDC as a sorbent has been suggested as an efficient means of metal removal from wastewater. SDC was previously shown to exhibit comparable or higher metal sorption capacity compared to that of commercial activated carbon (AC) sorbents (Smith et al., 2009). Extensive research has been performed with respect to SDC and other carbonised sorbents. However, the vast majority of studies were performed using artificial (aqueous) metal solutions, and thus there is a lack of studies considering real wastewater (Rangabhashiyam et al., 2022). Furthermore, several studies have examined optimisation of SDC sorption capacity through adaptation of pyrolysis conditions (temperature and duration) and activation (before, during, or after pyrolysis) (Smith et al., 2009). However, examination of metal removal capacities in dilute wastewaters are lacking. To predict how sorption capacity varies at different equilibrium sorbate concentrations, isotherm models are commonly applied. However, model predictions are generally not verified with respect to dilute wastewaters. Predictions in this range, based on the existing literature, are therefore highly uncertain.

With respect to metal removal from municipal wastewater, previous studies have examined: optimisation of process parameters of conventional treatment (Gardner et al., 2013); coagulation/flocculation as a tertiary treatment step (Hargreaves et al., 2018b, 2018a); microfiltration-reverse osmosis/nanofiltration (Garcia et al., 2013); and metal removal in constructed wetlands (Kröpfelová et al., 2009). Optimisation of the primary treatment process for enhancing the metal removal has been suggested (Petrie et al., 2014). The utilisation of SDC for treatment of municipal wastewater has previously been examined with regard to the removal of organic micropollutants and nutrients. Liu et al. (2018) suggested the use of SDC for removal of organic micropollutants and nutrients from secondary treated municipal wastewater and the use of nutrient-laden char for soil amendment. Jin et al. (2017) suggested the use of SDC in the biological treatment of municipal wastewater to support the removal of nitrogen (N) through sorption as well as acting as a carbon source and biofilm carrier. However, there is a lack of research on treatment technologies that enhance metal removal during primary settling. SDC as a potential in-house resource is an interesting option. Enhanced primary treatment could prevent metals from entering both secondary sludge and effluent.
Industrial emissions have historically been the main source of metals entering municipal wastewater. However, stringent legislation for industrial emission caused metal contamination to markedly decrease during the 1970’s and the early 1980’s (Cantinho et al., 2016). Based on the trends of metal contents in sludge, it has been deduced that diffuse emissions currently constitute the main contribution of metal input to municipal wastewater treatment plants (WWTPs) in some locations (Sörme et al., 2003). Diffuse emissions include, for instance, metals from the corrosion of pipes and roofs (containing Cu) and road runoff (where asphalt, tires, and brake linings may contain Cd, Pb, and Zn). Furthermore, households may contribute significantly to diffuse emissions; the use of amalgam in dental care was estimated to contribute a large part of Hg, and food was calculated to contribute 9% of Cd and 25% of Zn to a WWTP in Stockholm, Sweden (Sörme et al., 2003). To continue the reduction of metal loads, there is a need to further regulate the use of metals in different products. Meanwhile, it is also relevant to attempt to optimise municipal wastewater treatment systems to minimise the metal contents in sludge and effluent (Cantinho et al., 2016).

The energy use associated with sludge treatment and reuse, or disposal may constitute a major share of the total energy use for wastewater treatment (Longo et al., 2016). The energy balance of sludge pyrolysis is therefore relevant when considering SDC production. Furthermore, techno-economic analyses have been performed with respect to sludge pyrolysis (Barry et al., 2019; F. Cheng et al., 2020; Huang et al., 2022), however, the previous studies have not considered the demand for SDC.

1.1 Objectives and Research Questions

The aim of this thesis is to investigate the possible use of SDC as a metal sorbent in wastewaters which are dilute with respect to metal concentrations. The following objectives were formulated:

- Exploring the suitability of applying sorption technology during or following primary treatment of municipal wastewater with the purpose of decreasing metal concentrations in secondary sludge (excess sludge from biological treatment) and in effluent.
- Investigating SDC sorption capacity in relation to sorption capacity of other carbonised sorbents.
- Investigating the possibilities of applying SDC for enhanced metal removal during or following primary treatment of municipal wastewater (such a solution could utilise PS for on-site production of SDC while promoting reuse of secondary sludge). Furthermore, to investigate its’ demand with respect to dilute industrial wastewater and stormwater.
- Investigating the importance of pyrolysis conditions and sludge composition with respect to SDC sorption capacity.
- Investigating the energy balance of SDC production from primary and secondary sludge.

The following research question (RQ) were formulated:

**RQ1** Metal removal during municipal wastewater primary treatment:
Based on the typical composition of municipal wastewater, what is the suitability and expected performance of sorption technology for enhancing the removal of Cd, Cr, Cu, Hg, Ni, Pb, and Zn during primary treatment?

**RQ2** Metal sorption capacity of SDC:
How does wastewater composition influence the metal sorption capacity of SDC? With respect to the priority metal Pb, how does SDC perform in relation to other carbonised sorbents?

**RQ3** Aspects of SDC production and its’ implementation as a metal sorbent in dilute wastewaters:
Given the typical composition of municipal wastewater, how large metal removal could be expected when applying SCD as a sorbent during primary treatment of municipal wastewater (with respect to Cd, Cr, Cu, Ni, Pb, and Zn)? With respect to the priority metal Cd, how large is the total sorption capacity of SDC produced from a local WWPT compared to the local sorbent demand with respect to dilute industrial wastewaters and stormwater? To which degree is Cd sorption capacity and pyrolysis energy balance influenced by pyrolysis temperature and sludge composition?

In order to shed light on various practical aspects of implementing SDC as a sorbent, RQ3 includes several sub-questions. Furthermore, RQ3 focuses mainly on Cd as a priority metal from a toxicity perspective. Figure 1 illustrates the correlation between the research questions and the papers included in this thesis in relation to a typical municipal wastewater treatment process.
Figure 1. Research questions and related papers. The illustration is based on a simplified overview of Kungsängsverket WWTP, Västerås, Sweden. The solid arrows illustrate current flows of water and sludge in the WWTP, while the dotted arrows illustrate the flows investigated in the current thesis. Processes are given in capital letters and flows are given in small letters (AD = anaerobic digestion).

1.2 Contributions to Knowledge

Each underlying paper contributes in the following way to knowledge in the research field, in relation to the scope of this thesis:

- **Paper I** reviewed the metal speciation and removal in municipal wastewater treatment, focusing on primary treatment. This investigation highlights the potential of enhancing metal removal during primary settling and provides suggestions for removal technologies to be further investigated.
• **Paper II** experimentally investigated the sorption of metals by SDC from aqueous metal solutions, focusing on the sorption of Pb at µg/L concentrations. The results contribute to the understanding of sorption behaviour when sorbate concentrations are low and provide insight on the importance of considering metals initially contained in SDC. The paper also contributes to knowledge with respect to Pb sorption capacity of SDC in relation to that of other carbonised sorbents.

• **Paper III** investigated the sorption by SDC in real wastewater through experimental studies and sorption modelling. The paper provides insight with respect to SDC sorption capacity in the presence of wastewater dissolved organic matter (DOM) and particles. The potential of the suggested in-house use of SDC is revealed.

• **Paper IV** experimentally investigated the sorption of Cd onto SDC produced from different sludge types (primary and DS). It contributes to knowledge on SDC sorption capacity and pyrolysis energy balance in relation to sludge composition and pyrolysis temperature. To highlight the demand for SDC as a Cd sorbent, the local demand for Cd sorbent in Västerås city and possible replacement of current removal technologies by SDC sorption was assessed. The paper contributes to the understanding of the complex issue of matching SDC production and demand, with focus on Cd removal.

• **Paper V** reviewed life cycle assessments (LCA) with respect to sludge management options: agricultural use, incineration, and pyrolysis. The paper provides insight with respect to energy demand of SDC production in relation to other sludge management options as well as limitations with respect to comparability of LCA results.
2. Theoretical Background

2.1 Metal Contamination and Related Legislation

Typical concentrations of metals in raw municipal wastewater, treated wastewater effluent, and in municipal sludge are shown in Table 1 (Paper I). Rule et al. (2006) investigated 30 WWTPs in the UK and found that Cr concentrations in raw wastewater were higher in plants with more than 50% industrial load. With respect to the other metals investigated, no such correlation was found.

Table 1. Typical metal concentrations in municipal wastewater and sludge: raw wastewater; dissolved fraction in raw wastewater; effluent concentrations; and concentrations in sludge (DM = dry mass) (Paper I).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Raw wastewater (µg/L) (number of plants)</th>
<th>Dissolved fraction in raw wastewater (%)</th>
<th>Effluent (µg/L) (number of plants)</th>
<th>Sludge (mg/kg DM) (number of plants)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>2.7–12 (15)</td>
<td>-</td>
<td>1.6–4.9 (5)</td>
<td>4.2–40.4 (6)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.4–75 (18)</td>
<td>6–100</td>
<td>&lt;0.2–1.5 (6)</td>
<td>1.0–22 (11)</td>
</tr>
<tr>
<td>Cr</td>
<td>8–100 (17)</td>
<td>7–86</td>
<td>2–20 (8)</td>
<td>15.3–856 (10)</td>
</tr>
<tr>
<td>Cu</td>
<td>10–100 (18)</td>
<td>4–55</td>
<td>5–75 (8)</td>
<td>38.9–1200 (11)</td>
</tr>
<tr>
<td>Hg</td>
<td>0.7–3.6 (6)</td>
<td>8–58</td>
<td>0.25–2 (5)</td>
<td>0.9–3.2 (6)</td>
</tr>
<tr>
<td>Ni</td>
<td>3–100 (17)</td>
<td>57–79</td>
<td>1.9–25 (8)</td>
<td>16.6–621 (10)</td>
</tr>
<tr>
<td>Pb</td>
<td>2–100 (18)</td>
<td>5–70</td>
<td>&lt;1–27 (8)</td>
<td>3.1–330 (11)</td>
</tr>
<tr>
<td>Zn</td>
<td>100–1600 (17)</td>
<td>8–75</td>
<td>63–325 (7)</td>
<td>501–8900 (11)</td>
</tr>
</tbody>
</table>

Reference: (Cantinho et al., 2016) Paper I (Cantinho et al., 2016) (Cantinho et al., 2016)

Current metal removal from industrial wastewaters is primarily motivated by limiting the release of metals in treated wastewater effluents. This is to protect the surface water and groundwater as well as limit the effects on ecosystems and human health (Barakat, 2011; Carolin et al., 2017). However, it means that metals are generally accumulated in sludge. With respect to elimination of metals from municipal sludge, attempts are made to prevent them from entering municipal wastewater by regulating industrial release. Examples of regulation and standards for freshwater quality and sludge use are provided in Table 2 (Paper I).
Table 2. Freshwater quality standards and limit values for agricultural sludge use with respect to metals (DM = dry mass; EQS = environmental quality standards; EU = European Union; US EPA = United States Environmental protection agency; HaV = Swedish Agency for Marine and Water Management) (Paper I).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Limit values for sludge use in agriculture (mg/kg DM)</th>
<th>EU Directive</th>
<th>EU countries with stringent limits(^a)</th>
<th>US EPA</th>
<th>Freshwater standards (μg/L)</th>
<th>Water quality criteria, US (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>-</td>
<td>-</td>
<td>75</td>
<td>0.5 (-)</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>20–40</td>
<td>0.8–2.5</td>
<td>85</td>
<td>0.08–0.25</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.08–0.25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.4 (-)</td>
<td>74/11(^d)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1000–1750</td>
<td>300–1000</td>
<td>4300</td>
<td>0.5–2.6 (-)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>16–25</td>
<td>0.8–2.5</td>
<td>57</td>
<td>0.07 (0.07)</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>300–400</td>
<td>30–100</td>
<td>420</td>
<td>4.8–6.4 (4.8–6.4)</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>750–1200</td>
<td>100–250</td>
<td>840</td>
<td>1.2–1.3 (1.2–1.3)</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>2500–4000</td>
<td>800–4000</td>
<td>7500</td>
<td>1.1–5.5 (-)</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Denmark, Finland, Luxembourg, Slovenia, and Sweden.

