

Mälardalen University Press Licentiate Theses

No. 74

**METAL RETENTION FROM LEACHATE USING
INDUSTRIAL WASTE PRODUCTS**

Emma Nehrenheim

2007



MÄLARDALEN UNIVERSITY

Department of Public Technology
Mälardalen University

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ISSN 1651-9256

ISBN 978-91-85485-42-0

Printed by Arkitektkopia, Västerås, Sweden

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Licentiate Thesis

PART I

SUMMARY

Landfill leachate arises when water percolates through a landfill. The degree and type of pollution is dependent on the content of the landfill but also on a range of other factors, including the age of the landfill and the landfilling technique. In recent years, concerns about potentially hazardous compounds in landfill leachate have stimulated research into on-site treatment. Examples of new techniques for treatment are the sequent batch reactor technique (SBR), wetland systems and different forms of filter solutions.

Lilla Nyby landfill is the municipal landfill in Eskilstuna, Sweden. Leachate streams have been found on site that are weaker than the main stream. One of these has been investigated in the present study. It contains heavy metals, especially zinc, copper and nickel, in concentrations which require treatment. Low strength landfill leachate streams require special treatment. There are various reasons for this, but examples can be geological reasons or dilution problems in the treatment facility for the main leachate.

The technique chosen for the leachate stream, reactive filters, is rather new and few pilot scale experiments have been conducted. Therefore many questions still remain concerning the applicability of the method on site, and there was a need for more experimental data. Previous research has shown that many industrial by-products may be suitable to capture metals from leachate. Among the materials previously recommended, blast furnace slag and pine bark had advantages which were well suited for the present application. They were also available in large quantities near the site. A column experiment was set up at the landfill and three filter materials were chosen; pine bark and two types of blast furnace slag. In addition, one of the columns was filled with sand as a reference. As a complement to the column study, laboratory experiments were conducted at Mälardalen University. The aim of the laboratory experiments was to investigate factors that might limit metal retention by the filter materials. Different concentrations and contact times were tested as well as the presence of other substances (i.e. metals and organic carbon).

The results from the first laboratory experiments (initial metal concentration, competing metal ions and contact time) and the on-site column study were contradictory. Metal uptake in the laboratory was very efficient, as has also been found by other researchers. On-site, many factors influenced sorption and uptake was very unstable, especially for the slags. It was

found that pine bark is more effective and stable than the slags with respect to metal retention, especially at low concentrations. The contact time between the substrate and metals is important for effective retention. The final experiment, showed that dissolved organic carbon (DOC) can greatly inhibit metal retention. To further develop reactive filter technology, a method to reduce the DOC content may be necessary.

In contrast to what has been previously assumed, leaching of COD from the pine bark column at Lilla Nyby landfill was negligible. Finally, some suggestions for future work on reactive filter technology are made. For instance, it could be interesting to develop an alternative technique for filtration. Packed columns have been addressed with a series of problems, related to hydraulic parameters. By using fluidised reactors, a comparison with batch experiments becomes possible.

SVENSK SAMMANFATTNING (SUMMARY IN SWEDISH)

Lakvatten uppstår när regnvatten eller grundvatten infiltrerar genom en deponi. Omfattningen och typen av förorening beror på innehållet i deponin men också en rad andra faktorer, till exempel deponins ålder och deponeringsteknik. På senare år har kunskap om de potentiellt miljöfarliga föroreningarna i lakvatten gjort att utvecklingen av lokala behandlingsmetoder tagit fart. Exempel på nya tekniker som utvecklats är så kallad SBR (sequent batch reactor), våtmarker och olika sorters filterlösningar.

Lilla Nyby är Eskilstunas kommunala avfallsdeponi. På deponin har lokala lakvattenströmmar funnits som är svagare än det som kallas för huvudströmmen. En av dessa strömmar är lakvattenströmmen i den här studien. Den innehåller tungmetaller, speciellt zink, koppar och nickel, i koncentrationer som kräver någon form av behandling. Svaga lakvatten som uppstår i deponier kräver speciell behandling. Anledningen kan variera men exempel kan vara geologiska eller problem med utspädning i behandlingsanläggningen för den stora lakvattenströmmen på deponin.

Tekniken som valdes för lakvattenströmmen, reaktiva filter, är relativt ny och få pilotexperiment har genomförts. Därför finns många frågor obesvarade avseende teknikens tillämpbarhet i fält. Även i laboratorium står många frågor obesvarade och mer experimentdata krävs. Tidigare forskning har visat att flera olika industrirestprodukter kan användas för att fånga upp tungmetaller ur en lösning, exempelvis lakvatten. Bland materialen som rekommenderats återfanns masugnsslagg och furubarkflis, som båda hade lovande egenskaper för tillämpningen i den här avhandlingen. Dessutom fanns de tillgängliga i stora kvantiteter och i närregionen. Ett kolonnförsök sattes upp på deponin vid Lilla Nyby med fyra kolonner som fylldes med sand och tre filter material, furubarkflis och två typer av masugnsslagg. Som komplement till kolonnstudien utfördes kolonnförsök i laboratoriet på Mälardalens Högskola. Syftet med laboratorieförsöken var att finna vad som skulle kunna störa metallretentionen. Olika koncentrationer och kontakttider prövades, liksom störningar i form av andra metalljoner eller löst organiskt kol.

Resultaten visade att det fanns stora skillnader mellan laboratorie- och fältförsöken. Samma parametrar (initial metallkoncentration, konkurrerande metalljoner och kontaktid) var signifikanta för processen men upptaget i fält var avsevärt sämre. Den goda

upptagningsförmågan i laboratorieförsöken (d.v.s. skakförsöken) överensstämde väl med resultat från tidigare forskning. I fält var metallsorptionen däremot väldigt ojämn, speciellt till de två slaggmaterialen. Furubarkflis var däremot mer stabil och effektiv, speciellt avseende metallretention vid låga metalljonkoncentrationer.

Lång kontakttid var viktigt för att uppnå effektiv metallretention. Det sista experimentet visade att DOC spelar en viktig roll för metallretentionen och kan hindra upptaget avsevärt. I en vidare utveckling av den reaktiva filtertechniken behöver påverkan av DOC och eventuell reduktion av denna utvecklas vidare.

I motsats till vad som tidigare antagits av forskare, fanns inget signifikant läckage av COD från kolonnen med furubarkflis vid Lilla Nyby.

Slutligen har några förslag på fortsatt arbete inom området redovisats. Exempel på intressant vidarearbete är utvecklandet av tekniken för att optimera flödet i kolonnerna. Packade kolonner kan innebära problem med kanalbildning och kloggning, vilket kan undvikas med fluidiserade bäddar. Dessutom blir jämförelsen med skakförsöken lättare då de är lika i sitt utförande.

ACKNOWLEDGEMENTS

During the entire time I have spent so far at the Department of Public Technology I have had two supervisors, **Sylvia Waara** and **Lena Johansson Westholm**. Thank you for all the time you have spent in my project.

A year ago, my studies were also enriched by the knowledge and supervision of **Jon-Petter Gustafsson** at Royal Institute of Technology. It has been an honour and very interesting working with you.

When I first thought about continuing my education towards a higher degree **Erik Dahlquist**, professor and dean, was the contact I had. For a few months different projects were discussed and finally we decided to go on board with a project in collaboration with **Mälarenergi AB**, **VAFAB Miljö** and **Eskilstuna Energi och Miljö AB**. I would like to send many thanks to Erik for giving me this opportunity and the collaboration companies for the financial support.

Among the partner companies there are also a few persons that has become important for the project. In the initiation of the project **Carina Färm**, at Mälarenergi AB, was a great support. The co-operation with **Magnus Jacobsson** and **Jörgen Björnfot** at Eskilstuna Energi och Miljö AB has been very valuable as well as discussing problems with **Leif Linde**. I would also like to thank the members of the VAFIM group for discussions, advice and feed back to the project. During the construction of the research set up at Lilla Nyby landfill, **Tobbe Fagre** has been the handy-man. Tobbe was never afraid to try out new solutions to fit my design demands. It was really fun working with you, Tobbe!

SSAB Merox AB must be thanked for supplying the slag for free. Especially **Lotta Lind** is thanked for the help and support in the project.

Thank you, **Björn Widarsson**, **Anders Avelin**, **Christer Karlsson**, **Veronika Ribé** and **Fredrik Starfelt** for your support on our Friday morning meetings. Other PhD-student colleagues and friends at Mälardalen University are of course thanked for so many hours of laughs; **Thomas Nolte**, **Mia Kumm**, **Fredrik Wallin**, **Andrea Wallin**, **Andreas Kvarnström**, **Johan Kvarnström**, **Jenny Nyström**, and **Cajsa Bartusch**, just to mention a few. I would also like to give a thought to all other colleagues at Department of Public

Technology and especially to **Lars Wester** for making ISt a incredibly nice working environment. Great thanks also to **Adel Karim** for putting time and effort into explaining the physics of fluid dynamics, Gambit and Fluent. Thank you also, **Eva Thorin**, for help with the final polishing of the manuscript. Without laboratory support from **Christina Ingwall-Johansson** and **Ann-Sofie Magnusson**, I don't know what I would have done. Thank you! In the first months of the Lilla Nyby on-site project, **Karin Skütte** helped out within the frames of her diploma work. Thank you, Karin and good luck with your future plans!

Nick Jarvis has been my very fast and meticulous proof reader of manuscripts and thesis. Thank you!

Monica Odlare has been a very important friend and room mate. Thank you for always giving me advice and for working so hard with BIOREX, our common project.

Hans Wallin, my dear friend and mentor, has been a very important in my research carrier so far. I would like to thank you for always believing in me and for working hard also on rainy days.

Speaking about friends, I must send a special thought and thanks for being there to the “gal-pals” of mine; **Emma Carlsson**, **Sara Landerdahl**, **Charlotta Anger**, **Helena Carlsson**, **Marie Söderberg** and **Anna Thunblom**. You have all inspired me with you high ambitions and energy in life.

During all my days on earth my parents, **Zarah** and **Ingemar Rudgård**, have not only been great support but also role models to life. **Jenny** has always been the sister in need and she has become my best friend as well. Nowadays, she is accompanied by **Markus** who has also become a dear friend.

Finally my husband **Ville** must be thanked for always keeping me happy and for staying home with our daughter and joy in life, **Hedda**, so that I could finish my licentiate degree. I love you both!

