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the Built Environment

**ON-SITE WASTEWATER
TREATMENT – POLONITE AND
OTHER FILTER MATERIALS FOR
REMOVAL OF METALS, NITROGEN
AND PHOSPHORUS**

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Photo on cover: Interior view of the filter well Biop[®], using Polonite[®] as reactive material, for treatment of domestic wastewater.

PREFACE AND ACKNOWLEDGEMENTS

This thesis was produced as part of the requirements for a doctoral degree at the Royal Institute of Technology, Stockholm.

My Master's degree (in Engineering) is from Warsaw Agricultural University (SGGW), where my interest for ecotechnology began. Thanks to scholarships from the Swedish Institute I was able to join the ecotechnological research programme, which was established by Assoc. Prof. Gunno Renman in joint cooperation with my home university. During the first years I performed research together with Dr Lena Johansson Westholm until she graduated with a PhD in 1998. I also had the opportunity to work with my friends from SGGW, Dr Joanna Kwapisz and Dr Agnieszka Karczmarczyk. In 2001 I finally had the possibility to start my PhD studies at KTH.

This study was conducted in close cooperation with companies: Telge Återvinning AB, Hubbinettes Prefab AB and Biotech AB. In the very beginning of this research in which I assisted, I also had good cooperation with NCC AB. This latter contact has continued through Mr Magnus Alfredsson, who organised the preparation of the first generation of Polonite® for my experiments, and later on through Mr Claes Thilander, Biotech AB.

I would like to thank my advisor, Professor Per-Erik Jansson, for his support, especially in the last phase of thesis preparation. Secondly, I would like to thank Assoc. Prof. Jon Petter Gustafsson, Assoc. Prof. Lars Hylander and Assoc. Prof. Gunno Renman for their help, valuable advice, discussions and comments on manuscripts. Prof. Dr hab. Zygmunt Brogowski and Prof. Dr hab. Józef Mosiej from SGGW are acknowledged for challenging me and thus improving my work. I am also especially grateful to Engineer Bertil Nilsson and Research Engineer Monica Löwén for discussions and technical support in the laboratory. I wish to thank all my colleagues at the Department of Land and Water Resources Engineering for the enjoyable atmosphere. I thank Mr Börje Öhrvall and Mr Gustaf Persson, Viksta By, for their great help with the field-scale experiments and nice "fika" events in their houses. Many thanks are due to Dr Mary McAfee for revision of the English in this thesis.

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The deepest and warmest gratitude goes to my family, who have always supported and encouraged me along my way. I especially want to send my deepest love to my Mother, who is no longer with us, for being so very important to me. Thank you for everything.

Stockholm, May 2008

Agnieszka Renman

SAMMANFATTNING

Småskalig, lokal rening av avloppsvatten – Polonite och andra filtermaterial för avskiljning av metaller, kväve och fosfor

Infiltration, markbäddar och konstruerade våtmarker har länge varit en förhärskande teknik att rena avloppsvatten som genereras från enskilda hushåll. Dagvatten och lakvatten renas också ofta på motsvarande sätt.

I denna avhandling har en ny typ av reningsteknik undersökts som innebär att avloppsvatten aktivt filtreras genom kemiskt reaktiva material. Dessa kan omvandla eller binda ämnen så att de inte blir skadliga i miljön, t ex ammoniumkväve blir kvävgas eller binds genom jonbyte till materialet.

Sammanlagt filtermaterial undersöktes varav de viktigaste är restprodukten masungsslagg, Nordkalk Filtra P, Polonite[®] och wollastonite. Materialens förmåga att avskilja fosfor, kväve och metaller har studerats genom kolonn- och fullskaleförsök i långa tidsserier. Mekanismer för fosfors och metallernas fastläggning har också klarlagts genom skakförsök och kemisk modellering. Avloppsvatten härrörande från kommunalt nät och enskilda hushåll och lakvatten från avfallsdeponi har använts vid de experimentella försöken. Dessutom har ett konstgjort avloppsvatten med enbart oorganisk fosfor och kväve utnyttjats vid ett kolonnförsök.

Resultaten från skak- och kolonnförsöken med konstgjort avloppsvatten visade att Nordkalk Filtra P och Polonite är bra filtermaterial för avskiljning av fosfatfosfor. Långtidsförsök med Polonite i en patenterad typ av filterbrunn visade att detta material fungerar i praktisk tillämpning och binder fosfor så att godkända utsläppsvärden erhålls i renat vatten (reningsgrad < 90%; utgående genomsnittlig fosfor koncentration < 1 mg/l). Polonite i filterbrunnar ska bytas efter intervall som bestäms av den belastning som filtret utsatts för. Materialåtgången uppskattas till minst 1-2 kg Polonite (fraktion 2-5 mm) för varje renad kubikmeter avloppsvatten i optimerade system. De studerade reaktiva filtermaterialen är mindre lämpliga för avskiljning av kväve. I småskaliga reningssystem krävs kompletterande enheter som svarar för detta.

Kunskap som erhöles från skak- och krukförsök visade att den bundna fosfor i filtermaterialen är tillgängliga för växter eftersom den till viss del förelåg som kalciumfosfater. Samtidigt visade delstudier att metaller i avloppsvatten binds till filtermaterialen. Koncentrationerna var dock mycket låga i förhållande till vad som är godkänt i slam för spridning på åkermark. Det betyder att filtermaterial kan återföras till växtodling men fler undersökningar krävs för att en mer allmängiltig slutsats ska kunna dras.