\(^b\) Intervals represent inland and surface waters. Maximum allowable Hg concentration. Maximum allowed annual average values for other metals. Cd standards based on water hardness.

\(^c\) Continuous concentrations. Limit values are adapted based on water hardness.

\(^d\) Cr(III) and Cr(VI).

With respect to Cd, as one of the priority metals of concern, its’ concentration in different industrial wastewaters and in stormwater varies greatly. This is exemplified in Table 3 (selected literature data from Paper IV).

Table 3. Cd concentrations in various wastewater; industrial wastewaters and stormwater (CHP = combined heat and power plant).

<table>
<thead>
<tr>
<th>Type of wastewater</th>
<th>Cd (μg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storm water</td>
<td>0.05–0.13; 0.05–13,730</td>
<td>(Reddy et al., 2014; Rule et al., 2006a)</td>
</tr>
<tr>
<td>Landfill leachate</td>
<td>0.012–0.027; &lt;0.05–1.4; 1900</td>
<td>(Modin et al., 2011; Öman et al., 2000; Zand &amp; Aby- aneh, 2020)</td>
</tr>
<tr>
<td>Mine tailings leachate and drainage</td>
<td>0.06–0.4; 16,690–67,610</td>
<td>(Adolfsson et al., 2020; Fernández Pérez et al., 2022)</td>
</tr>
<tr>
<td>Flue gas condensate from CHP</td>
<td>0.54; 1.46</td>
<td>(Noor et al., 2020, 2021)</td>
</tr>
<tr>
<td>Car wash facilities</td>
<td>~5; 260</td>
<td>(Kichigin et al., 2018; Sörme &amp; Lagerkvist, 2002)</td>
</tr>
<tr>
<td>Textile factory wastewater</td>
<td>23; 969</td>
<td>(Mekuyie Fenta, 2014; Parihar &amp; Malaviya, 2023)</td>
</tr>
<tr>
<td>Tannery wastewater</td>
<td>&lt;1–2,900</td>
<td>(Whitehead et al., 2021)</td>
</tr>
</tbody>
</table>
Metal contamination in municipal sludge occasionally prohibits the use of sludge in agriculture (Hudcová et al., 2019). With respect to effluents, the surface water standards consider concentrations in the actual water course. Because of the dilution of water that occurs as it enters the water course, effluent release may be allowed even though concentrations in the effluent exceed the given limits or standards (Clara et al., 2012). Thus, local conditions determine the need for minimisation of metals in effluents and sludge. Furthermore, the permissible effluent concentrations from various industries are defined in the permits for the respective industrial site.

The variations in limit values and standards mirror the extent to which a precautionary approach has been taken. The precautionary approach considers unmeasurable or unknown hazards as well as perceived risks by the public, where scientific evidence of harmful effects may be lacking (Öberg & Mason-Renton, 2018).

2.2 Metal Speciation and Removal during Primary Settling

The speciation of metals is relevant for their possible removal during primary settling. For elucidating the speciation of metals in municipal wastewater, metal chemical speciation has not been measured directly. Instead, assumptions on the speciation were made based on knowledge of the presence of organic complexes in different size fractions and the elemental composition of wastewater samples. The different approaches to metal speciation that have been applied are: i) filtration (0.45 µm) and membrane separation (1 kDa) of wastewater samples followed by analysis of metals in the raw sample, filtrate, and membrane permeate (Hargreaves et al., 2017); ii) filtration (0.45 µm) followed by diffusion and dissociation into a permeable gel and subsequent analysis of metals in the raw sample, filtrate, and gel (Buzier et al., 2006; Gourlay-Francé et al., 2011); and iii) elemental analysis of wastewater particles through energy dispersive X-ray spectrometry (from which mineral species can be deduced based on known mineralogical compositions) (El Samrani et al., 2004). Metals analysed after sample preparation according to i) were referred to as particulate, colloidal, and truly dissolved, respectively. Metals analysed after sample preparation according to ii) were referred to as particulate, dissolved inert, and dissolved labile, respectively.

Metals in municipal wastewater have been suggested to occur mainly as organometallic complexes (Ziolko et al., 2011). Buzier et al. (2006) suggested that the dissolved labile fraction consisted of small inorganic metal complexes and small weak organic complexes, and that the dissolved inert fraction contained stronger inorganic complexes and larger organic complexes in the
DOM compartment (<0.45 µm). Wastewater DOM, to which truly dissolved and colloidal metals could be associated, is primarily composed of humic substances and non-humic macromolecules (including proteins, polysaccharides, and amino sugars) (Hargreaves et al., 2017). Metals may be trapped by chelates in these organic compounds, including chelating agents of natural origin (e.g., proteins and nucleic acids) and synthetic origin (e.g., nitrilotriacetic acid [NTA] and ethylenediamine tetraacetic acid [EDTA]) (Ziolko et al., 2011). El Samrani et al. (2004) investigated municipal wastewater (combined system including stormwater) and found that metals associated with sulphide particles were abundant. Metals were also encountered in the form of alloys, iron oxhydroxides, carbonates, phosphates (PO₄-P), sulphates and as associated with clays.

The truly dissolved or dissolved labile metals in raw municipal wastewater, depending on the pre-processing of wastewater samples as described above, have been examined in a few cases. Based on these studies, Ni is most likely to appear in the truly dissolved or labile fraction, with up to half of the dissolved Ni being truly dissolved or labile dissolved (Buzier et al., 2006; Gourlay-Francé et al., 2011; Hargreaves et al., 2017). The fraction of Zn in the truly dissolved or labile dissolved form was small or insignificant (Gourlay-Francé et al., 2011; Hargreaves et al., 2017). For Cu, around 10% was found to be truly dissolved in one study (Hargreaves et al., 2017), while less than 5% was found to be dissolved labile (Buzier et al., 2006; Gourlay-Francé et al., 2011). Pb and Cr were mainly found in the particulate fraction, and the concentrations of dissolved labile Pb and Cr were below the detection level (Buzier et al., 2006; Gourlay-Francé et al., 2011). Truly dissolved Pb was quantified to 5% in one study (Hargreaves et al., 2017). Dissolved labile Cd was evaluated in one study, and the amount was found to be below the detection level; however, the total concentration was only ~3 times the detection level, indicating that up to ~33% of the Cd may actually have been dissolved labile (Buzier et al., 2006).

The removal of metals during primary settling is ultimately determined by the removal of solids to which the metals are associated. A typical solids removal is 60% (Metcalf & Eddy, 2014). Removal is thus determined by the speciation of metals in the influent and the sorption and desorption (onto inherent particulate matter in wastewater) which may occur during primary settling (Pomiès et al., 2013; Ziolko et al., 2011). Volatilisation is a possible factor for removal of some metals (As, Hg, and Antimony [Sb]) (Cantino et al., 2016; Yoshida et al., 2015). Metal speciation is affected by wastewater hardness, alkalinity, pH, and redox potential (Ziolko et al., 2011), while hydraulic retention time (HRT) is one of the key parameters for solids removal in primary settlers. Typical pH and HRT in primary settlers are 7–8 (la Cour Jansen et al., 2019) and 1.5–2.5 h (Metcalf & Eddy, 2014), respectively.
If disregarding sorption and desorption during settling, the removal (R\%) of metals could be described by:

\[ R\% = \left( \frac{C_{part} \times 0.60}{C_{tot}} \right) \]

(1)

where \( C_{part} \) is the concentration metals sorbed onto wastewater particles and \( C_{tot} \) is the total influent concentration (particle bound and dissolved metals).

Based on on-site measurements of metal concentrations at different WWTPs, it is also relevant to consider the metal concentrations in return flows from sludge dewatering since these may significantly influence the metal and solids loads on primary settlers and thus influence the metal removal (Goldstone, Atkinson, et al., 1990; Goldstone, Kirk, et al., 1990b, 1990a; Gourlay-Francé et al., 2011; Innaa et al., 2014; Yoshida et al., 2015). It is also of importance to consider the possible contribution of metals from the addition of process chemicals (Buzier et al., 2006). In some WWTPs, secondary sludge is returned to the head of the primary settler. In those cases, the sorption of metals onto biomass may increase the metal removal capacity of the primary settler (Chipasa, 2003; Comte et al., 2008; Ziółko et al., 2011).

2.3 Metal Removal Through Sorption

Sorption is one of the most frequently applied technologies for metal removal due to its ease of operation, flexible design, and absence of toxic by-products (Carolin et al., 2017; Chai et al., 2021). Commercially available sorbents include AC which is available in various forms (e.g., pulvérised, granular, clothe, and fibrous form) and produced mainly from coal, wood, and coconut shells (Chai et al., 2021). The main characteristic of AC is its large specific surface area (SSA) due to its well-developed pore structure, which provides the basis for sorption to occur. AC production can be adapted with respect to the target sorbate. Activation techniques are referred to as physical (pyrolysis and steam) and chemical (using e.g., phosphoric acid or zinc chloride), generating SSAs of up to 3,000 m²/g (Koelhert, 2017).

Extensive research is being performed with respect to various biosorbents as an alternative to AC. The use of biosorbents is commonly motivated by potential cost savings compared to AC. Additionally, the use of biosorbents could reduce the reliance on fossil coal used for AC production. Potential biosorbents include algae, bacteria, fungi, and char (also referred to as biochar) (Chai et al., 2021).

Sorbents are often examined with respect to their maximum sorption capacity \( Q_{max} \), in the unit of milligram of sorbate per gram of sorbent (mg/g). With increased concentrations of sorbate in the solution, the sorption capacity approaches its maximum. This behaviour is modelled by so-called isotherm
models, which correlate the sorption capacity to the sorbate concentration in solution at equilibrium. The most commonly applied isotherm models are the Langmuir and Freundlich isotherms (Chai et al., 2021; Freundlich, 1906; Langmuir, 1918).