LIST OF APPENDED PAPERS

Papers included in the Thesis

Paper I

Nehrenheim E, Waara S and Johansson Westholm L (2006) *Metal retention to pine bark and blast furnace slag – on-site experiment for treatment of landfill leachate*, Accepted for publication in *Bioresource Technology*

Paper II

Nehrenheim E and Gustafsson J-P (2006) *Kinetic Sorption of metals to pine bark and blast furnace slag*, Manuscript submitted to *Bioresource Technology*

Paper III

Nehrenheim E, Waara S, Gustavsson J-P and Johansson-Westholm L, 2007, *The influence of dissolved organic carbon (DOC) on the metal sorption process to pine bark*, Manuscript

The papers are published with the kind permission of the journals concerned, and the papers are appended in Part II.

Papers and reports, not included in the thesis

Papers

Nehrenheim E (2005) *Metal Reduction from Landfill Leachate by using Blast Furnace Slag and Pine Bark – Discussion about the Parameters significant for Metal Removal*, Kalmar Eco-tech'05, The Second Baltic Symposium on Environmental Chemistry, Kalmar, Sweden, November 28-30

Nehrenheim E., Johansson Westholm L. and Waara S. (2005) *Treatment of landfill leachate using filter substrates*, Sardinia '05 10th international Waste and Landfill Symposium, Sardinia, Italy

Nehrenheim, E, Lind, L. and Johansson Westholm, L. (2006) *Sorption of phosphorus from domestic wastewater by blast furnace slag – theory and practical experiences* (manuscript submitted to Water Research)

Nehrenheim, E and Odlare, M (2006) *Biological degradation of explosives in columns - new research ideas*, 4th International Disposal Conference, Nov 13-14, Katrineholm, Sweden

Odlare, M and Nehrenheim, E (2006) *Microbiological degradation of explosives in bioreactor*, 4th International Disposal Conference, Nov 13-14, Katrineholm, Sweden

Nehrenheim, E. and Dahlquist, E. (2003), *Mass Detonation or Recovery - Environmental Impact of Different Ammunition Destruction Methods*, 3rd International Disposal Conference, Nov 10 - 11, Karlskoga, Sweden.

Dahlquist E., Nehrenheim E. and Eriksson P. (2003), *Environmental and economic aspects on Reuse of Explosives*, 3rd International Disposal Conference, Nov 10 - 11, Karlskoga, Sweden

Reports

Johansson Westholm L, Nehrenheim E and Waara S (2005) *Slutrapport avseende filterbehandling av lakvatten (L500) på deponin Lilla Nyby, Eskilstuna*, Fo-rapport 2005:4, Institutionen för Samhällsteknik Mälardalens Högskola

Nehrenheim E (2006) *Heavy metal removal by using by-products from world wide industry – a State Of The Art*, Fo-rapport 2006, Institutionen för Samhällsteknik Mälardalens Högskola

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1 INTRODUCTION

Finding new technologies for water treatment has become a top priority among global environmental concerns. Increased use of resources and energy as well as continuous waste production, means an increased risk of environmental contamination. Therefore, actions to minimize the impacts of human activities have to be constantly developed in order to prevent over-exploitation of planet earth. Water treatment is one example.

Examples of waste waters produced by human activities include industrial waste water, sewage water, storm water and the waste water addressed in the present thesis; landfill leachate. All these specific waste water types might require specially designed treatment systems. When different waste waters are mixed together, the resulting waste water might result in a dilution of one or several compounds which are more easily and efficiently removed if present at higher concentrations. Another outcome is the interference of one compound on the removal efficiency of another. Thus, it is possible that treatment of a particular waste stream with a few compounds or many compounds present at low concentrations might be solved by using a simpler technology than when mixed together. It can therefore be argued that on-site treatments, adapted to the specific contaminants and recipient sensitivity, are favourable, especially from a financial point of view.

Landfill leachate is formed when water percolates through a landfill. Depending on the content of the wastes, the leachate consists of many different types of compounds e.g. salts, metals and organic materials (Lagerkvist 2003). A municipal landfill can produce a series of leachate streams of different qualities or contents, and most of these require an advanced treatment plant, if they are to be treated together. It is however quite common that some part of a landfill produces leachate that has a very different composition or contains rather low levels of contaminants. For instance, an older part of the landfill can produce a leachate which requires some kind of treatment (e.g. due to high metal content), but not to the same degree as the main body of the leachate. It would then be impractical to treat this stream together with the main leachate stream.

Landfill leachate can contain many persistent compounds such as heavy metals. Some are toxic at large concentrations, including those that are essential for organisms in low concentrations. Some metals, such as Cr and Zn, are also suspected carcinogens and/or could

bioaccumulate (Öman et al 2000b). High concentrations of heavy metals are seldom a problem in drinking or sewage water treatment (Junestedt et al 2003), but often occur in industrial waste water, landfill leachate and storm water. Several different methods of removing metals from waste water have been suggested, including wetland treatment, detention ponds and filter technology (Reed et al 1995, Färm 2003, Thörneby et al 2006, Kietlinska et al 2005, Aziz et al 2003, Kargi and Pamukoglu 2003). Among these, metal retention on various substrates (i.e. reactive filter technology) has been evaluated for use as an on-site application due to its low cost, low maintenance needs and low demands on space. Several reports indicate that many materials show suitable properties for metal removal (Johansson Westholm and Färm 2004). The metal sorbing properties of many materials have been investigated in recent years and research in this field has been extensive. The materials tested can be categorized into natural, manufactured and by-products (this will be further described later, see Table 2-1). Of these, blast furnace slag and pine bark were considered the most interesting to use in the present study because of low cost, and local availability in large quantities. From a global perspective, they are also widely available in many parts of the world. Most importantly, both pine bark and blast furnace slag were available close to the landfill site as by-products. From the point of view of sustainable development, it can be argued that by-products are preferable to both manufactured materials and natural resources.

To begin with, some basic terms should be defined. There are three interacting units in a filter; the *solution*, *solute* and *sorbent*. The solution is the water or effluent from which the contaminant, or solute, is to be removed. The sorbent is the porous media to which the solutes attach. In the thesis, the solute will most often be a metal ion and the sorbent any of the industrial by-products studied. The thesis also refers to the term reactive filter, which means a material or substrate with surface properties well suited to attract ions.

1.1 Problem

Even though many materials have been tested and appear promising for the removal of contaminants such as metals, there are many questions remaining before they can be used in full scale applications for on-site waste water treatment. To date, most experiments have been conducted in the laboratory with the aim of evaluating the intrinsic sorption potential of the material, but very few studies have addressed the problem of designing a treatment facility with filter material where factors of importance for the functioning of the filter for a particular

waste water have been explored. The results of batch experiments conducted in the laboratory can only say something about the specific question that the experiment was designed to answer. One can design experiments for a series of potential problems, but not until the technique is tested on-site is it possible to determine its true potential.

1.2 Objective

The overall aim of the thesis is to evaluate reactive filter technology with a focus on understanding its performance and limitations under realistic field conditions.

The specific aims are to:

1. Evaluate the possibility of removing metals from a landfill leachate using pine bark and blast furnace slag in filter columns on-site (*Paper I*)
2. Confirm that the Swedish filter materials used in the study have a high potential to sorb metals (*Paper II and III*)
3. Investigate the relationship between contact time and metal retention capacity (*Paper II*)
4. Investigate the influence of dissolved organic carbon (DOC) on the metal retention capacity (*Paper III*)
5. Evaluate the risk of phenol leaching from pine bark (*Paper I and III*)

1.3 Thesis Outline

1.3.1 A two-part thesis

The thesis is divided into two parts. The first part gives an overview of previous research together with a presentation and a discussion of the research conducted within the framework of the project. In the second part, the research is described in more detail in published papers and submitted manuscripts.

1.3.2 Working progress and demarcations

In the research work presented in this thesis, low cost sorbents were chosen based on certain criteria. The materials should be available in large quantities close to the site. The availability of the materials from a global perspective was also taken into account. To fulfil the aims of

finding a low cost and operationally effective sorbent, the study focused on the use of untreated and poorly modified materials concerning particle size, chemical composition and moisture content. The materials were examined exactly as they were delivered from the suppliers, as would be the case in a future potential full scale application. Therefore, no pre-treatment or manipulation of the filter materials was conducted.

The main study was to evaluate the material properties from the perspective of an on-site application. Thereafter, the laboratory experiments were designed to answer specific questions that arose as the on-site study was conducted and evaluated. For example, laboratory experiments were conducted in order to establish the metal retention capacity of the specific materials used in the study. Even though similar materials have been tested by other researchers, it is important to ensure that the materials have the metal retaining properties expected. The 3 materials used were therefore evaluated for removal efficiency at different initial metal concentrations and solution pH. The metal retention capacity of filter substrates have often been tested with single metal solutions, but it is important to assess the effects of mixtures of many metals on the retention potential. The possible presence of competition of metals for sorption sites was therefore also explored. These results agreed with what was found by earlier studies, and so have not been included in the thesis.

One important parameter controlling metal retention is the time available for ions to sorb to particle surfaces. Therefore, the contact time as a parameter for metal removal by the materials was determined in laboratory batch experiments. From this, a kinetic sorption model was derived (*Paper II*).

The presence of DOC was identified as one of the most important factors that can limit the removal of metals from landfill leachate, but this is generally not considered in batch experiments. Therefore, the third study (presented in *Paper III*) was conducted to test the hypothesis that DOC might alter the speciation of metals and thus influence the metal removal efficiency of a sorbent. The figure below shows the way the work progressed within the project and how knowledge gained from the on-site experiment formed the laboratory work. The results from the laboratory studies then led to modifications in the on-site experiment (Figure 1-1).

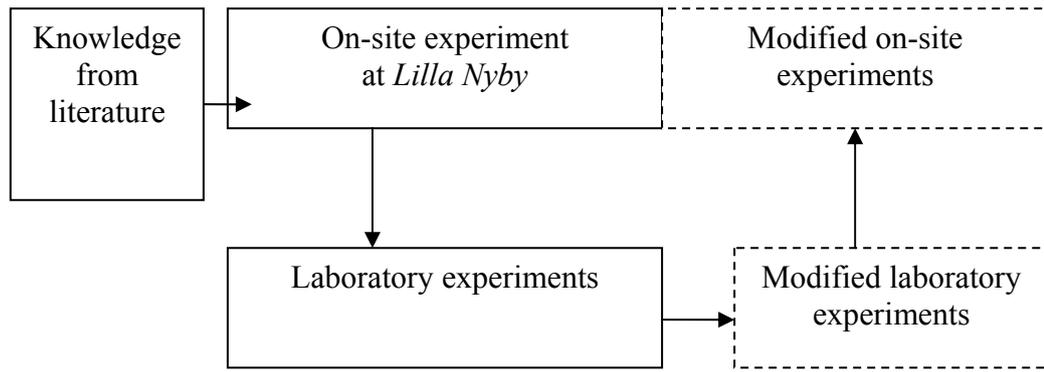


Figure 1-1 Working progress in the project

2 THEORY

This chapter aims to give an overview of previous research in the field of reactive filter technology with special regard to the two materials investigated in the thesis, blast furnace slag and pine bark. First, the mechanisms of sorption and the mathematics used to model them are described. It is important to fully understand the complexity of the sorption chemistry and the choice of a kinetic pseudo-model, described in later chapters (see also *Paper II*).

