Biochar adsorption for separation of heavy metals during municipal wastewater treatment

I. Sylwan*, E. Thorin* and J. Zambrano*

*The School of Business, Society and Engineering, Mälardalen University, Högskoleplan 1, Västerås, Sweden
(E-mail: *ida.sylwan@mdh.se; eva.thorin@mdh.se*; *jesus.zambrano@mdh.se*)

Abstract
The idea behind this study is to concentrate heavy metals in primary sludge during municipal wastewater treatment, and produce a bio-sludge with low metal contents from the secondary treatment step where nutrients are removed. We investigate a process concept where biochar, produced from primary sludge, is reused as a metal adsorbent in primary treatment. Biochar has been extensively studied as an efficient low cost-adsorbent of heavy metals in treatment of industrial wastewater. Metal concentrations are often many times higher in industrial wastewaters compared to municipal wastewater, therefore we investigate what importance diffusion and competition from other ions has for the adsorption capacity when the biochar is applied in municipal wastewater treatment.

Keywords
Biochar; Metal adsorption; Primary treatment; Sludge; Nutrient recovery.

INTRODUCTION

Heavy metals in municipal wastewater may cause adverse effects on human health and the environment. Strict limiting values apply to heavy metal concentrations in sludge for agricultural use. This calls for action both toward decreasing the metal release to municipal sewers (e.g. from local industries) and to design engineering solutions that decrease the metal concentrations in sludge.

One possible solution is separation of metals through adsorption before they end up in the sludge. Chars produced from organic residues (also called biochar) have been studied extensively as low cost adsorbents with high adsorption capacity (Inyang et al., 2015; Mohan et al., 2014). The idea behind this study is to remove metals during primary treatment of municipal wastewater, while nutrients are removed during secondary treatment (i.e biological treatment) – to produce a high quality secondary sludge that can be used in agriculture. An overview of the studied process concept is shown in Fig. 1.

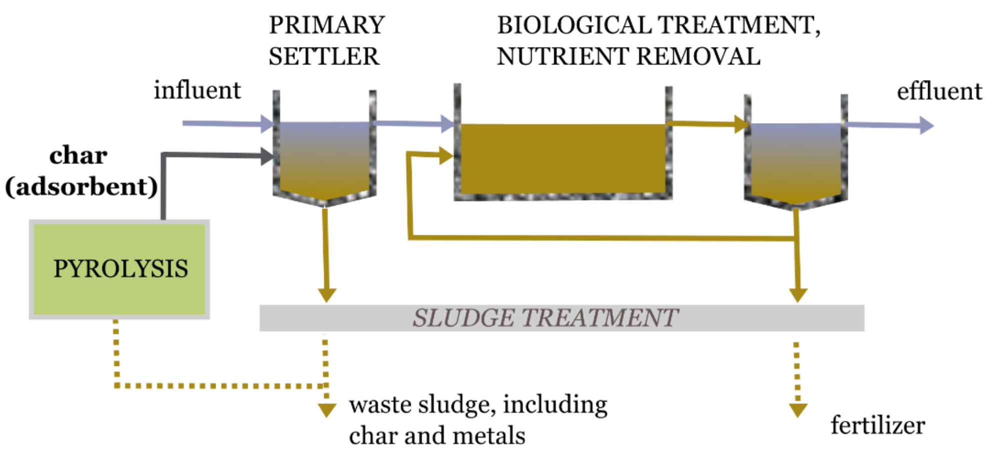

Figure 1. Process concept for improved quality of secondary sludge.

METHOD

This experimental study is performed by laboratory shake tests, where the adsorption capacity of different types of char is compared under different char dosages and adsorbate (metal) concentrations. The adsorption is determined by analysing the residue metal concentrations in the solution after the char treatment.