In addition to the sorbate concentration, sorption is also governed by temperature and pH of the liquid matrix (Chai et al., 2021). Increased sorbent dose enables increased sorbate removal; however, an increased dose may lead to non-optimal utilisation of sorption capacity (equilibrium sorption capacity, \( q_e < Q_{\text{max}} \)). Furthermore, a provision for full utilisation of the sorbent is that sufficient contact time between the sorbent and the liquid matrix is provided, in accordance with the time required to reach equilibrium.

With respect to terminology, there is some inconsistency in the literature, where the terms sorbent (or sorption) and adsorbent (or adsorption) are interchangeably used, for instance by Mohan et al. (2007). The term sorption encompasses both adsorption and absorption, which have been defined as follows (Hunt, 2013):

- Absorption “happens when a fluid soaks into the pores of a material, like water soaking into a sponge”.
- Adsorption “is a process in which atoms, molecules or ions are held on the surface of a solid”.

The adsorption of metals occurs through several mechanisms, as summarised in Figure 2 and explained as follows (Chai et al., 2021; Inyang et al., 2016; Rangabhashiyam et al., 2022; L. Wang et al., 2019):

- Physical sorption due to van der Waals forces, where no chemical reactions are involved.
- Electrostatic attraction, caused by opposite charge of the sorbent and sorbate (the substance to be removed). Thus, with respect to cationic metals negative charge on the sorbent surface supports electrostatic interactions.
- Ion exchange, where ionizable protons or cations are released and their place is taken by metals in solution. With respect to metal sorption onto char, the cations \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{K}^{+} \), and \( \text{Na}^{+} \) are often considered to be of importance.
- Precipitation, where ionic metals react to form solids, which are deposited on the sorbent surface or in other locations. With respect to metal sorption by char, the solids formed include compounds containing, e.g., phosphate (\( \text{PO}_4^{3-} \)), silicate (e.g., metasilicate, \( \text{SiO}_3^{2-} \)), and carbonate (\( \text{CO}_3^{2-} \)).
- Complexation, which is the formation of multi-atom structures, i.e., complexes. Considering metal sorption by char, functional groups such as carboxyl (\( \text{R-COOH} \)), hydroxyl (\( \text{R-OH} \)), phenol (\( \text{C}_6\text{H}_5\text{OH} \)), and amino groups (\( \text{R-NH}_2 \)) are typically involved.
Because absorption is not easily differentiated from adsorption in standard experimental setups, the term sorption (onto a sorbent) is used in the current work.

2.4 Sludge-Derived Char as Metal Sorbent

A large number of studies have investigated metal sorption by SDC, with a focus on topics such as: the effect of different pyrolysis conditions (temperature, duration) (W. Zhang et al., 2013); the effect of digesting the sludge prior to pyrolysis (Ho et al., 2017); the effects of temperature and ageing of the sorbent (W. Zhang et al., 2017); how the co-existence of humic acids affects the sorption capacity (F. Zhou et al., 2015); and the competition between different sorbates (W. Zhang et al., 2017). Table 4 shows sorption capacities with respect to Cd, Cr, Cu, Hg, Ni, Pb, and Zn in relation to the sludge type, sludge
amendments, pyrolysis conditions, activation type, and modification type (based on literature available until Jan 2022). Additionally, the sorption capacity of sorbents produced from sludge mixed with other feedstock materials, e.g., sugarcane bagasse, was investigated (Tao et al., 2015).

Table 4. Literature data with respect to sludge-derived char (SDC) metal sorption capacity in relation to sludge type, sludge amendment, sludge/char particle size, activation type, and modification type (^ = data taken from graph; * = several dwell times/temperatures were investigated; ns = not specified; N = no; Y = yes; M = sludge from municipal wastewater treatment, no further specification; PS = primary sludge; WAS = waste activated sludge; An = anaerobically digested; AGS = aerobic granular sludge; MBR = sludge from membrane bioreactor) (in the instances where improvement of sorption capacity is given but no capacity of unmodified/non-activated SDC is given, the study investigated the effect of optimised pyrolysis conditions).

<table>
<thead>
<tr>
<th>Sorption capacity (maximum [mg/g]/when unmodified and non-activated [mg/g]/improvement when modified or activated [times])</th>
<th>Sludge type/ sludge amendment/char or sludge particle size</th>
<th>Pyrolysis conditions (dwell time [min]/temperature [°C]/heating rate [°C/min])</th>
<th>Activation type; before or after pyrolysis (B/A)</th>
<th>Modification type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd²⁺</td>
<td>17.0^/-6.8 M/N/&lt;0.45 mm</td>
<td>20/800*30</td>
<td>-</td>
<td>-</td>
<td>(T. Chen et al., 2014)</td>
</tr>
<tr>
<td></td>
<td>58.0^/-1.12 M/N/&lt;2.0 mm</td>
<td>240/500*/ns</td>
<td>-</td>
<td>-</td>
<td>(L. Y. Gao et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>42.8/- M/N/&lt;0.45 mm</td>
<td>20/900/ns</td>
<td>-</td>
<td>-</td>
<td>(T. Chen et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>1.6/- M/N/ns</td>
<td>15/500/ns</td>
<td>-</td>
<td>-</td>
<td>(J. J. Zhao et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>61.83/- PS+WAS-An/N/0.5–1 mm</td>
<td>120/600/ns</td>
<td>-</td>
<td>-</td>
<td>(Ni et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>90.0^/- M/N/120 mesh</td>
<td>30/500/nsᵃ</td>
<td>-</td>
<td>-</td>
<td>(Xue et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>750.0^/- M/N/&lt;0.45 mm</td>
<td>120/400/ns</td>
<td>-</td>
<td>MgCl₂ and calcination</td>
<td>(Ngambia et al., 2019)</td>
</tr>
<tr>
<td></td>
<td>36.5/17.0/2.15 M/N/ns</td>
<td>ns/500/ns</td>
<td>-</td>
<td>CaCO₃</td>
<td>(Zuo et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>2.6^/1.5/1.73 WAS/N/&lt;0.2 50 mm</td>
<td>120/400/20</td>
<td>-</td>
<td>Zn(NO₃)₂</td>
<td>(J. Gao, Zhao, et al., 2020)</td>
</tr>
</tbody>
</table>

ᵃ The goal temperature was reached within 3 minutes
<table>
<thead>
<tr>
<th>Sorption capacity</th>
<th>Sludge</th>
<th>Pyrolysis conditions</th>
<th>Activation</th>
<th>Modification</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>M/N/60 mesh</td>
<td>120/550/5</td>
<td>-</td>
<td>Hydroxyapatite</td>
<td>(Y. Chen et al., 2021)</td>
</tr>
<tr>
<td></td>
<td>M/N/1–3 mm</td>
<td>ns/850/ns</td>
<td>ZnCl&lt;sub&gt;2&lt;/sub&gt;B</td>
<td>-</td>
<td>(Zhai et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>M/N/ns</td>
<td>15/350/ns</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;A</td>
<td>-</td>
<td>(Wongrod, Simon, van Hullebusch, et al., 2018)</td>
</tr>
<tr>
<td></td>
<td>M/N/ns</td>
<td>15/350/ns</td>
<td>KOH;A</td>
<td>-</td>
<td>(Wongrod, Simon, van Hullebusch, et al., 2018)</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>M/N/ns</td>
<td>15/500/ns</td>
<td>-</td>
<td>-</td>
<td>(J. J. Zhao et al., 2019)</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;6+&lt;/sup&gt;</td>
<td>WAS/N/&lt;0.2</td>
<td>120*/400*/20</td>
<td>-</td>
<td>-</td>
<td>(W. Zhang et al., 2013)</td>
</tr>
<tr>
<td></td>
<td>50 mm</td>
<td></td>
<td></td>
<td></td>
<td>(D. Zhou et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>M/N/&lt;0.2 mm</td>
<td>120/400/ns</td>
<td>-</td>
<td>-</td>
<td>(F. Zhou et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>WAS/N/&lt;0.2</td>
<td>120/400/20</td>
<td>-</td>
<td>-</td>
<td>(Fei et al., 2022)</td>
</tr>
<tr>
<td></td>
<td>50 mm</td>
<td></td>
<td></td>
<td></td>
<td>(Zeng et al., 2021)</td>
</tr>
<tr>
<td></td>
<td>M/N/&lt;0.250</td>
<td>120/500/ns</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M/N/200 mesh</td>
<td>120/600/5</td>
<td>KOH;B</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>WAS/N/ns</td>
<td>60/600*/ns</td>
<td>-</td>
<td>-</td>
<td>(Rio et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>WAS/Y&lt;sup&gt;b&lt;/sup&gt;/ns</td>
<td>60/800/ns</td>
<td>-</td>
<td></td>
<td>(Rio et al., 2005)</td>
</tr>
<tr>
<td></td>
<td>M/N/ns</td>
<td>30/650*/10</td>
<td>-</td>
<td>-</td>
<td>(Seredych &amp; Bandosz, 2006)</td>
</tr>
<tr>
<td></td>
<td>M/N/&lt;0.2 mm</td>
<td>120/400/ns</td>
<td>-</td>
<td>-</td>
<td>(D. Zhou et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>WAS/N/ns</td>
<td>240/500/5</td>
<td>-</td>
<td>-</td>
<td>(Shen et al., 2018)</td>
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<tr>
<td></td>
<td>M/N/several;</td>
<td>ns/600*/10</td>
<td>-</td>
<td>-</td>
<td>(Xu et al., 2018)</td>
</tr>
<tr>
<td></td>
<td>&lt;0.043–2.0 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M/N/ns</td>
<td>15/500/ns</td>
<td>-</td>
<td>-</td>
<td>(J. J. Zhao et al., 2019)</td>
</tr>
</tbody>
</table>