A description of potential materials for metal removal then follows, which gives a background to the choice of slag and pine bark. Thereafter the materials used in the experiments are described in more detail.

The origin and toxicity of landfill leachate is described in order to emphasize the importance of the treatment of landfill leachate from a perspective of sustainable development. This also explains why the leachate is so complex and the dynamics of leaching from a landfill.

The chapter also aims to evaluate the different experimental approaches used in the field of reactive filter technology. The purpose was to illustrate the need for on-site investigations (*Paper I*) and identifying limitations in the technique in practical application (*e.g. Paper III*). The theory chapter concludes with a discussion.

2.1 Diffusion

The random microscopically small movements of molecules, atoms or ions is called diffusion, and is one of the most important metal retention processes. Diffusion is caused primarily by concentration gradients, so that a species moves in the direction of high concentration to low concentration. Ions are transported by diffusion to the sorbent surface where adsorption processes can occur (see next section). In a binary system with zero velocity and no chemical reactions, diffusion in three dimensions is described by Fick's second law of diffusion:

$$\frac{\partial C}{\partial t} = D_s \nabla^2 C$$

, where C (mg/l) is the solution concentration of solute at time, t (s), D_s is the solute diffusivity or diffusion coefficient (m²/s).

Fick's law of diffusion is the basic expression, valid for gases in free spaces. A modified version of Fick's law, adjusted to describe diffusion of solutes into the boundary layer (i.e. the charged area covering the particle surface) and pores of a loaded particle, is given by (McKay 1996, Bird et al 2002):

$$N_t = D_s \left[\frac{\partial^2 C_t}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right]$$

, where N_t is the diffusion rate and r the radius of the particle (or more precisely the length of the available micropores). This equation assumes a uniform concentration of the solution surrounding the particle.

2.2 Sorption

Sorption is defined as any process that transports solutes between the solution and the sorbent. It includes several different processes described in this chapter, ranging from adsorption to precipitation with falling strength. The sorption process is most often very difficult to determine for natural sorbents or industrial by-products, and therefore a number of models or isotherms can be derived instead. In general, for reactive filter technology, adsorption is preferred to precipitation. At low pH, precipitated metal ions can re-dissolve into the leachate.

2.2.1 Adsorption

Adsorption is a sorption process which transport solutes from the solution to the particle surface. The diffuse double layer (DDL) or boundary layer surrounding the particles in reactive filter substrates, is occupied by *counter-ions* (ions of opposite charge from the one in the diffuse layer). These ions can be replaced by ions from the effluent, for instance metal ions (Gustafsson et al, 2004). In this ion-exchange process, it is expected that the most strongly adsorbed ion will be the first to occupy the charged sites of the particles. When concentrations in the effluent increase, and the sorption process approaches equilibrium, competition for the sites occurs. Pb, Cu and Hg are strongly absorbing metals in soils, while Zn, Ni and Cd are weakly absorbed (Gustafsson et al, 2004).

According to Langmuir (1997), researchers have proved that the adsorption affinity of different metal cations to clay, hydrous oxides, organic matter, soil and sediment follow the Irving –Williams order (i.e. geochemical metal ion complex stability);



The suggested adsorption process involved in metal uptake to pine bark is ion exchange, with metal cations replacing adjacent hydroxyl groups, forming a chelate (Bailey et al 1999).

2.3 Sorption modelling

A model of the sorption process contains the following three parts (McKay 1996):

- Fluid dynamics (transport through porous media)
- The rate of adsorption (kinetics)
- The sorption affinity (i.e. the amount of sorbate required to remove a unit of solute from solution)

The first part has not been addressed in this thesis. It is however important to bear in mind that fluid dynamics, especially through unsaturated columns, can significantly affect the filtration efficiency. The dimensions of the system must be carefully designed in order to avoid clogging or channelling effects (Färm 2003, Rastas 2003).

Due to the complexity of the sorption process, chemical modelling of the processes is impossible with the knowledge we have today. Therefore, laboratory experiments can be conducted in order to find mathematical relationships for the process, even though many of the involved reactions are unknown. The equations used in sorption modelling describe pseudo-order-reactions. The advantage of pseudo-order modelling is the use of empirical data, which summarise a large number of chemical and electrical reactions that are largely unknown (Zhu and Anderson 2002).

The two empirical modelling approaches are determination of sorption equilibrium and sorption kinetics. Sorption equilibrium is determined in order to estimate the amount of one or more given substances and their forms at equilibrium. In modelling terms, this is the boundary

condition for a model. A kinetic model, on the other hand, defines the time required to reach equilibrium and the reaction positions along the way (Langmuir 1997).

2.3.1 Kinetics

Diffusion was discussed in the previous section. The diffusion rate and the potential distance of metal diffusion into the particles will together determine metal uptake by the materials. Adsorption kinetics are estimated experimentally by determining the time elapsed before a given amount of solute is removed from solution. The data are then presented as the effluent concentration as a function of time, giving an exponential function.

The study of sorption kinetics in filter materials in batch experiments has led to a distinction between rapid and slow sorption processes. Initially, the sorption mechanisms in reactive filters are rapid on particle surfaces. With time, the sorption mechanisms become slower. These reactions are attributed to intra-particle diffusion in macro- and micropores of mineral particles (Makris 2004). Uptake onto the surface once the solute has been transferred into the boundary layer or into the micropores (e.g. by sulphide complex binding or ion exchange, Lundström 2002) is a rapid process that can be ignored in kinetic modelling.

Färm (2003) investigated the metal sorption capacity of pine bark at various contact times (1-1000 s) and concentrations (0.1-10 mg/l). The results of this study showed that very rapid sorption processes were involved, with no effect of contact time. At low concentrations (0.1 mg/l), the longer contact times instead appeared to offer a possibility for the metals in the pine bark to leach from the material. From this, Färm (2003) concluded that sorption is very rapid and increased retention time is of minor importance

Jang et al (2005) assessed the kinetic model approach for Cu, Pb and Zn retention to three species of bark mulch, including pine bark. The experiment was set up as a batch test where the sorbent and solution were shaken for different times ranging from 1 to 360 minutes. Metal removal as a function of time was described with a first-order kinetics model:

$$\ln C_t = \ln C_i - kt$$

, where C_t (mg/l) is the concentration of metal ions in solution at time t (s), C_i is the initial concentration of metal ions and k (-) is the rate of adsorption to pine bark at 25 °C (Jang et al

2005). For the first 100 seconds, the model fitted well to a first-order equation. After 100 seconds, the uptake rate decreased and the model was not valid.

Chatterjee et al (1995) compared Ni sorption to various sorbents at different contact times. A close to linear relationship was found for all sorbents during the first 30 minutes. After 30 minutes the uptake rate decreased.

Intra-particle diffusion rate has been evaluated in a model describing sorption to pine sawdust (Özacar and Sengil 2005). The diffusion rate was described as;

$$q_t = k_i \cdot t^{1/2} + C$$

, where q_t is the amount of solute (i.e. metals) sorbed at equilibrium (mg g^{-1}) and k_i is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$). C gives information about the boundary layer. The higher the value of C , the thicker is the boundary layer (Acemioglu 2004). This diffusion model was shown to work well for Fe removal by pine bark (Acemioglu 2004). Sorption of dye to sawdust was described better by a pseudo-second-order kinetics model and it was concluded that the diffusion model did not accurately describe the sorption rate (Özacar and Sengil 2005). The pseudo-second-order approach was also studied by Acemioglu and Alma (2004) for Cu retention by sawdust, and by Ho and Ofomaja (2006) for Cu adsorption on palm kernel fibre. In the pseudo-second-order kinetic model, the kinetics was expressed as the change of the mass of adsorbed metal with time:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

, where k is the rate constant of sorption ($\text{dm}^3/\text{mg}\cdot\text{s}$), q_e (mg/g) is the amount of metal ions adsorbed at equilibrium and q_t (mg/g) is the amount of Cu ions adsorbed at time t (s) (Ho and McKay 2000).

2.3.2 Equilibrium isotherms

In any sorption model, knowledge about the capacity or affinity of the adsorbent for the solute is required. The boundary conditions of a model are calculated by establishing the maximum amount of metal ions that will be adsorbed and/or absorbed at equilibrium.

In terms of solute transport through and into micropores of particles, there exists an equilibrium state where the concentration in the micropores corresponds to the solution concentration. Kinetic studies have shown that this equilibrium is reached after a certain time that varies for different sorbents. The suggested time for pine bark was found to be 8 hours in an experiment carried out by Curkovic et al (2001), while Dimitrova and Mehandgiev (1998) assumed equilibrium after 5.5 hours in experiments on metal sorption to slag. However, the shaking procedure is most often carried out for 24-48 hours (Al-Asheh and Duvnjak 1997, Vázquez et al 1994), in an attempt to ensure that equilibrium is reached.

Apart from the isotherms discussed above, there are a series of mathematical expressions, e.g. NICA or Gaines-Thomas (Gustafsson et al 2004), Ideal Adsorbed Solution Theory (IAST) and Sips model (Al-Asheh et al 2000), that might be applicable to the study of sorption on reactive filter materials. However, there are only a few examples of the application of these models to low cost sorbents in the literature.

Langmuir adsorption isotherm

The Langmuir isotherm has been used by many researchers to model potential sorption of contaminants to particulate media such as soil. The isotherm was originally developed for sorption of gas and vapour onto particles (Dullien, 1979) and it has been found to give varying results when used for metal sorption onto particles in water treatment systems (Al-Asheh and Duvnjak 1998, Al-Asheh et al 2000, Jang 2005). This is further discussed in the conclusions chapter (see Chapter 5.1.2. – *Methodology development*). The Langmuir isotherm assumes a homogenous sorbent surface, and equally active sorption sites (Curkovic et al 2001). The Langmuir isotherm can be expressed as;

$$\frac{q}{Q} = \frac{bC}{1+bC}$$

, where C (mg/l) is the equilibrium adsorbate concentration, q (mg/g) is the mass of adsorbate concentration per mass of adsorbent at equilibrium and Q (mg/g) the maximum mass adsorbed at saturation conditions per mass unit of adsorbent. b (l/mg) is an empirical constant with units the inverse of concentration C . The Langmuir adsorption maximum (Q) is calculated from the slope obtained by plotting q against q/C . Q is the upper limit of q . Converting the Langmuir equation to a linear form allows the calculation of b and Q .