RESULTS AND CONCLUSIONS

The adsorption dynamics of char include kinetics (the rate of adsorption) and adsorption isotherms (the dependency on metal concentration). Langmuir and Freundlich are models which are often used to describe the adsorption capacity of an adsorbent as a function of adsorbate/metal concentration (Inyang et al., 2016). At low metal concentrations, these models give a near linear correlation between metal concentration and adsorption of metal. In this experiment the adsorption capacity is investigated at low metal concentrations, comparable to concentrations in raw municipal wastewater in Sweden (~0.1-100 µg/L). Adsorption capacity at these low concentrations is not expected to be linearly dependent on the metal concentration, as suggested by the Langmuir and Freundlich models, but is expected to be limited by diffusion. More complex models could be applied to describe the adsorption isotherm.

Competition for adsorption sites could occur in raw wastewater, which contains many different metals and other ions. Compared to previous experiments with raw municipal wastewater, it is expected that the adsorption capacity of metals is higher in aqueous metal salt-solutions.

Initial experimental data on wastewater, containing many different metals and other ions, indicates that Swedish char produced from wood could adsorb significant amounts of cadmium (Cd) (Sylwan et al., 2017). In this study, results from experiments on metal salt-solutions are presented. The aim is to better understand the adsorption capacity for each metal. From the results of the initial experiments, Cd, Pb and Zn are identified as the metals of highest interest.

Further, based on adsorption of metals *and* nutrients (phosphorus and nitrogen), conclusions can be drawn regarding the possibility to improve the quality of secondary sludge.

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BIOCHAR ADSORPTION FOR SEPARATION OF HEAVY METALS IN MUNICIPAL WASTEWATER TREATMENT

Ida Sylwan[1], Hanna Runtti[2], Eva Thorin[1] , Jesús Zambrano[1], Lena Johansson Westholm[1]

[1]School of Business, Society and Engineering, Mälardalen University, [2]Research unit of Sustainable Chemistry, University of Oulu

INTRODUCTION

- **Heavy metal adsorption capacity of sludge based biochar (Linz) was studied** and compared to adsorption potential of wood based biochar (Vindelkol) and a commercial activated carbon (Norit) (fig. 1).
- Biochar produced from sludge could be a potential low cost adsorbent, efficient for adsorption of heavy metals from wastewater (Lu et al., 2012).
- Few studies on metal adsorption to biochar have examined the potential adsorption at initial metal concentrations less than 5 mg/L.
- Metal concentrations in municipal wastewater are generally below 0.1 mg/L (Cd, Cr, Cu, Hg, Ni, Pb, Zn) (Cantinho et al., 2016).

METHOD

Batch adsorption tests were performed at:

- initial metal concentration 0.005 to 150 mg/L,
- pH 2, to avoid precipitation,
- adsorbent dose 5 g/L.

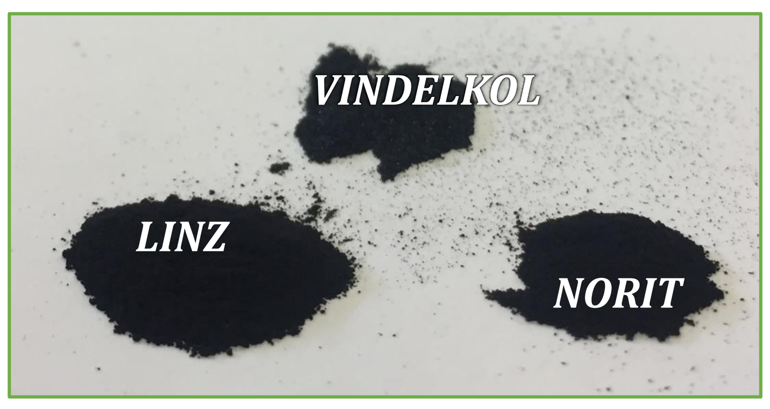

FIGURE 1. Linz, Vindelkol and Norit, particle size <0.125 mm.

Commonly applied adsorption **isotherm models were fitted to the experimental results** and evaluated based on root mean square deviation: $RMSD = \sqrt{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2/n}$, where $\hat{y}$ is the model value, y is the experimental value and n is the number of observations.