<sup>b</sup> Lime
Table 4, continued

<table>
<thead>
<tr>
<th>Sorption capacity</th>
<th>Sludge</th>
<th>Pyrolysis conditions</th>
<th>Activation</th>
<th>Modification</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.6/-/1.82</td>
<td>MBR/N/ &lt;0.15 mm</td>
<td>240/300*/5</td>
<td>-</td>
<td>-</td>
<td>(Fan et al., 2020)</td>
</tr>
<tr>
<td>37.5/25.2/1.49</td>
<td>PS+WAS/N/ 0.074–0.149 mm</td>
<td>60/500/ns</td>
<td>-</td>
<td>Amino-functionalised</td>
<td>(Tang et al., 2019)</td>
</tr>
<tr>
<td>89.9/-/-</td>
<td>M/N/60 mesh</td>
<td>120/550/5</td>
<td>-</td>
<td>Hydroxyapatite</td>
<td>(Y. Chen et al., 2021)</td>
</tr>
<tr>
<td>18.5/-/-</td>
<td>AGS/N/ns</td>
<td>120/650/ns</td>
<td>ZnCl₂;B</td>
<td>-</td>
<td>(Wei et al., 2018)</td>
</tr>
<tr>
<td>83.3/43.5/1.91</td>
<td>M/Y&lt;1 mm</td>
<td>ns/ns/10</td>
<td>K₂CO₃;   A</td>
<td>FeCl₂, FeCl₃, and NaOH (magnetisation)</td>
<td>(B. Zhao et al., 2021)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>769.2/87.0/2.41</td>
<td>M/N/0.3 mm</td>
<td>120/400/ns</td>
<td>-</td>
<td>Carboxymethyl chitosan</td>
<td>(Ifthikar et al., 2018)</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36.0/20.4/1.74</td>
<td>M/N/0.074 mm</td>
<td>120/500/10</td>
<td>-</td>
<td>FeCl₃, FeSO₄, and NaOH</td>
<td>(Yang et al., 2019)</td>
</tr>
<tr>
<td>9.1/-/-</td>
<td>M/N/1–3 mm</td>
<td>ns/850/ns</td>
<td>ZnCl₂;B</td>
<td>-</td>
<td>(Zhai et al., 2004)</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.0^-/-1.5</td>
<td>WAS/N/0.2 50 mm</td>
<td>120*/400*/5</td>
<td>-</td>
<td>-</td>
<td>(W. Zhang et al., 2013)</td>
</tr>
<tr>
<td>31.0/-/-</td>
<td>M/N/0.85–1.0 mm</td>
<td>120/550/10</td>
<td>-</td>
<td>-</td>
<td>(Lu et al., 2012)</td>
</tr>
<tr>
<td>187.7/-/1.55</td>
<td>WAS/Y&lt;1 ns</td>
<td>90/600/15</td>
<td>-</td>
<td>-</td>
<td>(Y. di Chen et al., 2018)</td>
</tr>
<tr>
<td>49.9/-/-</td>
<td>WAS-An/N/ ns</td>
<td>90/600/15</td>
<td>-</td>
<td>-</td>
<td>(Ho et al., 2017)</td>
</tr>
<tr>
<td>15.6/15.6/1.73</td>
<td>WAS/N/0.2 50 mm</td>
<td>120/400/20</td>
<td>-</td>
<td>-</td>
<td>(W. Zhang et al., 2017)</td>
</tr>
<tr>
<td>7.0/-/-</td>
<td>M/N/ ns</td>
<td>15/500/ns</td>
<td>-</td>
<td>-</td>
<td>(J. J. Zhao et al., 2019)</td>
</tr>
<tr>
<td>233.3/196.7/1.19</td>
<td>WAS/N/0.2 50 mm</td>
<td>120/400/20</td>
<td>-</td>
<td>-</td>
<td>(F. Zhou et al., 2015)</td>
</tr>
<tr>
<td>155.4/-/-</td>
<td>PS+WAS-An/N/0.5–1 mm</td>
<td>120/600/ns</td>
<td>-</td>
<td>-</td>
<td>(Ni et al., 2019)</td>
</tr>
</tbody>
</table>

^c Hazelnut shell
^d Persulfate zero-valent iron
Table 4, continued

<table>
<thead>
<tr>
<th>Sorption capacity</th>
<th>Sludge</th>
<th>Pyrolysis conditions</th>
<th>Activation</th>
<th>Modification</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.0^//-</td>
<td>M/N/several; &lt;0.025– &gt;0.165 mm</td>
<td>ns/600/ns</td>
<td>-</td>
<td>-</td>
<td>(H. Chen et al., 2022)</td>
</tr>
<tr>
<td>54.1/-3.69</td>
<td>M/N/ns</td>
<td>60/800*/10</td>
<td>-</td>
<td>-</td>
<td>(S. Li et al., 2019)</td>
</tr>
<tr>
<td>9.7/-1.3</td>
<td>WAS/N/3–5 mm</td>
<td>120/500*/ns</td>
<td>-</td>
<td>-</td>
<td>(Hong et al., 2019)</td>
</tr>
<tr>
<td>110.0^//-</td>
<td>M/N/120 mesh</td>
<td>30/500/ns(^a)</td>
<td>-</td>
<td>-</td>
<td>(Xue et al., 2019)</td>
</tr>
<tr>
<td>239.2/-2.31</td>
<td>M/N/&lt;0.3 mm</td>
<td>120/400/ns</td>
<td>-</td>
<td>Carboxymethyl chitosan</td>
<td>(Ifthikar et al., 2018)</td>
</tr>
<tr>
<td>1800.0^/-5.65</td>
<td>M/N/&lt;0.45 mm</td>
<td>120/400/ns</td>
<td>-</td>
<td>MgCl(_2) and calcination</td>
<td>(Ngambia et al., 2019)</td>
</tr>
<tr>
<td>226.1/-</td>
<td>M/N/ns</td>
<td>120/550/ns</td>
<td>-</td>
<td>Layered double hydroxide</td>
<td>(X. Cheng et al., 2022)</td>
</tr>
<tr>
<td>17.0^/4.0/4.25</td>
<td>WAS/N/&lt;0.2 50 mm</td>
<td>120/500/10</td>
<td>ZnCl(_2);B</td>
<td>-</td>
<td>(L. Y. Li et al., 2019)</td>
</tr>
<tr>
<td>241.6/-</td>
<td>M/N/&lt;0.3 and &lt;0.45 mm</td>
<td>120/400/ns</td>
<td>ZnCl(_2);A</td>
<td>-</td>
<td>(Ifthikar et al., 2017)</td>
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<tr>
<td>80.0^/6.5/12.31</td>
<td>M-An/N/ns</td>
<td>15/350/ns</td>
<td>KOH;A</td>
<td>-</td>
<td>(Wongrod, et al., 2018)</td>
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<tr>
<td>22.4/7.6/2.96</td>
<td>M/N/0.1–0.6 mm</td>
<td>60/700/10</td>
<td>CO(_2);A</td>
<td>-</td>
<td>(J. Zhang et al., 2019)</td>
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<tr>
<td>47.6/7.6/6.29</td>
<td>M/N/0.1–0.6 mm</td>
<td>60/700/10</td>
<td>CH(_3)-COOK;A</td>
<td>-</td>
<td>(J. Zhang et al., 2019)</td>
</tr>
<tr>
<td>57.5/7.6/7.6</td>
<td>M/N/0.1–0.6 mm</td>
<td>60/700/10</td>
<td>KOH;A</td>
<td>-</td>
<td>(J. Zhang et al., 2019)</td>
</tr>
<tr>
<td>27.0^/-6.75</td>
<td>WAS/N/&lt;0.2 50 mm</td>
<td>120/500/10</td>
<td>ZnCl(_2);B</td>
<td>HNO(_3)</td>
<td>(L. Y. Li et al., 2019)</td>
</tr>
<tr>
<td>135.5/18.0/7.53</td>
<td>M/Y(^e)/200 mesh</td>
<td>30/800/10</td>
<td>KOH;B</td>
<td>HNO(_3)</td>
<td>(Tao et al., 2015)</td>
</tr>
</tbody>
</table>

| Zn\(^{2+}\)      |        |                      |            |              |           |
| 5.5^/-          | M/N/<0.2 mm | 120/400/ns | -          | -            | (D. Zhou et al., 2017) |

\(^a\) The goal temperature was reached within 3 minutes
\(^e\) Sugarcane bagasse
Table 4, continued

<table>
<thead>
<tr>
<th>Sorption capacity</th>
<th>Sludge conditions</th>
<th>Pyrolysis conditions</th>
<th>Activation</th>
<th>Modification</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$^{2+}$</td>
<td>WAS/N/&lt;0.2</td>
<td>120/400/20</td>
<td>-</td>
<td>-</td>
<td>(W. Zhang et al., 2017)</td>
</tr>
<tr>
<td></td>
<td>50 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>M/N/several;</td>
<td>ns/600/ns</td>
<td>-</td>
<td>-</td>
<td>(H. Chen et al., 2022)</td>
</tr>
<tr>
<td></td>
<td>&lt;0.025–&gt;0.165 mm</td>
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</tbody>
</table>

From the literature data in Table 4, it is evident that Cd, Cu, and Pb are the most frequently investigated metals. In several cases, different types of activation and/or modification were shown to more than double the sorption capacity with respect to these metals. Some extreme improvements were shown by, e.g., Wongrod, Simon, van Hullebusch, et al. (2018), where the sorption of Cd increased by almost 20 times after KOH-activation. However, in that case the sorption capacity of non-activated SDC was low (1.7 mg/g), probably due to the short pyrolysis residence time (15 min) and low temperature of pyrolysis (350°C). Pyrolysis conditions are of essential importance to the sorption capacity, and their optimisation could more than double the sorption capacity for Cd, Cu, and Pb, compared to non-optimal conditions (T. Chen et al., 2014; S. Li et al., 2019; Seredych & Bandosz, 2006). The sorption capacity of SDC, which was neither amended, modified, nor activated, was in the ranges of 1.5–90, 3.6–146.7, and 4.0–196.7 mg/g for Cd, Cu, and Pb, respectively. Its sorption capacity when amended, modified, or activated was in the ranges of 2.6–750, 18.5–131.8, and 17.0–1,800 mg/g for Cd, Cu, and Pb, respectively.

With respect to dilute wastewaters, Agrafioti et al. (2014) examined metal removal (As$^{5+}$, Cr$^{3+}$, and Cr$^{6+}$) in the µg/L range. However, higher concentrations, where saturation of the sorbent occurs, were not considered which means that the isotherm parameters were not estimated in a precise way.

Metal sorption capacity of SDC correlates positively with SSA (T. Chen et al., 2014; Wongrod, Simon, van Hullebusch, et al., 2018; Xu et al., 2018; J. Zhang et al., 2019). Smaller particle size generally increases the available SSA. Ho et al. (2017) and Chen et al. (2015) found that precipitation and ion exchange were the dominating mechanisms for Pb and Cd sorption onto SDC. In contrast, Lu et al. (2012) found that Pb sorption by SDC was mainly attributed to complexation with hydroxyl and carboxyl functional groups as well as surface precipitation (e.g., co-precipitation with phosphates, silicates, or carbonates).

In addition to the properties of the sorbent, the amount of metal that can be sorbed is also governed by the composition of the liquid matrix (as given in Chapters 2.2-2.3).
2.5 Sludge Pyrolysis and Energy Balance

Pyrolysis is the thermal decomposition of organic matter in oxygen-free or oxygen-limited atmosphere, which prevents complete combustion. Pyrolysis generates liquids (tar or oil and an aqueous fraction), gases, and solid residues, the latter referred to as char or biochar (Mohan et al., 2014). Pyrolysis reduces sludge mass, eliminates pathogens, and reduces the mobility of various pollutants (Paz-Ferreiro et al., 2018). Sludge pyrolysis, and the related process of gasification, have been implemented since the 1970s’. However, many installations have been decommissioned due to the complexity of handling the combustion of off-gas (gas and tar in vapor form) and associated heat recovery. Corrosion issues and fouling have led to high maintenance requirements for these systems (Winchell et al., 2022). Recent research indicates that, due to high temperatures, pyrolysis could reduce or destroy emerging contaminants such as PFAS in sludge. Based on this benefit and technological developments, pyrolysis has recently gained renewed interest from the wastewater industry (Winchell et al., 2022).