Freundlich adsorption isotherm

The Freundlich isotherm is based on an exponential distribution of sorption sites and energies (Curcovic et al 2001). It considers monolayer coverage and assumes a heterogeneous balance distribution of the sorption sites (Al-Asheh et al 2000). Dimitrova and Mehandgiev (1998) investigated Pb uptake to crystalline slag and found a linear relationship between the logarithmic concentration at equilibrium and solute uptake to the particles at equilibrium (mg/g), which confirmed that the sorption isotherms were of Freundlich type. No equilibrium constants were presented in the study. The Freundlich isotherm is given by:

$$q = KC^n$$

, where n (l/mg) the empirical constant with units of adverse of concentration, C . Some parameters, such as Ca-concentration or pH can have such a large influence on sorption that the isotherm would be too limited if they were not taken explicitly into account. An extension of the isotherm is described by;

$$q = KC^n + C^b$$

, where b can be pH or any other relevant parameter that is valid for the model. (Gustafsson et al, 2004).

Linear isotherms

Apart from the use of these isotherms, a linear relationship can be found between the rate of uptake and the concentration which can be described by a regression of the data. Using a linear sorption isotherm however requires accuracy in defining the boundary conditions for the model. Otherwise it can be misinterpreted as if the uptake to each mass unit of material

continues to increase without limits if the concentration in solution increases, which is physically impossible. It can be assumed that sorption affinity decreases and eventually the model will take the form of one of the equilibrium models described above. Linear isotherms were used by Färm (2003) and by Acemioglu and Alma (2004) to describe Cu sorption to pine sawdust.

2.4 Sorbents

2.4.1 Metal retaining materials

The theory and practical experience of the use of different porous materials as sorbents for removal of metals and P from polluted waters was described thoroughly in a recent literature review by Johansson Westholm and Färm (2004). Metal sorbing materials were divided into natural materials (biomass), marine materials, minerals and rocks, industrial waste products and agricultural by-products. The classification of materials by Johansson Westholm and Färm is presented in Table 2-1. Sawdust was considered as both natural biomass and industrial waste, but in this thesis it is classified as the latter. It should also be noted that not all material of biological origin is placed in the natural (biomass) group (see Table 2-1).

Table 2-1 Materials investigated for metal sorption capacity
(Johansson Westholm and Färm 2004)

<i>Natural (biomass)</i>	<i>Rocks and minerals</i>	<i>Industrial waste</i>	<i>Agricultural by-products</i>
Peat	Clays	Paper mill sludge	Agricultural waste
Barks	Zeolites	Paper industry waste	Peanut shells
Spruce wood, coal, cork	Coal	Blast furnace sludge	Olive mill residues
Fungal biomass	Polonite®	Electric furnace slag	Cassava waste
Cactus		Fly ashes	Maize starch
Cocoa shells		Activated sludge	Oat by-products
Juniper fibre		Sawdust	Agro-based fibres
Seaweed			Grape stalk fibres
Marine algae			Husk of black gram

2.4.2 *Blast furnace slag*

Blast furnace slag (BFS) is a by-product from steel manufacturing. This is an industry with a significant production worldwide and only in China, around 15 million tonnes of BFS is produced annually (Ling, 2004). In Sweden, 240 000 tonnes of slag is produced yearly by the steel industry in Oxelösund. The slag in this study was supplied by SSAB Merox AB.

When the slag exits the furnace it has a temperature of 1500 °C. The cooling procedure then determines whether the slag becomes crystalline or amorphous in its structure. The crystalline slag (BFS-C) resembles a slightly different form of natural species of rock consisting of mainly silica and lime. BFS-C is characterized by its low density, high friction as well as large insulation and cement properties. The crystalline structure is obtained by air cooling the slag when it is released from the furnace. Amorphous slag (BFS-A), on the other hand, is cooled rapidly in water basins to give a glassy-sandy solid property. Apart from this, the chemical composition is rather similar to BFS-C.

The chemical composition of the BFS produced by SSAB Merox AB is given in Table 2-2 and example of the physical properties in Table 2-3. Generally, steel by-products can vary depending on the manufacturing process and the raw product. For example, the slag studied by Dimitrova and Mehanjiev (1998) contained twice the amount of calcium and silicate and ten times less magnesium and sulphur than the slag in the present study. The iron content was however the same. Alkaline reactions and high Ca-solubility are known to be beneficial for metal removal. Another interesting application is the use of BFS for removal of P in solution. Johansson (1998) examined the removal efficiency of BFS and found that up to 90 % of P can be sorbed to the material under optimal conditions. P-removal has also been studied in a pilot-scale research project described by Nehrenheim et al (2006). The uptake rate in the pilot scale facility was not as high as in the laboratory. There were several reasons for this, including a high concentration of suspended solids and the presence of dissolved organic carbon (DOC).

Scanning Electron Microscopy (SEM) pictures of BFS-A, before and after treatment of municipal sewage water, were presented by Nehrenheim et al (2006). These pictures showed that after treatment with municipal sewage, the pore structure on the surface of the particles had decreased significantly. Rather similar pictures were presented by Feng et al (2004) of

Cu-saturated steel and iron slag. In both series of pictures one can observe a fuzzy layer of solute ions (P or Cu) on the particle surfaces.

Studies have shown that metals are sorbed efficiently by BFS. Among others, Kietlinska and Renman (2005) conducted an experiment to determine the metal retention capacity of filter substrates such as BFS-A. The removal efficiency of BFS-A was determined for Zn, Cu and Ni in columns (\emptyset 98 mm) fed with landfill leachate. The approximate flow rate was equivalent to 9 pore volumes each day and the total amount of leachate fed to the columns was approximately 300 l. It was found that more than 60 % (\pm 30) of Zn and Cu was removed. The equivalent figure for Ni was approximately 20 % (\pm 9).

Table 2-2 Examples of the chemical composition and pH of BFS-A and BFS-C and the metal content of pine bark (*Paper II*)

Element (mg/kg)	Crystalline BFS	Amorphous BFS	Pine bark
Ca	210000	210000	n.a.
Fe	2700	3600	n.a.
K	4200	4200	n.a.
Mg	105000	99500	n.a.
Na	3870	4000	n.a.
Si	159000	160000	n.a.
Al	68000	67000	n.a.
As	0.53	0.97	0.11
Ba	370	360	n.a.
Cd	0.019	0.015	0.6
Co	11	< 2	0.25
Cr	42	30	1.8
Cu	< 2	4.6	6
Hg	0.13	0.14	n.a.
Mn	4500	4200	n.a.
Ni	< 2	2.4	0.8
Pb	0.60	0.54	2.5
Sr	300	300	n.a.
S	10900	12900	n.a.
V	610	490	0.54
Zn	3.4	3.5	83

Table 2-3 Physical parameters of BFS-A and BFS-C (*Paper II*, Johansson 1998*)
and pine bark (*Paper II*)

Parameter	Crystalline BFS	Amorphous BFS	Pine bark
Density (g/cm ³)	1.2-1.61*	0.8-1.47*	0.6-0.9
Porosity (%)	40-58*	44-55	38-49
Hydraulic conductivity (m/day)	0.8-15.9	3.2-40.6	n.a.
Specific surface area (m ² /g)	0.5-0.7	n.a.	n.a.

2.4.3 Pine bark

Pine bark is a by-product from a global industry, namely manufacturing pulp and paper, cellulose and other woods products. The sorption mechanisms to pine bark are expected to differ from other materials, being mainly controlled by complexation with humic material on the sorption sites. Previous studies have investigated the use of pine bark to remove metals from solution (Al-Asheh and Duvnjak 1998) and from storm water run-off (Färm 2003, Jang et al 2005). An example of the metal content in pine bark is given in Table 2-2 (Färm 2003) and the physical parameters are given in Table 2-3. Pine bark has also been shown to remove phosphate ions from water. The maximum uptake was determined by Tshabalala et al (2004) to be 12.65 mg phosphate per gram pine bark.

SEM and Energy-Dispersive X-ray (EDX) can provide some information on the rate of diffusion into a sorbent. For example, Al-Alsheh and Duvnjak (1998) found that only a small fraction of the sorbed metal diffused into the particles of pine bark. Most of the metal ions sorbed on the cell wall of the bark.

Apart from heavy metals, pine bark has been investigated for its capacity to remove pentachlorophenol from industrial waste water (Bras et al 2005, Edgehill and Lu 1998) and uranium from aqueous systems (Freer et al 1989). Lindane and heptachlor adsorption to pine bark was studied by Ratola et al (2003) who found that the metal retention was 80.6 % and 93.6 % for lindane and heptachlor, respectively.

2.5 Landfill leachate

Landfill leachate arises when groundwater or precipitation percolates through a landfill. The composition of the leachate depends primarily upon the following parameters; the landfill content (i.e. the waste material and the degradation stage), the environment in and surrounding the landfill and the technique used to construct the landfill (Lagerkvist 2003). Generally speaking, the leachate is usually contaminated by organic material, nutrients and metals. The landfill content will be further described below.

The landfill environment (e.g. pH, moisture content, temperature and redox potential) influence, and in turn are influenced by, degradation in the landfill. Landfill degradation is divided into five phases; aerobic, acidogenic, methanogenic, oxidation and weathering (Lagerkvist 2003).

The age of the landfill exerts an important control on the character of the leachate, for two reasons. Firstly, the landfill changes with time and thereby the chemistry and microbiology changes. Secondly, landfilling has been modernised and together with the legislation of today, this means that landfills are characterised by a larger content of solids. In old landfills and to some extent also in landfills in use, organic material contributes to the majority of the contaminants in leachates. In the present study, metals were of primary concern in the weak leachate at Lilla Nyby.