Pb AND Ni REMOVAL CAPACITY

Figure 2 shows the removal/release of Pb.

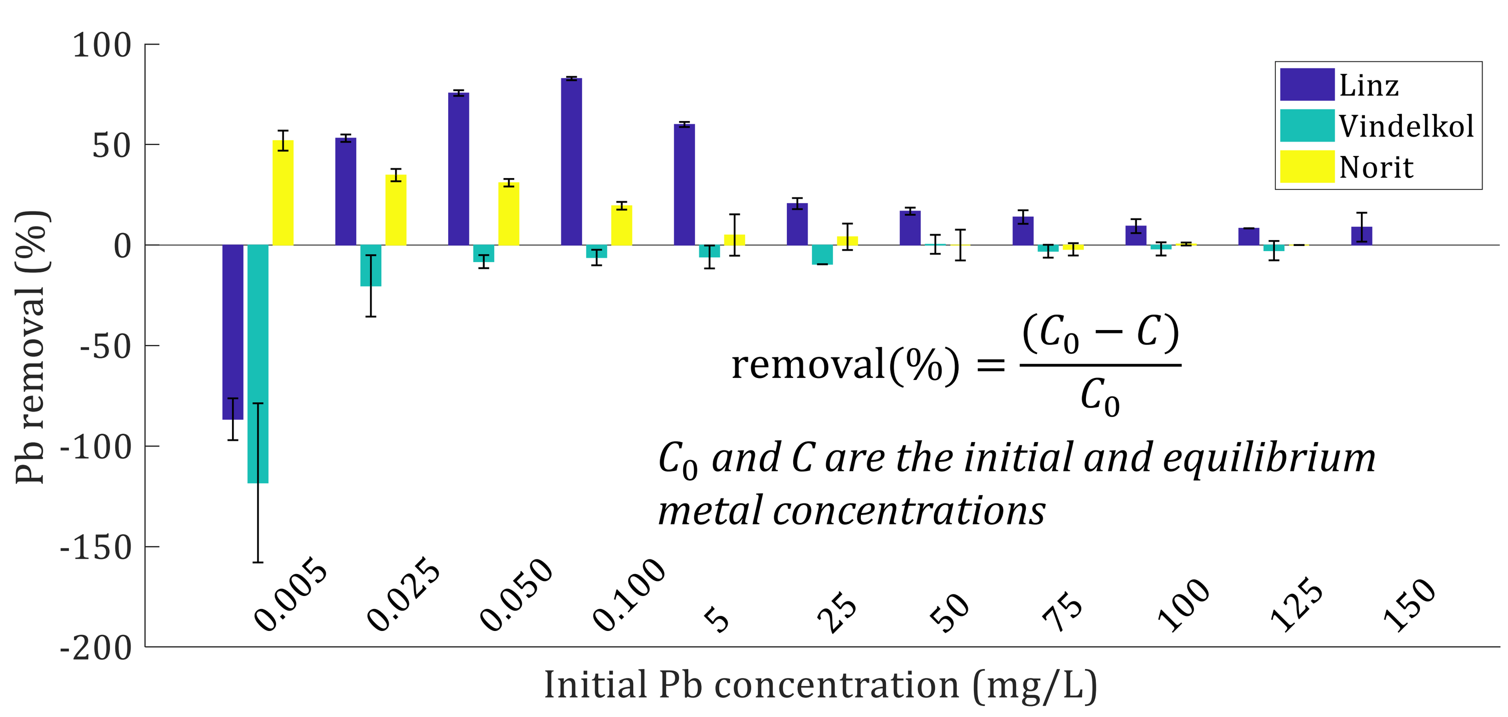

FIGURE 2. Removal capacity of the different adsorbents tested.