The thermal decomposition occurring during pyrolysis is an endothermic reaction. Organic constituents in sludge undergo aromatisation, where molar ratios of H-O-N/C decrease (Paz-Ferreiro et al., 2018). The off-gas contains a complex mixture of compounds, including aromatic hydrocarbons (e.g., toluene [C₇H₈], benzene [C₆H₆]), aliphatic hydrocarbons (e.g., methane [CH₄], acetylene [C₂H₂], propane [C₃H₈]), furans, N and sulphur (S) containing compounds, alcohols, steroids, esters, hydrogen (H₂), carbon monoxide (CO), and carbon dioxide (CO₂) (Shahbeig & Nosrati, 2020; Winchell et al., 2022).

A technological screening found about 300 companies around the world that provide pyrolysis technology for various types of biomasses, including sludge (Enell et al., 2020). Many of these technologies were in the start-up or demonstration stage; however, several manufacturers have installations up and running in Europe. While an inert atmosphere is commonly used in laboratory scale, full-scale technologies rely on preventing air from entering the pyrolysis chamber. At least one full-scale sludge pyrolysis plant is in operation in Europe and at least one in the US (Geraats et al., 2020; McNamara et al., 2023). At these sites, the off-gas is combusted and the heat generated is used to support the drying and pyrolysis of sludge. Off-gas combustion minimises air emissions, and its combustion prior to tar formation reduces the issue of fouling (Winchell et al., 2022).
Figure 3 gives a schematic overview of the components required for sludge pyrolysis, including drying, the pyrolysis reactor, and the off-gas combustion involving heat recovery. Slow pyrolysis is typically applied with respect to sludge; this promotes the formation of char over liquid and gas. Typical conditions of slow pyrolysis are atmospheric pressure, a heating rate of less than 100°C/min, a temperature of 350–850°C, and a dwell time of up to a few hours (McNamara et al., 2023; Mohan et al., 2014; Winchell et al., 2022).

![Figure 3. Typical configuration of sludge pyrolysis, based on systems in operation in the US. Illustration adapted from Winchell et al. (2022).](image)

Besides feed-stock composition, pyrolysis temperature is the most critical parameter with respect to char characteristics. The char pH and its concentrations of phosphorus (P) and potassium (K) increase with increased temperature, while N concentrations decrease (Winchell et al., 2022). Typical SDC yields are 40–54% (500–700 °C) (Zielińska et al., 2015). Yields decrease with increased temperature (Barry et al., 2019; Winchell et al., 2022). Due to the mentioned decomposition and aromatisation, a porous structure is created, providing increased SSA (Rosales et al., 2017). With respect to SSA, the optimal temperature of sludge pyrolysis was found to differ depending on the dwell time applied. At a dwell time of 20 min, the largest SSA (68 cm²/g) was found for char produced at 900°C (T. Chen et al., 2014), while optimum temperature was 400°C at a dwell time of 120 min (SSA: 24 cm²/g) (W. Zhang et al., 2013). Due to loss of carbon, metal concentrations in char are higher compared to concentrations in sludge. However, the recovered mass of the metals Pb, Zn, and Cd has been found to be smaller compared to the mass of the respective metal in the sludge substrate (Vali et al., 2021). The removal of these metals was greater at higher temperatures (500–900°C). Furthermore, the mobile forms of Cu, Ni, Zn, Cd, and Pb were found to be smaller in char compared to sludge substrate (Méndez et al., 2012).
Resource consumption associated with wastewater treatment is expected to increase with population growth, economic development, ageing infrastructure, and more stringent regulations. Sustainable wastewater treatment requires resource recycling, minimised waste generation, and reduced dependence on non-renewable resources (e.g., fossil energy) (Mo & Zhang, 2013). The energy balance of sludge pyrolysis depends on the sludge composition and pyrolysis conditions. Direct combustion of off-gases can theoretically provide heat in excess of that needed for drying and pyrolysis. However, operational data from full-scale applications are not yet publicly available (Winchell et al., 2022). Important aspects with respect to pyrolysis energy balance are the feedstock moisture content, the type of drying applied, and the radiant heat losses from the pyrolysis reactor (Winchell et al., 2022).
3. Methods

The suitability and expected performance of sorption technology for enhancing the metal removal during primary treatment (RQ1) was assessed based on the data collected in a literature review (Paper I; Chapter 3.1). A separate review (Paper V) was conducted with respect to the energy aspects of sludge pyrolysis (Chapter 3.1). Furthermore, experimental studies coupled with isotherm modelling were performed with respect to the metal sorption capacity of SDC (Paper II, III, and IV; RQ2; Chapter 3.2 and 3.3). Aspects of the production and implementation of SDC (RQ3) were investigated through experimental studies coupled with calculations and static modelling (Paper III and IV; Chapter 3.2 and 3.3).

3.1 Literature Review, Data Collection, and Assessment

To provide background knowledge on metal concentrations, speciation, and processes of removal during the primary settling of municipal wastewater, a literature review (Paper I) was conducted. The findings related to this topic were summarised in Chapters 2.1-2.2 of the Theoretical Background. The review was based on scholarly published articles.

Paper I also includes the identification of appropriate technologies for enhancing metal removal during primary settling of municipal wastewater. Furthermore, to estimate the sorption technology performance (RQ1) a simplified assumption was made that the sorbent could accumulate and completely remove all the dissolved metals from the wastewater. Based on this simplified assumption, Equation 2 describes the maximum removal of metals if sorption is implemented:

\[ R\% = \left( C_{part} \times 0.60 + C_{diss} \right)/C_{tot} \tag{2} \]

where \( C_{diss} \) are the dissolved metals and other parameters are according to Equation 1. The removal of particle bound metals was assumed to be unaffected by sorbent addition.

To complement the experimental findings (Chapter 3.2) and calculations with respect to energy aspects (Chapter 3.3) (RQ3), a review was performed
with respect to the energy balance of pyrolysis compared to other sludge management options (Paper V). For this thesis, the underlying publications were revisited to extract further information.

To assess the theoretical possibility of utilising SDC as a Cd sorbent in dilute wastewaters, other than municipal wastewater, literature data was collected and information was acquired with respect to Cd concentrations and mass flows in wastewater generated locally around Västerås city, Sweden. Further details are given in Paper IV. The assessment of sorption potential was based on Cd concentrations in these wastewaters and did not consider the impact of organic matter, wastewater particles or other competing ions.

### 3.2 Experimental Investigations

To investigate the metal sorption capacity of SDC, batch sorption experiments were conducted. Batch experiments are a standard tool for sorption experiments as it facilitates the evaluation of varying conditions with respect to the liquid matrix used as well as the comparison of different sorbents. Figure 4 depicts the sample setup during batch tests and the separation of sorbent. The emphasis was on examining the importance of initial metal concentrations (using artificial metal solution) as well as municipal wastewater composition (using real municipal wastewater) with respect to the inherent content of particulate matter and DOM (RQ2). The SDC’s performance in relation to that of other carbonised sorbents (RQ2) and the impact of pyrolysis temperature and sludge composition (RQ3) were also considered. In Papers II and IV, aqueous metal solutions were used, i.e., metal salts mixed in ultrapure water to form an artificial wastewater. In Paper III, sorption from both aqueous metal solutions and municipal wastewater (real wastewater) was investigated.
Figure 4. Sample setup during batch sorption tests: a) shake tests for determination of metal removal and isotherm model parameters; b) examination of sorption kinetics; and c) separation of sorbent from matrix through filtration. Photos: Ida Sylwan.

For Paper II and III, the SDC was collected from Linz WWTP, Germany, where one of the few full-scale sludge pyrolysis plants in Europe is located. To enable investigation of sludge composition and pyrolysis temperature, the char used in Paper IV was generated in-house. Pyrolysis was performed under an inert atmosphere, using a tube furnace (Figure 5). Furthermore, SDC sorption capacity with respect to Pb was investigated in relation to that of AC and wood-derived char (WDC) (Paper II).
Table 5 summarises the experimental conditions with respect to liquid matrices, origin of SDC, metals considered, and the char characterisation performed in the respective Paper (II–IV). Char characterisation was performed to enable correlation of the char properties and sorption capacities and thus shed light on the sorption mechanisms. Characterisation of chars was performed according to commonly used methods. The analysis was done both in-house (pH, ash content, C/H/N/S, cation exchange capacity [CEC], Fourier transform infrared spectroscopy [FTIR], and calorific value) and by collaborators or external parties (SSA, porosity, metal/P/Si content, and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy [SEM-EDS]).
Table 5. Experimental conditions: matrices, sludge-derived char origin, metals considered, and sludge-derived char characterisation (CEC = cation exchange capacity; FTIR = Fourier transform infrared spectroscopy; SEM-EDS = scanning electron microscopy coupled with energy dispersive X-ray spectroscopy).

<table>
<thead>
<tr>
<th>Paper</th>
<th>Matrix</th>
<th>SCD origin</th>
<th>Metals considered</th>
<th>Char characterisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Metal solution</td>
<td>Produced from digested sludge at Linz WWTP, Germany</td>
<td>Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, Ni$^{2+}$, and Zn$^{2+}$; (focusing on Pb$^{2+}$)</td>
<td>SSA, porosity, pH, ash content, metal content, and C/H/N.</td>
</tr>
<tr>
<td>III</td>
<td>Metal solution and municipal wastewater collected from primary settler</td>
<td>Produced from digested sludge at Linz WWTP, Germany</td>
<td>Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Cr$^{3+}$, Ni$^{2+}$, Zn$^{2+}$, Hg$^{2+}$, and Ag$^{+}$</td>
<td>SSA, porosity, pH, ash content, metal/P/Si content, C/H/N/S, CEC, FTIR, and SEM-EDS.</td>
</tr>
<tr>
<td>IV</td>
<td>Metal solution</td>
<td>Produced in-house from primary and digested sludge</td>
<td>Cd$^{2+}$</td>
<td>SSA, porosity, pH, ash content, metal content, C/H/N/S, FTIR, and calorific value.</td>
</tr>
</tbody>
</table>

The following describes the batch sorption experiments step by step: i) char was mixed with metal solution and/or wastewater of appropriate concentration; ii) samples were shaken or mixed during a set time interval; and iii) the char was separated from the liquid through filtration (0.45 µm). Metal concentrations were determined in the filtrate (analysis performed by an external laboratory). The sorption of metals per mass unit of sorbent, $q$ (mg/g), and the removal efficiency, $\Delta C$ (%) were calculated as follows:

$$q = \frac{m_{Me}}{m} + q_i \quad (3)$$

$$\Delta C = \frac{(C_0 - C)}{C_0} \times 100 \quad (4)$$

where $m_{Me} = (C_0 - C) \times V$ (mg) is the total amount of metal sorbed, $C_0$ (mg/L) is the initial concentration of metal, $C$ (mg/L) is the final metal concentration in the liquid after separation of sorbent, $V$ (L) is the sample volume, $m$ (g) is the mass of sorbent, and $q_i$ (mg/g) represents the initial amount of sorbed metal per mass unit of sorbent.