Öman et al (2000b) studied the concentration of metals commonly occurring in Swedish landfill leachate. Based on this study, it was suggested that a series of metals (Al, Ag, As, Ba, Ca, Co, Cr, Cu, Fe, Hg, Ka, Mg, Mn, Na, Ni, Pb, S, Sb, V and Zn) should be analyzed frequently in order to characterize the toxicity of leachate (Öman et al 2000a). Based on a consideration of their environmental hazard, it is of specific interest to remove some of these metals (i.e. Cr, Cu, Ni, Pb and Zn) from the leachate stream at Lilla Nyby landfill, Eskilstuna.

Cr is a toxic metal which can bioaccumulate. It is common in two forms, Cr III and Cr VI, with the latter being more toxic. The acute toxicity of Cr III to green algae is 0.4 mg/l and to fish 67 mg/l. Cr VI, on the other hand, affects crustaceans at concentrations of only 20 µg/l. Cu is also considered to bioaccumulate. Cu affects algal growth in concentrations larger than 2 µg/l but the limit for drinking water in Sweden is 2 g/l (Öman et al 2000b). Pb occurs in

several forms, of which the organic complexes are more toxic. For some organisms, Ni is also acutely toxic. Toxicity, mobility and bioavailability is however dependent upon a series of factors, including pH, redox potential, ionic strength and the presence of organic substances. Pb concentration in leachate varies greatly in Sweden (Öman et al 2000b). In aquatic environments, Pb occurs in complexes or adsorbed to sediment or other particular matter. Therefore, the availability and toxicity of the metal depends on the degree of hardness and salt content in the leachate (Öman et al 2000b). Zn is an essential metal for most organisms. But the metal is still considered to be toxic to aquatic organisms. For example, acute effects have been shown for algae at concentrations of only 30 µg/l, which is less than the mean concentration in Swedish landfill leachates, and for crustaceans at 500 µg/l (Öman et al 2000b). Some typical leachate concentrations for the metals considered in this thesis, found in Sweden and internationally, are given in Table 2-4.

Table 2-4 Metal concentration in Swedish landfill leachates (Öman et al 2000b) and international examples (Lagerkvist 2003)

	Swedish mean (min-max)	International interval
Cu	22 (5.8-80)	4-1400
Cr	17 (1.5-45)	30-1600
Ni	30 (9.8-91)	20-2050
Zn	63 (16-340)	30-6700
Pb	4.9 (0-15)	8-1020

2.6 Experimental methods

Most experiments to date have been carried out in the laboratory, with the aim to determine the sorption capacity or metal retention capacity. The experimental methods, both laboratory and on-site, used by researchers studying the use of slag and pine bark as reactive filters are shown in Table 2-5. It is clear that the batch experiment is the dominant method used in sorption research. Small columns are defined as columns with $\text{Ø} < 0.1\text{m}$, while studies are classified as pilot scale, if larger columns are used or if it in some respects aims to test the possible functioning of a full-scale facility.

On-site experiments are here defined as those taking place at the discharge source. This means that all factors involved are assumed to be relevant in a full scale water treatment application. Parameters that might be relevant and different from the laboratory experiments described in the previous chapter are climate variations, operational problems and economic issues. If they are neglected, these practical issues may result in many years of wasted research. Examples of metal sorption studies carried out as on-site studies were described by Färm (2003).

Table 2-5 Experimental methods used by researchers examining slag (S) and pine bark (P).

Batch	Small columns	Pilot scale	Reference
P			Acemioglu (2004)
P			Al-Asheh and Duvnjak (1997)
			Al-Asheh and Duvnjak (1998)
P			Al-Asheh et al (2000)
S			Curcovic et al (2001)
	S		Deja (2002)
S			Dimitrova (1996)
S			Dimitrova and Mehangiev (1998)
			Dimitrova and Mehangiev (1999)
	S		Dimitrova (2002)
P		P*	Färm (2003)
S			Feng et al (2004)
P	P	P	Gaballah and Kilbertus (1998)
	P		Gloaguen and Morvan (1997)
P			Jang et al (2005)
	S*		Kietlinska and Renman (2005)
P			Montes (2003)
P			Özacar and Sengil (2005)
S	S		Smith (1996)
S	S		Smith (1998)
P		P	Vazquez et al (1994)

* Pilot studies performed using landfill leachate or storm water as metal solution

Table 2-6 Sorption variables for slag (S) and pine bark (P) examined by researchers

pH	Initial concentration	Equilibrium concentration	Contact time	Temperature	Other parameters	Reference
P	P	P	P			Al-Asheh and Duvnjak (1997)
P						Al-Asheh et al (2000)
S				S		Curcovic et al (2001)
S	S			S		Deja J, (2002)
S	S				sorbent concentration	Dimitrova (1996)
S	S	S				Dimitrova and Mehandgiev (1999)
S	S		S			Dimitrova and Mehandgiev (1999)
					thermal treatment of sorbent	Dimitrova and Mehandgiev (2001)
S					grain size, bed height	Dimitrova (2002)
P			P			Färm (2003)
S	S	S				Feng et al (2004)
P	P					Gaballah and Kilbertus (1998)
					sorbent ion competition, grain size	Gloaguen and Morvan (1997)
P		P	P			Jang et al (2005)
P			P		pre-treatment sorbent	Montes et al (2003)
S	S		S	S	concentration	Ortiz et al (2000)
S	S					Smith (1998)
S	S					Smith (1996)
P		P	P			Vazquez et al (1994)

2.6.1 Batch Experiments

The batch experiment approach, where the sorbent and solution are shaken together in flasks and parameters such as pH or sorbent concentration are varied systematically, was described by Catts and Langmuir (1986). A large number of laboratory batch experiments have been carried out by researchers all over the world (see Table 2-6) to investigate various sorbents and their metal retention properties. Contact time, pH, and sorbent and solute concentration are examples of batch variables that vary between the different studies. As can be seen in Table 2-6, the relationship between pH and rate of sorption has been examined by several researchers. Metal retention as a function of initial or equilibrium concentration has also been well investigated. However, some contradictions can be noted in the results obtained from different studies, and these are discussed in the following chapters.

Batch experiments were used in this thesis, despite their limitations. In the first experiment, described in *Paper II*, batch experiments were used to determine the contact time required to achieve maximum adsorption. By using the same approach as other researchers it is possible to compare the results to other studies using other sorbents. In the study presented in *Paper III*, the batch approach was used to give a first indication as to whether DOC would have a significant effect on the sorption process.

2.6.2 Column experiments

Few authors have investigated the retention of metals by filter substrate in small columns ($\emptyset < 0.1\text{m}$) in the laboratory (see Table 2-5). Kietlinska and Renman (2005) used columns of \emptyset 98 mm in an experiment, which aimed to determine metal retention capacity for several filter substrates, among them BFS-A. In this study, landfill leachate was used instead of metal solution, but it was transported to the laboratory where the experiment was carried out. The approximate flow rate was 9 pore volumes each day and the total amount of leachate fed to the columns was approximately 300 l. Gloaguen and Morvan (1997) performed a series of small scale column experiments to assess binding capacities to pine bark for the metals Pb, Zn, Cr, Fe and Cu. The columns used were \emptyset 20 mm and they were subjected to a downwards directed flow.

It is not clear why so many authors have chosen to perform batch experiments rather than column experiments. One reason could be the effects of tube walls on the retention process.

However, column experiments can be considered to yield more reliable data for future on-site applications than batch experiments.

2.6.3 *On-site experiments*

From this literature overview, it can be concluded that pilot experiments are very rare compared to laboratory batch tests. A large pilot-scale experiment was carried out by Färm (2003). The aim was to find the best sorbent for metal uptake from storm water runoff. Another pilot-scale experiment was carried out by Gaballah and Kilbertus (1998) in which the metal sorbing properties of both pre-treated and raw pine bark were investigated. Solutions could either be shaken or percolated through the bark in this semi-pilot plant, which was 500 l in size .

Only a few studies have reported the results of column and pilot scale experiments, compared to the number of published reports on batch experiments. To my knowledge, no studies have included the hydrological aspects of the filtration process. In a full-scale application, knowledge and understanding of the practical properties of the materials used can be crucial for the final outcome of the treatment. On-site experiments are the only way of determining whether the materials are reliable as sorbents for leachate treatment. Therefore, this approach was used in *Paper I*.

2.7 Conclusions from literature survey

The literature concerning reactive filter materials is extensive. Researchers all over the world have successfully identified various sorbent materials that are suitable for column filtration processes. Most of the research conducted has been rather similar, using either batch experiments or column studies. On the other hand, despite these similarities, the experimental conditions in the studies vary considerably, with respect to:

for batch experiments;

- contact time (i.e. shaking time)
- sorbent/solute ratio

for column studies;

- height and diameter of the columns
- column experiment design
- direction of flow (upwards or downwards)
- flow rate and retention time

and for all experiments;

- sampling procedures
- concentration of metal(s)
- starting procedures
- particle size distribution of sorbent and solute
- pH and other physical-chemical parameters

These differences make it too difficult to compare the sorbent materials. It also makes it impossible to validate research results by comparing with similar studies. An interesting continuation of the present research project would therefore be to develop and agree on a standardized batch experiment method for testing filter materials (see Further Research chapter 5.1).

Most of the experiments described above were summarized and quantified by calculating equilibrium isotherms, typically the Freundlich or Langmuir isotherm. Even if the modelling isotherms generate quantitative variables, the results say little about the usability of filter materials in a full scale application, for a number of reasons. Firstly, the equilibrium time is often set to between 24-48 hours, which is much longer than is possible on-site without having to sacrifice one of the main advantages of filter boxes, namely their low space requirements. Secondly, the experiments used to derive the isotherms were not carried out using standardized procedures. This can be elucidated by just glancing at their results, which vary by order of magnitudes. As mentioned above, the experiments vary considerably with respect to important parameters, such as grain size and the volumetric relationship between substrate, solution and metal concentrations in the solution. The final reason for questioning isotherm modelling as a method for assessing the retention capacity of filter materials is the

experimental procedure. Whereas laboratory experiments most often are performed by shaking flasks containing the metal solution with the filter substrate of interest, reactive filters in the field are constructed differently, as percolation boxes packed with a filter substrate. This is discussed further in the last chapter of the thesis, among the proposed topics for future work.

As a result of this literature review, the approach for the experiments presented in this thesis became clear. Laboratory results all point in the same direction – the materials have high potential for metal removal. The questions raised are for instance, do they work on-site and when do they not work?