- **Linz removed maximum 82.8 % Pb**, at initial concentration 0.1 mg/L.
- Norit removed maximum 52.0 % Pb, at initial concentration 0.005 mg/L.
- Vindelkol did not remove Pb.
- **Linz released substantial amounts of Pb** (and so did Vindelkol)**, at initial Pb concentration 0.005 mg/L**

IDA SYLWAN
PhD-student
ida.sylwan@mdh.se
www.mdh.se

ISOTHERM – Pb REMOVAL PER GRAM ADSORBENT

Adsorbents typically reach a maximum adsorption capacity (fig. 3).

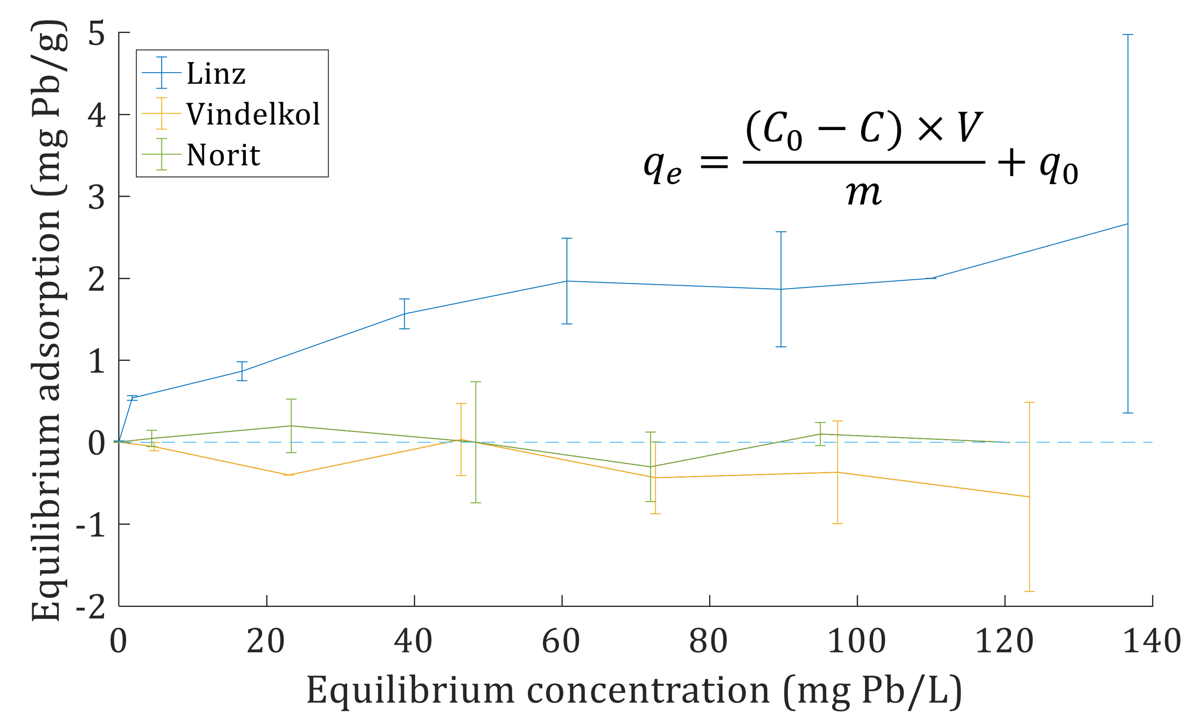

FIGURE 3. Adsorption capacity of Linz, Vindelkol and Norit.

- *q_e is the equilibrium adsorption,*
- *m is adsorbent dose*
- *V is sample volume and*
- *q_0 is estimated amount of metal in the adsorbent at the start of experiments*

- **Maximum adsorption of Pb per gram of Linz (~2 mg/g) occurred at initial metal concentration 75 mg/L or higher.**
- Vindelkol and Norit did not show any statistically significant adsorption of Pb at equilibrium concentrations above 1 mg/L.

ISOTHERM MODELS

Isotherm models are illustrated in Figure 4. **The Redlich-Peterson model gave the best fit**. Equations and parameter values are shown in Table 1.