The final amount of sorbed metal per mass unit and the final concentration of the metal solution are denoted by $q_e$ and $C_e$ respectively if the experiment is continued until equilibrium has established in the solution, or as $q_t$ and $C_t$ if the experiment is ended before equilibrium has established.
The metal removal after adjustment of pH (without any addition of sorbent) in metal solutions and wastewater was also considered; this was to examine the removal of metals through precipitation of metal hydroxides.

3.3 Modelling

Isotherm models are a standard tool to correlate the sorption of metals by SDC \((q)\) to the final concentration in liquid \((C)\). As previously mentioned, commonly applied isotherm models include the Langmuir isotherm:

\[
q_e = \frac{Q_{\text{max}}K_L C_e}{1 + K_L C_e} \tag{5}
\]

and the Freundlich isotherm:

\[
q_e = K_F C_e^n \tag{6}
\]

where \(Q_{\text{max}}\) (mg/g) represents the maximum sorption capacity of the investigated sorbent, \(K_L\) (L/mg) is the affinity between sorbent and sorbate, \(K_F\) (L/mg) represents the strength of adsorption, and \(n\) (dimensionless) indicates the driving force for sorption or heterogeneity of the sorption sites. These and additional models were assessed with respect to their predictive capacity in terms of dilute wastewater. Isotherm models do not allow for the equilibrium sorption \((q\) or \(q_e)\) to be negative. For isotherm modelling purposes, the parameter \(q_i\) (mg/g) was therefore introduced (in Equation 3) to represent the initial amount of sorbed metal per mass unit of sorbent.\(^1\) This parameter has not been considered in previous studies because desorption is not likely to be significant at higher initial metal concentrations in solution.

To assess the potential of using SDC for enhancing metal removal during the primary settling of municipal wastewater (RQ3), experimental results were coupled with modelling. The removal of metals during primary settling after addition of SDC \((\Delta C_{PS, BC, i}, \%)\) was modelled as follows:

\[
\Delta C_{PS, BC, i} = (\Delta S_{PS} C_{part, i} + C_{char, i} + \Delta DOM_{char} C_{DOM, i})/C_{0, i} \tag{7}
\]

\(^1\) Calculation of \(q_i\) was based on two assumptions: a) with no metals in the solution at equilibrium, there would be no sorbed metal \((q\) is 0 when \(C\) is 0, in agreement with the Langmuir and Redlich-Peterson isotherms); and b) \(q\) increases linearly at low sorbate concentration (Tran et al., 2017). “Low sorbate concentration” is relative to the sorption capacity of the sorbent. The maximum concentration for which a linear behaviour was assumed to be valid was determined based on experimental results for \(m_{Me}/m\) in relation to \(C\).
where $\Delta S_{PS}$ is the solids removal in the settler, $c_{part,i}$ are the metals sorbed onto wastewater particles, $c_{char,i}$ are the metals sorbed onto SDC, $\Delta DOM_{char}$ is the removal of DOM after SDC addition, and $c_{DOM,i}$ are the metals complexed with DOM. The respective metal investigated is denoted by $i$. The sorption onto SDC was determined experimentally, while the sorption onto wastewater particles and the complexation with DOM were modelled based on literature data. Further details are given in Paper III. The typical HRT and pH in primary settlers as well as possible char yield (which will determine the maximum possible dosing) were also considered.

The energy balance of pyrolysis ($E_{\text{net}}$, kJ/kg dewatered sludge), with respect to PS and DS, was modelled as follows:

$$E_{\text{net}} = E_{\text{vap}} \times 0.85 - (E_{\text{drying}} + E_{\text{heating}} + E_{\text{pyro}})$$  \hspace{1cm} (8)

where $E_{\text{vap}}$ is the energy content in pyrolysis vapours, and $E_{\text{drying}}$, $E_{\text{heating}}$, and $E_{\text{pyro}}$ is the energy required for drying, heating, and pyrolysis of sludge, respectively. To consider radiative heat losses and incomplete combustion, $E_{\text{vap}}$ was multiplied by 0.85 (Marazza et al., 2019; Z. Wang et al., 2012). The energy in pyrolysis vapours was taken as the difference in energy between feedstock sludge and the char, based on calorific values determined experimentally according to Chapter 3.2. The energy balance of PS pyrolysis was calculated given the estimate decrease in biogas production when exempting PS from anaerobic digestion (AD) ($E_{\text{net}} - E_{\text{CH}_4}$). Further details are given in Paper IV.
4. Results and Discussion

4.1 Sorption Technology in Primary Settling

This chapter addresses RQ1 and highlights the related findings from Paper I. Based on criteria formulated in Paper I, coagulation/flocculation and sorption were identified as the most attractive technologies for enhancing metal removal in primary settling, as they could:

- Be suitable for wastewater with high solids and organic matter concentration.
- Have a low impact in terms of energy use and sludge production.

Calculations of the optimal removal of metals through the addition of a sorbent, based on Equation 2, indicated the highest possible improvement with respect to Ni (~7–50% removal without sorbent and ~65–98% removal with sorbent), followed by Cu (~10–70% removal without sorbent and ~45–85% removal with sorbent). Literature data and calculations are summarised in Figure 6 (Paper I). For Pb, Cd, and Zn possible improvement of around 50% or more was calculated in some cases. The assessment indicates that sorption may be an appropriate technology for enhancing the removal of these metals. While for Cr and Hg, the possibilities of improving metal removal through the addition of a sorbent seem limited. The dissolved metals may in reality be partly unavailable for sorption (as mentioned in the previous discussion on the fractioning between colloidal and truly dissolved/labile metals); however, the calculated potential removal gives an indication of the possible performance of the sorption processes in primary treatment.
Sludge-derived char, utilisation as a metal sorbent

Total metal concentrations and fractions of dissolved metals in raw wastewater give an indication of the applicability of enhancing metal removal through sorption. The collected literature data indicated that the fraction of dissolved metals in raw wastewater may be lower at higher total influent metal concentrations. Such a trend was observed for Cr, Pb, Cd, Zn, and Hg (Figure 7; Paper I). The negative correlation remained when one study at a time was left out, with the exception for Hg, and Zn. An explanation of this trend may

Figure 6. Current removal during primary settling (according to references and calculated removals) and potential for improved removal of dissolved metals. Under the idealised assumption of 100% removal of dissolved metals (data from Paper I). The calculated removals, according to Equation 2, were based on the concentrations given (not on mass flows) and therefore differ from the removal according to reference in some cases. References: [1], Karvelas et al. (2003); [2], Buzier et al. (2006); [3], Goldstone, Kirk, et al. (1990a, 1990b); [4], Hargreaves et al. (2017) [5], Oliver & Cosgrove (1974); and [6], Gardner et al. (2013).
be that high concentrations of total metals coincide with high solids concentrations in the wastewater. Nielsen and Hrudey (1983) found similar types of trends: increased solid concentrations decreased the concentrations of dissolved metals (Ag, Cd, Cr, Cu, and Thallium [Tl]). Though the number of studies performed is limited, this correlation indicates that sorption may be more efficient at lower total influent metal concentrations.

Figure 7. Fraction of dissolved metals in raw municipal wastewater at different total metal concentrations; each data point for the respective metal collected from literature data (Buzier et al., 2006; Cecchini et al., 2015; Gardner et al., 2013; Goldstone, Atkinson, et al., 1990; Goldstone, Kirk, et al., 1990b, 1990a; Gourlay-Francé et al., 2011; Hargreaves et al., 2017; Karvelas et al., 2003; Oliver & Cosgrove, 1974; Toumi et al., 2003) (dotted lines = linear regression between percentage removal and log concentration of the different metals; adjusted R² values) (Paper I).

4.2 Sludge-Derived Char Sorption Capacity

This chapter addresses RQ2 and highlights the main related findings based on Papers II and III.

4.2.1 Pb Sorption from Dilute Artificial Wastewater

Pb sorption was modelled using isotherm models (examples in Equations 5 and 6) over a wide concentration range, Figure 8 (Paper II). The sorption of Pb at concentrations below 1 mg/L (dilute wastewater), could not be predicted based on experimental data collected at higher initial metal concentration (> 1 mg/L). The disagreement between isotherm model predictions and experimental data is illustrated in Figure 8a (Paper II). The isotherm model that best correlated with experimental data over the whole concentration range examined was the Redlich-Peterson model (Figure 8b; Paper II), with a coefficient
of determination ($R^2$) of 0.98 (Paper II). The assumption behind the Redlich-Peterson model is that the sorption sites that first become occupied have similar sorbate affinity, while at higher sorbate concentrations, sites of decreasing sorbate affinity successively become occupied. When considering initial concentrations larger than 1 mg/L, the Freundlich model and Redlich-Peterson model had similar correlations with the experimental data ($R^2$ of 0.98). The Freundlich model assumption is that each successively occupied sorption site has a lower sorbate affinity compared to the sorption sites previously occupied, irrespective of the sorbate concentration. The lack of accurate prediction based on concentrations $>1$ mg/L and associated model disagreement may thus be due to the heterogeneity of sorption sites (in line with the Redlich-Peterson isotherm).

Figure 8. Isotherm models for Pb$^{2+}$ sorption onto sludge-derived char: a) modelling based on equilibrium concentrations $>1$ mg/L (Freundlich, Langmuir-Freundlich, and Redlich-Peterson curves overlapping); and b) modelling based on the whole concentration range (Paper II). Equation 3 was applied to calculate “Experimental data” from analytical results ($q_t = 0.0137$ mg/g).

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4.2.2 Impact of Dissolved Organic Matter and Particles in Municipal Wastewater

The sorption of Cu, Ni, and Cd onto SDC was smaller in the presence of wastewater DOM than in an aqueous metal solution (Figure 9; Paper III; Equation 4). Thus, the sorption of these metals was inhibited by DOM. The size of Cu and Ni ions (smaller compared to Pb, Cd, Cr, Hg, and Ag ions), was identified as a possible explanation of their tendency to form complexes with the negatively charged DOM. A smaller size could enable a larger number of sites in DOM to be available for the sorption or complexation of these metals. Another possible explanation for the inhibition of Cu, Ni, and Cd sorption is DOM blocking of SDC surfaces (Guillossou et al., 2020).

Figure 9. Metal removal from aqueous metal solution (multiple metal solution) and municipal wastewater spiked with metals, collected at primary settler inlet (filtered and raw wastewater) (Paper III).