3 MATERIALS AND METHODS

3.1 On-site column experiment

3.1.1 Lilla Nyby landfill

Lilla Nyby is the municipal landfill of Eskilstuna, Sweden. There are several leachate streams at the site, originating from different parts of the landfill. The main leachate stream was at the time treated in a high technology treatment facility on-site. However, another leachate stream, with smaller contaminant concentrations than in other streams at the site, was identified in an older part of the landfill. In the autumn 2004, the investigation of the leachate started with a screening of the low strength leachate (see Table 3-1). A series of five samples were collected during winter/spring of 2005. These samples were analysed for physical-chemical parameters, metals and some organic substances. In general, it was concluded that the leachate was rather weak and no environmentally hazardous, persistent, organic compounds were detected. In *Paper I*, the procedure and results of the screening are described more in detail.

Table 3-1 Physical and chemical characteristics of the untreated landfill leachate from the screening. Data is presented by means together min minimum and maximum values.

<i>Character of the leachate in the screening, n = 5</i>	
pH	7.3 (7.0-7.7)
el. cond mS/m)	1300 (600-1700)
COD (mg/l)	180 (16-520)
N-tot (mg/l)	16 (5.6-22)
P-tot (mg/l)	0.54 (0-2.0)
SS (mg/l)	57 (16-190)
SO ₄ (mg/l)	79 (31-120)
Cl (mg/l)	41 (22-52)
Cr (µg/l)	1.4 (0.72-2.7)
Cu (µg/l)	14.0 (6.1-33)
Zn (µg/l)	88 (33-260)
Pb (µg/l)	2.2 (0.17-8.1)
Ni (µg/l)	12 (4.7-16)

The leachate stream probably mixed with the groundwater since the concentrations of metals and especially other leachate contaminants were so small. The only pollutants in the leachate-groundwater stream were metals, especially Zn, Cu and Ni. The authorities in Eskilstuna conducted a parallel screening of the leachate and decided that some kind of treatment was required with regard to the metal content. The concentrations of metals measured during the monitoring period are given in Table 3-2. As can be noted in the table, the concentrations varied significantly, especially for Zn. The concentration was largest at the beginning of the study, and then decreased throughout the project period. One reason was that the water had been re-circulated back up on the landfill for a certain period before the study began. Another reason might be a decrease in percolation through the landfill in the summer, so that the groundwater/leachate ratio in the well was high.

Table 3-2 Leachate metal concentrations during the research period

Metal	Concentration in Leachate ($\mu\text{g/l}$), n=29
Pb	0-8.1
Zn	0.001-260
Cu	2.0-33
Ni	2.0-16

3.1.2 Column set up

Four columns were constructed from plastic tubes and filled with pine bark, BFS-A, BFS-C and inert sand. The column set-up is described in more detail in *Paper I*, which also includes a figure showing the basic principles underlying the column set-up. The sand column was used as a reference and assumed to have neither reactive nor intra-porosity properties.

The columns were installed in a pump house on-site (see Figure 3-1) at Lilla Nyby landfill. The leachate was pumped into a well under the building and from there into a small container with a volume of approximately one hundred litres. The columns were supplied with the leachate from below by using a volumetric pump with parallel tubes which ensured the same flow rate to each column. During the four months of operation, three different flow rates were tested, starting with a high flow rate which was gradually decreased.

Replicate samples were collected from the container and from the outlet of each column, twice or three times a week during the experimental period. All samples were analysed for metals and some physiochemical parameters in the laboratory. The toxicity of some samples before and after treatment was also assessed. This is described in more detail in *Paper I*.

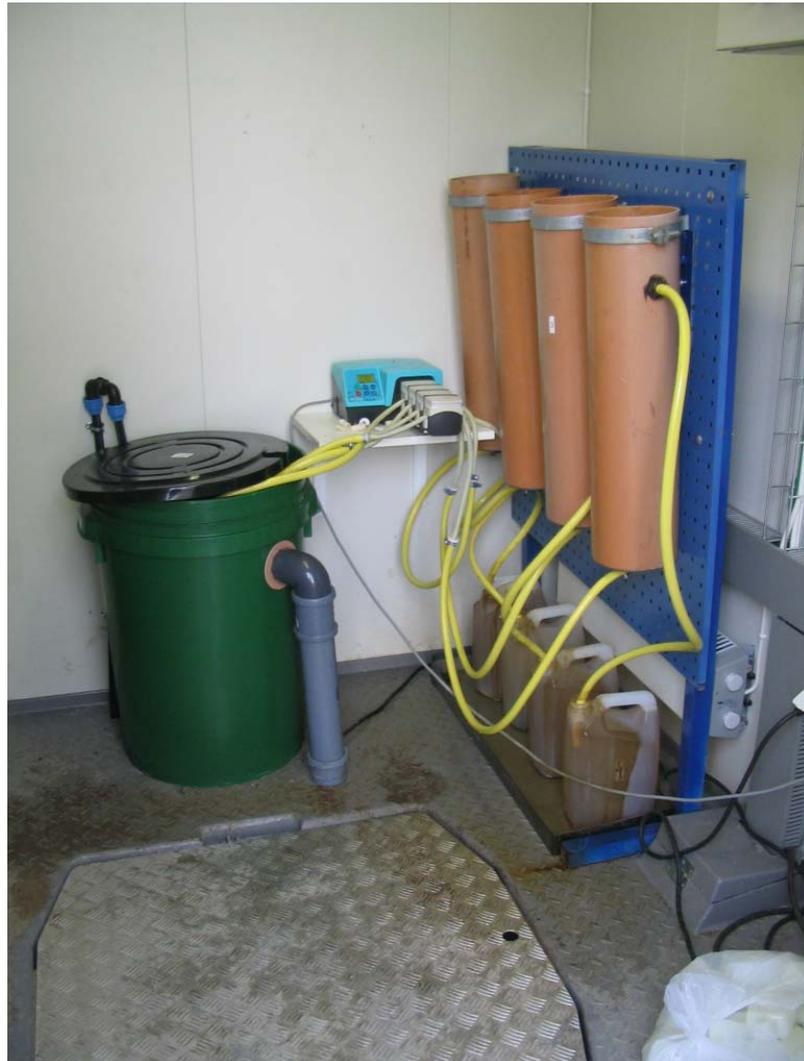


Figure 3-1 The columns in the pump house at Lilla Nyby landfill

3.2 Laboratory experiments

3.2.1 In general

Batch experiments have been carried out by research teams all over the world (see section 2-5). Nevertheless, it was considered necessary to complement this research in order to understand the processes involved in a full-scale application. Firstly, the materials used in this thesis were assumed to differ slightly from the materials tested in other parts of the world. Even batches from the same production plant can have different chemical or physical properties (see chapter 2.2.1 – *Blast furnace slag*). Secondly, the experimental design used in published studies varies significantly, which makes it difficult to compare results from one study to another. Three replicates flasks per treatment were used in all batch experiments reported in this thesis. The batch experiments were carried out to investigate the effects of different metal concentrations and shaking times (*Paper II*) as well as concentrations of DOC (*Paper III*). The percentage retention (R) in the material was calculated according to;

$$R = \frac{100 \cdot (C_i - C_t)}{C_i}$$

where C_i is the initial metal concentration in the solution and C_t the concentration in solution after shaking. The metals retained in the sorbent phase during the experiments were calculated according to the mass balance;

$$m(Q_e - Q_i) = V(C_i - C_e)$$

where m (g) is the sorbent mass, Q_e (mg/g) is the sorbed concentration of metal ion, Q_i (mg/g) is the initial metal ion concentration on the sorbent surface, C_e (mg/l) is the metal concentration remaining in solution and V is the solution volume.

3.2.2 Contact time

Paper II describes experiments to test the effects of contact time. Metal solutions were prepared containing larger concentrations of metals than are found in Swedish landfill leachate. Four different times were chosen from a logarithmic scale, 1-1000 seconds. The

flasks for shaking times of 1 and 10 seconds were shaken manually, whereas the remaining flasks were shaken mechanically (150 rpm).

In *Paper II*, the results from the batch experiments were fitted to kinetic models in order to describe the relationship between contact time and metal retention capacity. The results for the first 100 seconds of sorption fitted well to the first-order kinetic model described in section 2.3.1 – *Kinetics*. However, for the entire period examined (1-1000 s), a pseudo-second-order kinetic model gave a better description of the data. In the second-order kinetic model, the change in concentration with time was related to the dissolved concentration.

3.2.3 *Influence of DOC*

In the experiments on metal retention in pine bark at different concentrations of DOC, a simpler form of synthetic landfill leachate (SLL) was prepared from salts and metals commonly present in landfill leachate (see *Paper III* for details on the SLL). The metal concentrations were chosen in accordance with average leachate concentrations found in a survey of 14 landfills conducted by the Swedish Environmental Protection Agency (Öman et al 2000a). In this batch experiment, the pine bark was rinsed with deionised water by shaking (150 rpm) for 10 hours in order to reduce easily soluble organic compounds, which otherwise could have affected the results.

4 RESULTS AND DISCUSSION

4.1 Lilla Nyby on-site experiment

Three out of the four columns installed at the landfill did not remove metals to any significant extent; the sand column and the two slag columns. The pine bark column showed variations in sorption rate during the period, but its potential as a metal sorbent was promising compared to the other materials (see *Paper I*). The pine bark column did not reduce Zn and Cu concentrations under high flow rates. One reason may be that the contact time was not long enough for metal diffusion from the solution to the particle surfaces. The flow rate through the columns during the first experimental period was rather large, which resulted in a short retention time (c. 10 minutes). During this period, desorption of metals occurred, resulting in larger concentrations at the outlet than at the inlet. The uptake to pine bark appeared to stabilize when the flow rate was decreased to double the retention time (see Figure 4-1) and finally, as the flow rate was decreased again, the uptake of Zn, and to some extent also Cu, was significantly improved. Ni uptake was less than 20 % during the entire period. These results correspond well to the Irving-Williams order presented in chapter 2.2.1 – *Adsorption*.