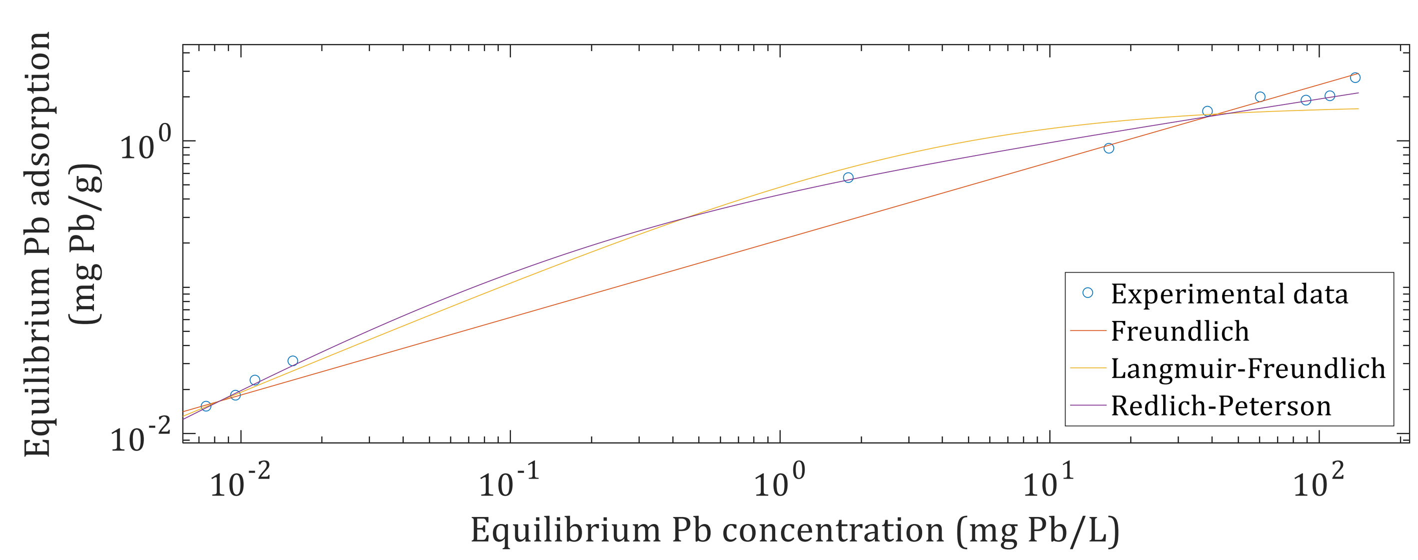

FIGURE 4. Isotherm models for Pb adsorption to Linz.

TABLE 1. Isotherm models, equations and parameter values.

Model	Equation	Parameter values	RMSD
Redlich-Peterson	$q_e = \frac{K_{RP}C_e}{1+a_{RP}C_e^g}$	$K_{RP} = 2.27, a_{RP} = 4.29, g = 0.716$	3.08
Langmuir-Freundlich	$q_e = \frac{K_{LF}C_e^{n_{LF}}}{1+(a_{LF}C_e)^{n_{LF}}}$	$K_{LF} = 0.665, n_{LF} = 0.769, a_{LF} = 0.283$	4.39
Freundlich	$q_e = K_F C_e^n$	$K_F = 0.211$, n= 0.530	7.33

CONCLUSIONS

- **Linz biochar showed significant removal capacity for Pb at C_0 of 0.025-150 mg/L**. While leaching of Pb (and Ni) occurred at the lowest C_0 tested – 0.005 mg/L.
- Results indicate that**, due to risk of leaching, it is relevant to consider metals contained in the adsorbent material "pre-adsorption" when adsorbents are applied at low C_0.**
- **The Redlich-Peterson isotherm model gave a good prediction of the adsorption capacity** over the whole concentration span**.**

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