Because metal hydroxide formation is an important aspect of metal removal from water, Figure 9 also shows the metal removal under pH adjustment but with no SDC addition (similar final pH as in the samples containing SDC). Addition of SDC resulted in a larger removal of metals from the filtered wastewater and aqueous metal solution compared to the mere pH adjustment. This indicates that metal hydroxide formation could be one of the mechanisms, but not the only one, of metal removal after the addition of SDC. This confirms previous studies with respect to metal sorption mechanisms (as were shown in Figure 2). Removal of Zn deviated from this pattern, with an increased concentration in the aqueous metal solution after the addition of SDC.
(compared to the mere pH adjustment). The increased concentrations of Zn were mainly due to the release of Zn from SDC (though some Zn contamination during sample handling was also found).

The removal of metals after sorption from raw wastewater was similar to the removal from filtered wastewater with respect to all metals except Cu and Zn. Presence of wastewater particulate matter appeared to promote the release of Zn from SDC, which was hypothesised to be due to the ion exchange with inherent ions in wastewater, e.g., $\text{Fe}^{3+}$ which has a similar radius but larger charge than $\text{Zn}^{2+}$. The increased removal of Cu under the presence of wastewater particulate matter (in raw wastewater compared to filtered wastewater) is explained by the particulate matter affinity for Cu which according to J. Wang et al. (2003) is larger than the particulate matter affinity for Ni and Cd.

4.2.3 Sludge-Derived Char Characteristics and Pb Sorption Capacity Compared to Other Carbonised Sorbents

The characteristics of SDC and other carbonised sorbents used in experiments (Papers II–IV) in relation to literature data with respect to SDC characteristics are summarised in Table 6 (Paper III).
Table 6. Characteristics of sorbents prior to sorption experiments and literature data with respect to sludge-derived char (DSC = digested sludge char; PSC = primary sludge char; AC = activated carbon; WDC = wood-derived char; SDC = sludge-derived char; DM = dry mass).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>DSC</th>
<th>DSC</th>
<th>PSC</th>
<th>AC</th>
<th>WDC</th>
<th>SDCs, literature data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals (mg/kg DM)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>99.3</td>
<td>20.6</td>
<td>8.22</td>
<td>0.295</td>
<td>0.854</td>
<td>n.d.–51</td>
</tr>
<tr>
<td>Cd</td>
<td>1.21</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>n.d.–3.7</td>
</tr>
<tr>
<td>Cr</td>
<td>84.3</td>
<td>59.4</td>
<td>33.4</td>
<td>19.7</td>
<td>0.314</td>
<td>100–115</td>
</tr>
<tr>
<td>Cu</td>
<td>569</td>
<td>872</td>
<td>632</td>
<td>25.5</td>
<td>16.0</td>
<td>184–242</td>
</tr>
<tr>
<td>Ni</td>
<td>61.4</td>
<td>45.2</td>
<td>23.6</td>
<td>19.4</td>
<td>0.430</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>2170</td>
<td>919</td>
<td>406</td>
<td>2.25</td>
<td>37.4</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.05</td>
<td>&lt;0.02</td>
<td>0.0248</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>6.6</td>
<td>10.39</td>
<td>11.33</td>
<td>6.5</td>
<td>5.6</td>
<td>8.8–12.2</td>
</tr>
<tr>
<td>Ash (% of DM)</td>
<td>68</td>
<td>73.8±0.2</td>
<td>38.8±0.2</td>
<td>8</td>
<td>1</td>
<td>74–88</td>
</tr>
<tr>
<td>CEC (cmol/kg)</td>
<td>72</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30–247</td>
</tr>
<tr>
<td>SSA (m²/g)</td>
<td>12.7±0.7</td>
<td>87.13</td>
<td>30.24</td>
<td>1010±20</td>
<td>75.7±23.5</td>
<td>25–68</td>
</tr>
<tr>
<td>Pores</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vol. (cm³/g)</td>
<td>0.032</td>
<td>0.010</td>
<td>0.047</td>
<td>0.55±0.02</td>
<td>0.04</td>
<td>0.053–0.099</td>
</tr>
<tr>
<td>Av. size (nm)</td>
<td>10.2±0.2</td>
<td>4.11</td>
<td>4.97</td>
<td>2.18±0.01</td>
<td>2.23±0.15</td>
<td>3.7–3.8</td>
</tr>
<tr>
<td>Micro/ meso/ macro (%)</td>
<td>10/71/19</td>
<td>25/70/5</td>
<td>17/78/5</td>
<td>76/23/1</td>
<td>75/25/&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>Pyrolysis temp. (°C) and duration</td>
<td>550–600; 16–30 min</td>
<td>800; 70 min</td>
<td>800; 70 min</td>
<td>Data not available</td>
<td>~500; 8–14 h</td>
<td>500–900; 20 min</td>
</tr>
<tr>
<td>Origin</td>
<td>Linz (DE)</td>
<td>Produced in-house</td>
<td>Produced in-house</td>
<td>Amersfoort (NL)</td>
<td>Vindeln (SE)</td>
<td>Beijing (CN)</td>
</tr>
</tbody>
</table>

a In Papers II–III, with respect to pore widths 1.5–300 nm; in Paper IV, with respect to pore widths >0.7 nm.

b Fraction of micro (<2 nm), meso (2–50 nm), and macropores (>50 nm).
AC and WDC had larger SSAs and pore volumes compared to SDC (Table 6). However, they were less effective than SDC in terms of Pb$^{2+}$ sorption, Figure 10 (Paper II). Except for the initial concentration of 0.005 mg Pb/L (pH 2), where SDC was less effective than AC since Pb$^{2+}$ was not sorbed but released from SDC at this initial concentration. Mohan et al. (2014) showed that chars produced from various organic substrates may exhibit a high affinity for metals, although their SSA is typically not as high as that of commercial ACs.

![Figure 10](image-url)  
Figure 10. Removal of Pb$^{2+}$ in aqueous metal solution (a) and its corresponding sorption onto sludge-derived char (SDC), wood-derived char (WCD), and activated carbon (AC) (b). Experimental conditions: initial pH 2; sorbent dose 5 g/L; sorbent particle size <0.125 mm; and contact time 24 h.

While large SSA and porosity of carbonous sorbents theoretically could indicate a larger number of sorption sites, the current work and previous studies
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indicate that the surface chemistry is of greater importance than the SSA with respect to metal sorption. The surface chemistry of chars and AC depends on the substrate used and production conditions. The high metal removal capacity of SDC could be associated with a high content of phosphates and carbonates compared to other sorbents studied (assumption, not measured in experiments), which promotes precipitation of metal phosphates and carbonates (Lu et al., 2012). Furthermore, the CEC of SDC (72 cmol/kg) (Paper III) was higher than that reported for WDC and AC (J. Gao, Liu, et al., 2020), which may support Pb$^{2+}$ sorption through ion exchange. SEM-EDS results confirmed the sorption of Pb$^{2+}$ (Paper III).

In comparison to the collected literature data, the SDCs used in this study (Papers II–IV) had comparable content of most metals. However, the Cu contents were in the higher range, and the content of Cr was in the lower range. Zn contents were in the higher range with respect to SDC used in Papers II–III. The SSA was in the lower range with respect to SDC used in Papers II–III, while in the higher range for DS-SDC produced in-house (Paper IV). The average pore size was comparable to literature data, and pH was comparable to literature data when considering the respective temperatures of pyrolysis (Papers II–IV). SSA and pH correspond with the pyrolysis duration and temperature for the respective SDCs. Literature data indicated that increased pyrolysis dwell time resulted in increased SSA, irrespective of pyrolysis temperature (W. Zhang et al., 2013).

4.3 Sludge-Derived Char Application and Pyrolysis Energy Balance

This chapter addresses RQ3 and highlights the main related findings based on Papers III–V.

4.3.1 Enhanced Removal during Primary Settling of Municipal Wastewater

Modelling based on experimental and literature data (Equation 7) indicated that the removal of Cd during primary settling of municipal wastewater could be enhanced through addition of SDC, Figure 11 (Paper III). The maximum possible dosing of char, given that the char is produced on-site at the WWTP, was estimated to ~0.1 g/L (Paper III). The Cd removal with this SDC dosing was estimated to 65% (compared to 39% with no SDC addition). Cd removal was enabled due to the availability of dissolved Cd in the primary settler influent. Based on the typical HRT of primary settlers and the sorption kinetics (>90% Cd removal achieved within 2 h; paper III), the sorption process may be sufficiently quick for sorption to occur during primary settling.
In contradiction to the results in Chapter 4.1, modelling indicated that the use of SDC could not enhance the removal of Ni and Cu. The cause is the DOM affinity for these metals. With respect to Ni, its large affinity for DOM (based on modelling) could result in a release of Ni from SDC, causing increased concentrations of Ni in primary settler effluents.

As was described in Chapter 2.2, the speciation of metals, in particular the fraction of dissolved metals, was expected to be of importance for the potential of improving metal removal. As shown in Figure 11, the model predicted a small fraction of dissolved Pb, Cr, and Zn. The dissolved fraction of these metals could be larger locally; however, adjusting the model (Equation 7) accordingly (based on literature data) did not alter the conclusions with respect to potential of enhancing removal of these metals using SDC.

![Figure 11](image_url)

Figure 11. Modelling of metal fractioning and removal during primary settling (based on wastewater composition at Kungsängsverket, Västerås): a) no addition of sludge-derived char (SDC); and b) addition of 0.1 g SDC/L (Paper III).
Optimisation of the SDC sorption capacity was considered, and modelling based on literature data indicated that this could further improve Cd removal (up to 79%, compared to 39% with no SDC addition). Modelling also indicated the possibility to improve Cu removal to 43% if an optimised SDC was used (30% with no SDC addition) (Paper III). Literature data indicated that the removal of the other metals investigated (Pb, Cr, Ni, Zn) could not be enhanced under the given wastewater composition.

A possible means of enhancing the removal of Pb, Cd, and Cr could be to increase the dosing of SDC (above the capacity of internal production of SDC). However, modelling indicated that this could also result in increased concentrations of Ni, Cu, and Zn in primary settler effluents.

4.3.2 Cd Removal from Dilute Industrial Wastewater and Stormwater

The following types of dilute wastewater were identified in the study site chosen (the vicinity of Västerås city, Sweden): municipal wastewater, waste site leachate, flue gas condensate from a combined heat and power plant, mining wastewaters, and stormwater. The flows and Cd concentrations of these wastewaters indicated that the local demand for Cd removal in the area of Västerås (estimated to 13 kg/yr.) could be covered by the char produced at the local WWTP (sorption capacity estimated to 3–71 kg/yr.). However, it was estimated that large SDC volumes would be required for replacement of a current treatment (ion exchange resins). Thus, the use of SDC could be less feasible compared to current treatment (details given in Paper IV).