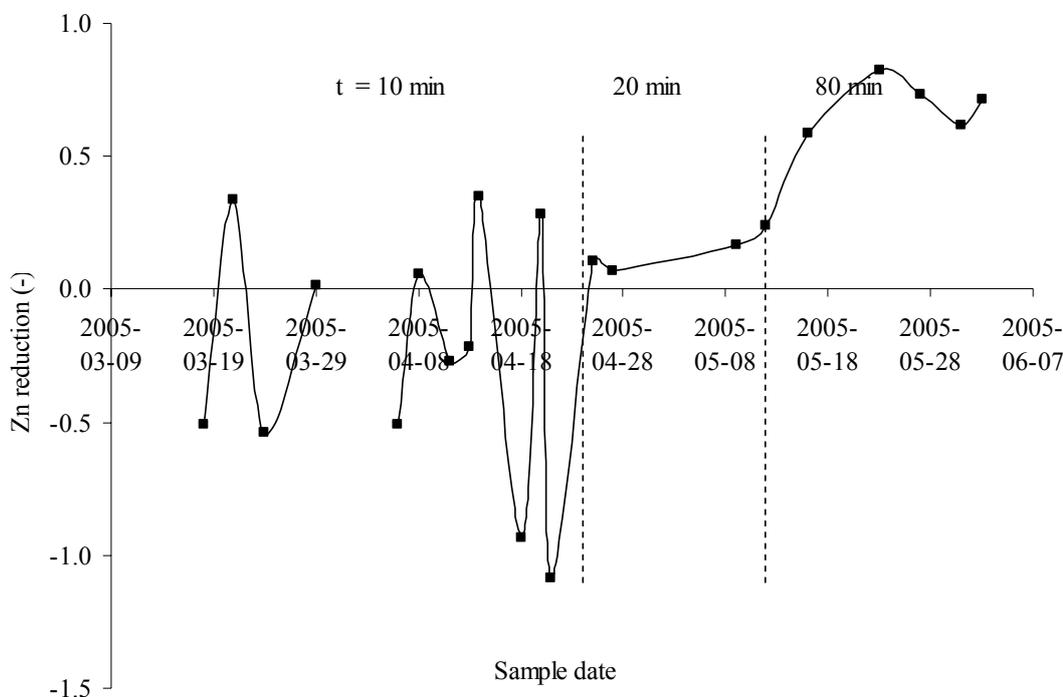


Figure 4-1 Retention of Zn on different sampling occasions during the column study at Lilla Nyby landfill. The dotted lines mark the days when the flow rate changed.

4.1.1 Leaching of organic compounds from the pine bark column

No discoloration could be observed after filtration through any of the four columns. Other researchers (Bailey et al. 1999 and Vázquez et al. 1994) have concluded that pine bark might be an unsuitable sorbent for storm water and landfill leachate, due to its release of soluble organic compounds that might be hazardous in the environment (e.g. phenols). Therefore, some of the samples from the pine bark outlet sample battery, were chosen randomly on seven different sampling occasions, and were analysed with regard to chemical oxygen demand, COD. COD is assumed to give an indication of the total content of organic substances in the wastewater. No significant change of the concentration of organic substances measurable by COD was detected (see Figure 4-2). Additional data collected from another pine bark filter, showed similar results, except that COD increased directly after start-up. Samples from this experiment (a large filter tank at Lilla Nyby landfill) were analysed for COD during the first two weeks after set-up but not later (Magnus Jacobsson, unpublished data). Thus, phenols might leach from pine bark, but this is only expected during a short period after start-up.

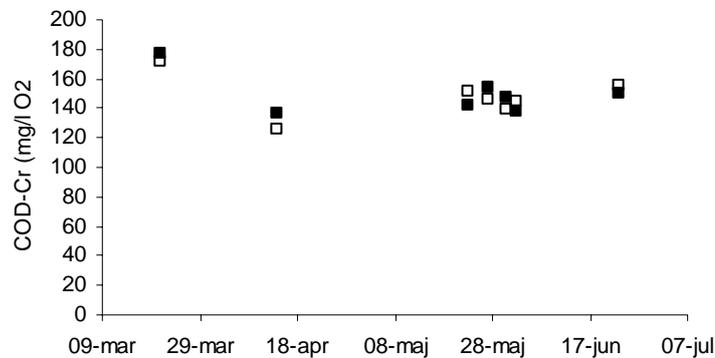


Figure 4-2 COD concentrations in samples from the inlet (□) and the outlet (■) of the pine bark column at Lilla Nyby

4.2 Laboratory experiments

4.2.1 Contact time

One alternative to measuring equilibrium isotherms is to determine the time elapsed for a metal ion to move from the solution to the surface of the substrate particle. In *Paper II*, the experimental results were interpreted with a second-order kinetic model for the five metal ions; Zn, Cu, Ni, Pb and Cr. An example of a model fit is displayed below (see Figure 4-3).

From the laboratory batch experiment presented in *Paper II*, it was found that all three materials could sorb the metals effectively. At initial concentrations varying between 2 and 20 mg/l, all three materials tested retained up to 100 % of the metal ions in solution, given no disturbance and sufficient shaking time.

In the laboratory experiment, the contact time was the same as the shaking time of the flasks, equal to the time each water unit was in contact with any of the substrate particles. In a percolation column, the same contact time can easily be achieved by calculating the time elapsed when each water unit passes through the column. However, the flow through a column differs significantly from the turbulent flow of a liquid in a shaken flask. It is therefore easier to optimize metal sorption in batch experiments than in a column. For instance, there might be a risk that some fraction of the material in a column will never come into contact with the metals in solution, since the flow is unidirectional (downwards or upwards). At large flow rates, vertical convective transport through the column may dominate the forces of diffusion. Another problem that might occur in a column is the formation of channel flows in the material, which allows the solution to pass through without being filtered. The batch method is, however, applicable if the purpose is to compare the material to other filter materials already tested in the literature. It also gives a good indication of sorption potential and, from a practical point of view, allows large experimental set-ups.

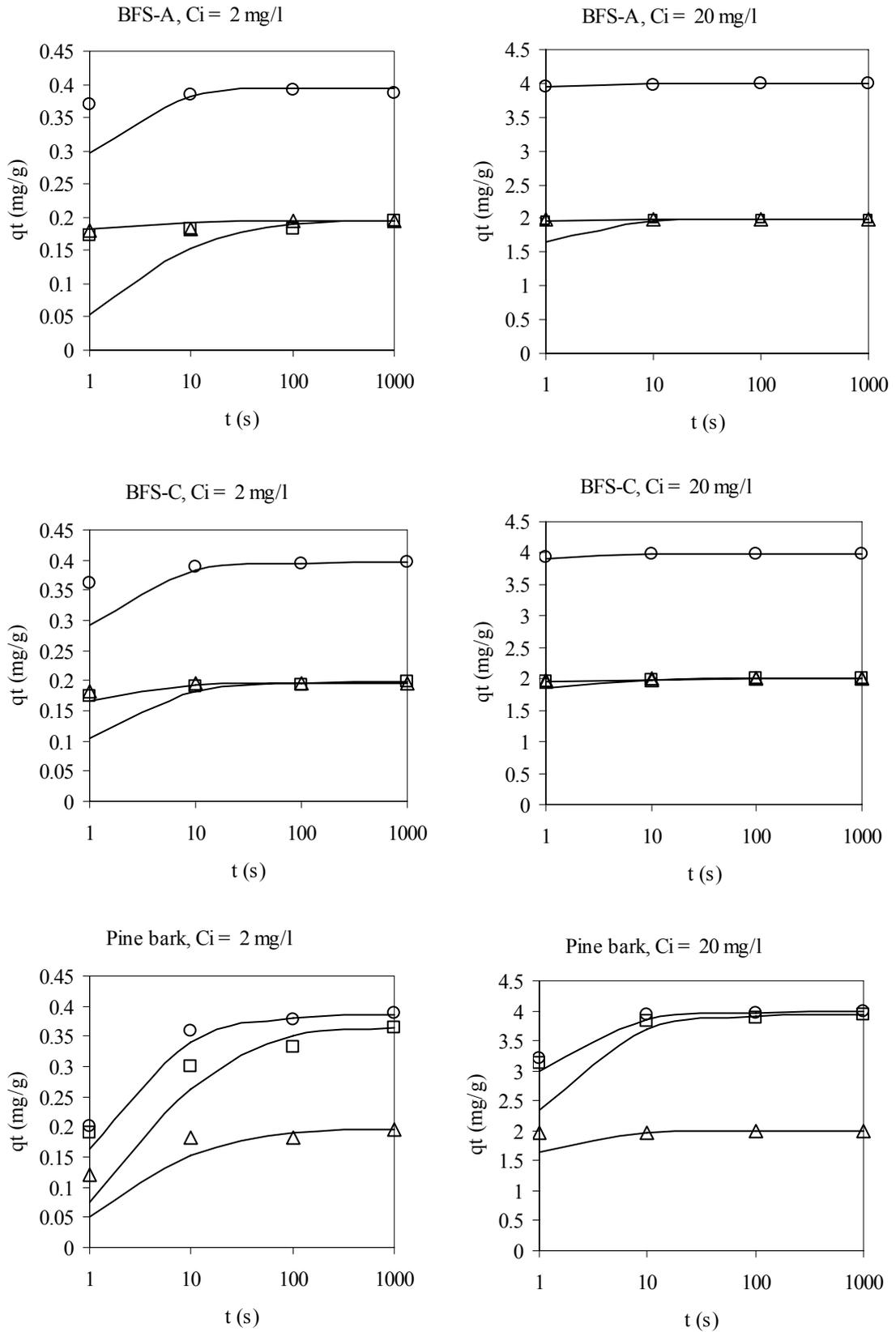


Figure 4-3 Pseudo-second-order model (curves) and data (symbols) describing metal uptake to the sorbent materials (mg/g). The metals in the model are; Pb (Δ), Zn (\circ) and Cu (\square) and the initial concentrations are 2 and 20 mg/l.

4.2.2 Dissolved organic carbon, DOC

An experiment was conducted on the effects of organic material on metal retention using a solution similar to leachate, by adding humic acid and salts. It was found that the influence of dissolved organic carbon on Cu, Cr and Ni sorption to pine bark, was significant and that the sorption potential to pine bark decreased with increased inlet concentration (see Figure 4-4, and *Paper III*). Therefore, the presence of dissolved organic carbon is believed to be one of the reasons for a low uptake of metals in the column experiment at Lilla Nyby Landfill. Unfortunately, DOC was not analysed in the leachate. The concentration of COD was however determined and found to be present in significant concentrations (see Figure 4-2). It can be argued that the experiment with DOC present gives more reliable information on the possibilities of leachate treatment than with metal solutions, since the solution composition was more similar to landfill leachate than the metal solutions traditionally used (see Chapter 2). Low metal retention could also partly depend upon the low concentrations of metals in the solution, compared to metal solutions used in batch experiments in previous research. It can perhaps be argued that the combination of high organic content and low concentration of metals, makes landfill leachate difficult to treat only with low cost sorbents.