4.3.3 Importance of Sludge Composition and Pyrolysis Conditions for Cd Sorption

Char produced from primary sludge (PSC) was compared to char produced from digested sludge (DSC). Despite having a smaller SSA, the sorption capacity of PSC was superior to that of DSC (Figure 12; Paper IV). Characterization of the respective chars showed that PSC had a higher pH, a larger content of cationic elements, and a greater presence of oxygen-containing functional groups (FTIR data) on the char surface (Paper IV). This indicates that PSC had a larger capacity for precipitation, ion exchange, and complexation of Cd compared to DSC. Precipitation could occur in the form of, e.g., metal hydroxides, carbonates, and phosphates (Lu et al., 2012).

The SSA (as well as pore volume and fraction of micropores; results given in Paper IV) increased with increasing pyrolysis temperature, which was in line with the increase in Cd sorption capacity. The decreased char yield with increased temperature was compensated by its increased sorption capacity.
Figure 12. Surface area (SSA) and Cd sorption capacity of char derived from primary (PSC) and digested sludge (DSC) under various pyrolysis conditions (400–800°C; 70–120 minutes) (char dose, 1 g/L; initial Cd concentration, 150 mg/L; only one replicate with respect to DSC400-70 Cd sorption capacity).

From a practical perspective, it may also be relevant to consider the bulk volume of the sorbent, which was considerably larger for the PSC compared to the DSC. The PS, DS, and respective chars are depicted in Figure 13 (Paper IV).

Figure 13. Dried primary sludge (top left), char derived from primary sludge (bottom left), dried digested sludge (top right), and char derived from digested sludge (bottom right); 0.15 g of each (chars produced at 800°C, 70 min; Paper IV).
4.3.4 Energy Demand of Sludge Pyrolysis

Literature data indicated that pyrolysis increased the energy demand of sludge treatment compared to land application of sludge in agriculture or sludge incineration (Figure 14; Paper V). The main driver of the increased energy demand is the drying of sludge required prior to pyrolysis. Accounting for the combustion of off-gas for supporting sludge drying and pyrolysis, the increases in energy demand were estimated at 20 and 13% by von Bahr (2016) and Houillon & Jolliet (2005), respectively. The data from Hospido et al. (2005) indicated an increase in energy demand of >700%, however, they considered only the recovery of heat from tar combustion (not pyrolysis gas). As indicated by both the pyrolysis and incineration scenarios, the possibility of recovering heat has a major impact on the overall energy balance. Another aspect of relevance is the recovery of nutrients for the substitution of mineral fertilisers, as illustrated by the data from Houillon & Jolliet (2005).

An LCA study by Li and Feng (2018) found that AD combined with pyrolysis could generate a net energy output when sludge organic content was 61% or higher (typical values 40–70%). Furthermore, they found that pyrolysis and AD as standalone technologies require sludge organic contents of at least 63% and 52%, respectively. Thus, standalone AD was the preferable option from a
strict energy perspective. Barry et al. (2019) found that the combustion of off-gas could support the drying and pyrolysis of sludge at initial sludge moisture content of up to 78% and organic matter content of 72%.

The results from Paper V highlight that outputs from different LCA studies cannot be directly compared due to variations with respect to the system boundaries applied in the analysis. Furthermore, the variations in LCA methods and inventory data contribute to variations between studies (Teoh & Li, 2020).

In contrast with the LCA data, the experimental study and calculations according to Equation 8 indicated that the combustion of off-gas could cover the energy needed for drying and pyrolysis of sludge, including an energy loss of 15% due to radiative loss and incomplete combustion (losses could be expected to increase when the pyrolysis dwell time is extended) (Figure 15; Paper IV). The contradiction compared to the LCA studies could be related to the assumed off-gas yield (though such details were not reported in the LCA studies). Furthermore, the organic contents of the experimentally examined PS and DS were 91.6 and 66.2%, respectively. The latter is similar to that assumed by Houillon & Jolliet (2005) (65% organic matter, unit of measurement not specified). In line with the organic matter content, the experimental data showed that the initially larger energy content in PS generated larger amounts of pyrolysis off-gas. This could generate larger net excess output of heat (or excess pyrolysis vapours) compared to the pyrolysis of DS. However, the pyrolysis of undigested PS will decrease biogas production; resulting in a net negative energy balance of PS pyrolysis (estimated to -1,450 kJ/kg de-watered sludge; 800°C).
Results and Discussion

4.4 Risk of Contaminants Increase?

In addition to the metal removal, typical wastewater contaminants such as P, N, organic matter, and inorganic matter were also investigated in parallel with metal sorption experiments in filtered wastewater (Paper III). SDC addition (5 g/L) promoted the removal of chemical oxygen demand (COD), total organic carbon (TOC), and N-compounds from filtered wastewater. However, P-compounds and inorganic carbon (TIC) were released from SDC in some samples (Figure 16; Paper III). This indicates that char washing prior to application as a sorbent could be appropriate to avoid the increase of wastewater P and inorganic concentration. However, washing could potentially affect the sorption capacity of the char negatively due to the loss of minerals and exchangeable cations (T. Chen et al., 2015).

Figure 15. Energy use and energy balance with respect to pyrolysis of primary (PS) and digested sludge (DS) (Paper IV).
Another challenge is the potential release of metals from SDC when the concentration of metals in the liquid matrix is low. In Paper II, a release of Pb was detected when initial concentrations in the aqueous metal solution were below 50 µg/L, at initial pH 2. However, release of Pb was drastically reduced at initial pH 4 and no release was detected at initial pH 8 (details given in Paper II).

![Graphs showing release of phosphorous compounds (PO$_4$-P and tot-P) and inorganic carbon (TIC) during sorption of metals.](image)

**Figure 16.** Release of phosphorous compounds (PO$_4$-P and tot-P) and inorganic carbon (TIC) during sorption of metals (A = initial metal concentrations ~25 µg/L; B = initial metal concentration ~50 µg/L; C = initial metal concentration ~100 µg/L) (data from Paper III).
5. Conclusions

SDC could be an efficient metal sorbent, comparable or even superior to some other carbonised organic substrates. Under laboratory conditions and using aqueous metal solutions of dilute concentration, a high-grade metal removal can easily be achieved. However, in a real implementation, the impact of co-existing pollutants in wastewater could be expected to interfere with the sorption and lessen the sorption capacity for some metals. The large volumes of sludge available grant the potential of the char being used as a low-cost sorbent. However, the investment in pyrolysis technology is a possible barrier from the wastewater utilities side, given the uncertainties in the market demand for SDC as a sorbent.

**Metal removal during municipal wastewater primary treatment**

Based on the metal speciation with respect to particulate and dissolved metals in municipal wastewater, sorption could be an appropriate technology to improve the removal of Ni, Cu, Cd, Pb, and Zn during or following primary settling. However, implementing sorption requires consideration of the metal speciation within the dissolved fraction (colloidal, and truly dissolved). These fractions were shown to vary, with different speciation at different WWTPs. Some general patterns could, however, be distinguished: Ni and Cu are the metals that are most prone to be truly dissolved (up to 50% and 10%, respectively), while the truly dissolved fractions of Cr, Zn, and Pb are generally small or below detection level, and there was limited data with respect to truly dissolved Cd. Furthermore, the dissolved fraction (colloidal and truly solved) generally decreased with increased total metal concentrations, indicating that successful removal during primary settling could require a combined approach of sorption and coagulation-flocculation.

**Metal sorption capacity of SDC**

Due to the heterogeneity of sorption sites, the accurate prediction of sorption capacity in dilute wastewater requires experimental data at the relevant concentrations. From a practical perspective this is contradictory since dilute concentrations do not allow for determining the maximum sorption capacity ($Q_{\text{max}}$) often sought in sorbent assessment. The current study has demonstrated the lack of prediction capacity, with respect to dilute wastewater, considering the bulk of scientific literature available.
Sludge-derived char, utilisation as a metal sorbent

In real wastewater, the sorption of Ni and Cu to SDC is restricted due to their tendency to complex with DOM. The presence of DOM may also promote the release of metals from char, especially Zn, which was hypothesised to be due to ion exchange with inherent wastewater ions (e.g., Fe$^{3+}$). The metal (lead) sorption capacity of SDC could exceed that of commercial AC and WDC, even when the SSA of WDC and AC is larger than that of SDC. This confirms the importance of sorbent composition with respect to surface functional groups and mineral composition.

Aspects of SDC production and its implementation as a metal sorbent in dilute wastewater

The in-house use of SDC for the removal of metals during primary settling could enhance the removal of Cd and Cu (from 39 to 79% and 30 to 43%, respectively), and the sorption kinetics are sufficiently quick for the sorption to occur during primary settling. There is a concurrent risk of increased Ni concentrations in primary settler effluent. The effect with respect to Pb, Cr, and Zn was predicted to be small, as these are preferentially associated with wastewate particulate matter.

Assessment of the regional demand for Cd sorbent in the Västerås area indicated that the volumes of SDC from the local WWTP could cover the local demand for Cd sorbent (municipal wastewater, stormwater, waste site leachate, flue gas condensate, and mining drainage). However, the SCD volumes required indicated that the use of SDC may be less feasible compared to the current treatment.

The SDC sorption capacity increases with a higher pyrolysis temperature due to increased porosity and SSA. A larger char sorption capacity could be expected when using PS as feedstock than when using DS. This was linked to its higher pH (promoting precipitation), larger cation content (promoting ion exchange), and larger functional groups content (promoting complexation).

In line with previous research, sludge pyrolysis could theoretically generate a net excess of heat when off-gas is incinerated to support the drying and heating of sludge. The net excess heat (per kg of dewatered sludge feedstock) was found to be greater with respect to PS (compared to DS), due to higher calorific value as well as larger off-gas generation. However, given the estimated loss of biogas production, the energy balance with respect to PS pyrolysis was negative. Higher pyrolysis temperature generated a more positive energy balance with respect to both sludges due to increased volumes of off-gas. However, because only a few full-scale sludge pyrolysis plants are currently in operation, the energy balance in full-scale and energy demand in relation to that of other sludge disposal options (agricultural use or incineration) remains uncertain.
6. Future Directions

SDC is a promising metal sorbent. However, to transfer from a promising research topic to actual implementation, further assessment and practical evaluation are needed. Important aspects to consider at the current stage are:

• The variability of sludge composition over time may affect the char sorption capacity. To the authors knowledge, this factor has not been investigated. The potential quality variations could affect the reliability of using SDC as a sorbent and thus the viability of selling the char as a sorbent.

• In the current work, the choice was made to consider only non-activated, unmodified SDC. However, there are many suggested processes for enhancing the metal sorption capacity of SDC (activation, modification, or co-pyrolysis of sludge and other feedstocks). Nonetheless, the techno-economic assessment of these processes deserves increased attention to avoid continued exploration of processes that are not economically feasible.

• The risk of leaching was demonstrated in this work. However, given the limited number of elements and compounds considered in the wastewater characterisation, future studies should explore additional contaminants such as organic micropollutants.

• The disposal or regeneration of spent SDC deserves attention, including the final fate of the metals accumulated in char.

• As previously mentioned, the energy balance in full scale is yet to be verified. Finally, in a pilot or full-scale implementation of SDC sorption, the appropriate process configuration is yet to be determined.
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