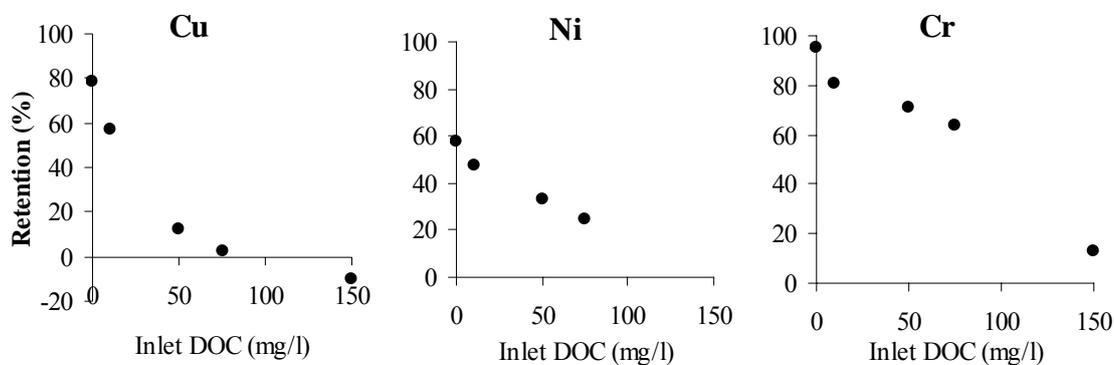


Figure 4-4 Percentage retention of Cu, Ni and Cr, plotted against the DOC concentration in solution.

4.2.3 Leaching of organic substances from pine bark

In the previous section, which described the results from the on-site study at Lilla Nyby landfill, the determination of COD leaching from the pine bark column was described. The detection of DOC gives another measure of the content of organic substances in a water solution. In the experiment presented in *Paper I*, the concentrations of DOC were measured before and after shaking with pine bark. The results from the study (see Figure 4-5) showed that the DOC concentration in the synthetic landfill leachate increased after shaking, especially when the DOC concentration was low before shaking. However, since the results from Lilla Nyby showed no leaching of COD under long-term operation, the relevance of the results from short-term shaking experiments can be questioned.

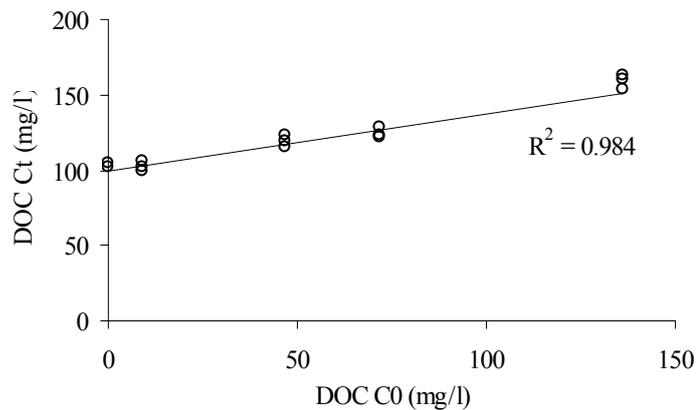


Figure 4-5 DOC leaching analysis results from the batch experiments. The graph shows outlet DOC concentration after shaking plotted against the inlet DOC concentration in solution.

5 CONCLUSIONS

The laboratory experiments confirmed the results of previous studies that showed that BFS-A, BFS-C and pine bark, have a high potential for metal retention. The field experiment, however, showed a smaller percentage uptake of the metal concentration in the solution/landfill leachate. From a comparison of the on-site column study and the laboratory experiments, it can be concluded that many questions still remain to be answered before this method can be recommended for treatment of landfill leachate. On the other hand, other polluted waters (e.g. storm water or waste water from industrial processes), which contain a more homogenous matrix of compounds, could be successfully treated with the reactive filter method. These possibilities will be discussed later in the chapter (see Further studies – *5.1.1 Technology development*).

The following possibilities and advantages were found with the technique:

- At small or varying concentrations of metals, pine bark appears to be a more reliable sorbent than blast furnace slag. According to the laboratory results, the slags might be more effective in retaining metals from solutions with large concentrations.
- Pine bark may retain metals even at small inlet concentrations
- Contact time is an important parameter, for all three materials. Sorption rates showed a good fit to a second-order kinetic model. This implies that metal removal efficiency could be enhanced by reducing the flow rate
- During an initial period of filtration through pine bark there is a risk of increased COD in the outlet water. This risk appeared to decrease after a short time.

Apart from the conclusions mentioned above, the following problems were found:

- Using blast furnace slag as sorbents for metal retention requires a continuous sampling programme due to the high risk of metal leaching at low concentrations
- Dissolved organic carbon (DOC) play an important role in inhibiting the sorption of heavy metals to filter substrate surfaces.

5.1 Further studies

5.1.1 *Technology development*

Since the results from batch and column experiments presented in this thesis differ significantly, it would be interesting to explore a new technique in reactive filter research. The batch experiments are conducted by shaking a small amount of filter material together with the metal solution or waste water. Results from these studies are often very promising and it is not unusual to achieve a metal retention close to 100 % in these experiments. Therefore, it would be very interesting to up-scale a batch experiment. By using the same proportions of materials and wastewater, a batch-type sorption process would be constructed. This technique would require waste water storage and a suitable site.

In agreement with the scope and objectives of the thesis work, the particle size was not manipulated. However, another design-related research task is to identify the grain size and shape that optimizes sorption, by maximizing the specific surface for metal ions to attach, and at the same time optimizing the fluid dynamic in the columns (e.g. avoiding problems with clogging and decreased hydraulic conductivity with time). Grain size distribution is important because the smaller the particles the larger the specific surface which in turn gives a larger area for the metals to be attracted. The particle form can also be assumed to play an important role as well as surface roughness and intra particle porosity. These parameters are however rarely investigated and this should be an important factor in future research work. According to Langmuir (1997), particles less than about 1 μm (1 cm^4) have a significant percentage of their atoms on their particle surface. This gives them particle properties associated with an extremely high sorption capacity. The explanation of this is their unsatisfied surface charge which is related to their colloidal behaviour. This argues for an evaluation of finer-grained materials. By using a fluidised reactor technique, described above, clogging can still be avoided.

As mentioned also in the conclusions chapter, other polluted water could potentially be treated with the reactive filter technique. The problem identified in this thesis was the presence of competing substances, especially DOC, which reduced sorption affinity. Industrial wastewater may contain only one pollutant (e.g. a metal or any other substance found in the process), which can be successfully captured in a filter.

5.1.2 Methodology development

Many materials have been evaluated to determine their metal-retaining capacity. There is a great need for simple methods focusing on the use of by-products, especially in developing countries. It is therefore likely that more materials than those studied in this thesis will be tested, both in laboratory experiments and on-site.

As described above, there is a great need for a common method for batch and column studies. A standardized method would certainly help researchers in experimental design and comparisons between materials and their application. This was also suggested by Johansson Westholm (2006) and *Ádám* (2006). In a standardized method, parameters influencing sorption (e.g. pH, grain size and solution/solute ratio), would be given and the procedure described.

5.1.3 Model development

In the theory chapter (see Chapter 2) many different types of models were discussed. There are software programmes available that model flow through porous media. It would be possible to adapt these programmes to fit the processes involved in leachate treatment by filter columns. This might make it possible to predict treatment performance in the filter substrate. There are however many questions to answer by experimental work before a valid model can be built. An interesting approach to modelling sorption kinetics would be to describe the kinetics in continuous processes (e.g. by using columns).

Another modelling approach that would help the future development of filter technology, is the use of chemical modelling in combination with fluid dynamics modelling.

5.1.4 Experimental work

Concerning laboratory experiments, it would be interesting to further investigate the relationship between presence of DOC and metal sorption to pine bark. Both the experimental work and modelling using Visual Minteq gave interesting results that are significant for the choice of material for treatment of landfill leachate.

The phenomenon of competing metal ions was only touched upon in this thesis (see Results and discussion – Competing metal ions). The effect was less than expected, but Cu appeared

to be more affected than Zn and Pb. To further investigate the effect of competing ions an extensive research set-up would have to be designed with two specific main outlines;

- adding other metal ions likely to be found in landfill leachate or storm water run off
- increasing concentrations of all the metal ions gradually to explore which ions will first be excluded from the sorption process.

5.1.5 Solutions for Lilla Nyby landfill

A full-scale test of the filter technique at the landfill site could be possible by taking account of the knowledge gained from this study. The suggestion would be to use pine bark as a sorbent, but with a dispersion layer of coarse sand both in the bottom and the top of the filter/column. By doing so, some of the organic material might be removed before filtrating the leachate through the reactive part of the filter. At the landfill, there is another leachate stream that ends up in a pond. This leachate has a higher metal content and pH which might imply a better chance of achieving good results. The stream will however need additional treatment due to its high content of organic substances (Nehrenheim 2006, unpublished data).

5.1.6 Potential for used sorbents

One important task in developing new techniques for metal retention using filter substrates is to find out how to treat the used sorbents when they are saturated with metal ions. Pine bark is a natural fibre, commonly used in municipal power plants in Sweden. Used pine bark could be sent to the plants, using a model for the mass balance of the metal ion to calculate the maximum metal ion concentration that would fulfil the allowable limit values of the ashes. Using this method it would be possible to bring important trace metals to the forest. A known problem in using biofuel for energy production is *fouling*, that is the formation of alkaline corrosive layers on the super-heater surfaces inside the boiler. This phenomenon is specific for biofuels due to reactivity in the organic or ion forms of K, Na, Ca, Mg, S, Cl, P and H₂O (Widarsson et al 2004). Many of these are easily exchangeable positive ions which can be replaced by metal ions. Further research can reveal if it is possible to reduce fouling problems by replacing fouling related ions with other metal ions.

5.2 Final words

Research on low cost sorbents for treatment of landfill leachate, storm water runoff and other potential applications has just begun. Many promising results have been published, especially concerning the metal retaining capacity determined in batch experiments. Now that we know the potential and the advantages, we must also address the problems. What can we do with used materials? How can we optimize the treatments on-site? What are the limitations with the technique? Interesting enough, the reactive filter technology for P removal from single household sewage has come a long way. Nowadays, authorities in Sweden recommend the use of P-sorbing materials as an alternative to sand. With more knowledge and research, reactive filter technology can also become the preferred treatment for landfill leachate.

My overall conclusion is that more field experiments must be conducted, for longer periods and with different types of effluents. The research presented in Chapter 2 (Table 2-6), describing experimental approaches, must be more balanced between laboratory experiments and full-scale approaches. By taking one step forward, finding applications for each of the low cost sorbents, we can also start treating weakly contaminated effluents at low cost. And we would also find new applications for many residual waste products from industry.

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