De reaktiva materialens metallavskiljande förmåga kan utnyttjas avsiktligt i andra reningssammanhang, nämligen vid filtrering av lakvatten och dagvatten. Masungsslaggen släppte vissa metaller t ex mangan till vattenfasen vilket är en nackdel.

Fortsatt forskning krävs så att den reaktiva filterbäddstekniken kan förfinas och appliceras i större skala och omfattning.

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LIST OF PAPERS

This thesis is based on a summary of the following six articles, which are referred to throughout the text, by their Roman numerals. The two first papers are published under my former surname of Kietlińska.

- I. **Kietlińska, A.**, Renman, G., 2005. An evaluation of reactive filter media for treating landfill leachate. *Chemosphere* 61: 933-940.

The author was responsible for planning and conducting column experiment and wrote most of the manuscript in co-operation with the second author.

- II. Hylander, L.D., **Kietlińska, A.**, Renman, G., Simán, G., 2006. Phosphorus retention in filter materials for wastewater treatment and its subsequent suitability for plant production. *Bioresource Technology* 97: 914-921.

The author was responsible for conducting the study at laboratory (except pot experiment) and writing the paper.

- III. Gustafsson, J.P., **Renman, A.**, Renman, G., Poll, K., 2007. Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment. *Water Research* 42(1): 189-197.

The author's contribution was to conduct the experiment, make laboratory analyses and, write part of the paper.

- IV. **Renman, A.**, Hylander, L.D., Renman, G., 2008. Transformation and removal of nitrogen in reactive bed filter materials designed for on-site wastewater treatment. *Ecological Engineering*, (submitted).

The author's contribution was to conduct the analyses at laboratory and write the paper in co-operation with the other authors.

- V. **Renman, A.**, Renman, G., Gustafsson, J.P., Hylander, L. D., 2008. Metal removal by filter materials used in domestic wastewater treatment. *Journal of Hazardous Materials*, (submitted).

The author's contribution was the same as in paper I and IV.

- VI. **Renman, A.**, Renman, G., 2008. Phosphorus removal by Polonite[®] from wastewater column experiments and a compact bed filter trial. Manuscript.

The author's contribution was to make all laboratory work, work up the material and, write the first version of the paper.

Reprints are published with the kind permission of the journals concerned, and the papers are appended at the end of the thesis.

ABSTRACT

Bed filters using reactive materials are an emerging technology for on-site wastewater treatment. Chemical reactions transfer contaminants from the aqueous to the solid phase. Phosphorus is removed from domestic wastewater by sorption to filter materials, which can then be recycled to agriculture as fertilisers and soil amendments. This thesis presents long-term column and field-scale studies of nine filter materials, particularly the novel product Polonite®. Phosphorus, nitrogen and metals were removed by the mineral-based materials to varying degrees. Polonite and Nordkalk Filtra P demonstrated the largest phosphorus removal capacity, maintaining a PO₄-P removal efficiency of >95%. Analysis of filter bed layers in columns with downward wastewater flow, showed that phosphorus, carbon and nitrogen content was vertically distributed, with decreasing values from surface to base layer. Polonite and Filtra P accumulated 1.9-19 g P kg⁻¹. Nitrogen in wastewater was scarcely removed by the alkaline filter materials, but transformation from NH₄-N to NO₃-N was >90%. Pot experiments with barley (*Hordeum vulgare* L.) revealed that after wastewater treatment, slags and Polonite could increase plant production. Batch experiments and ATR-FTIR investigations indicated that amorphous tricalcium phosphate (ATCP) was formed in the materials, so some of the accumulated PO₄-P was readily available to plants. Low heavy metal contents occurred in the materials, showing that they can be applied as soil amendments in agriculture without contamination risks. A full-scale treatment system using Polonite as filter material showed an average PO₄-P removal efficiency of 89% for a 92-week period, indicating the robustness of the filter bed technology.

Key words: alkaline materials; heavy metals; mechanisms; nutrient removal; sorption; speciation modelling

INTRODUCTION

Background

This thesis deals with the use of reactive bed filters for on-site treatment of wastewater. The focus is on ecological engineering systems that are more environmentally friendly than many systems based on traditional techniques, as they usually require little or no input of chemicals and electric energy for the process (Mitsch & Jørgensen, 1989; Jenssen, 1996). They are also characterised as more cost-effective in the long run. These properties are beneficial for developing ecotechnological treatment processes as an interesting alternative to on-site wastewater treatment, urban stormwater and landfill leachate. However, in some cases advanced and expensive treatment systems (Renou *et al.*, 2008) have to be used together with ecotechnological systems to meet treatment goals.

There is a reason to raise the level of ambition when it comes to the domestic wastewa-

ter treatment of the close to one million on-site wastewater treatment facilities in Sweden. Such facilities in sparsely populated rural areas are responsible for considerable discharges of phosphorus (P) to lakes, rivers and streams. About 40% of these systems are considered unacceptable by the Swedish Environmental Protection Agency (SEPA). The situation in other countries surrounding the Baltic Sea is, for instance, the same or even worse. On a global scale the sanitation problem in rural areas of developing countries is large and the need for sustainable technical solutions is urgent (WHO & UNICEF, 2006). During many years, different technologies have been tested that may improve the P removal efficiency in private wastewater treatment systems (Crites & Tchobanoglous, 1998) This development is likely to accelerate because of the new requirements for small-scale wastewater treatment (less than 25 person equivalents connected) issued by SEPA, according to which 70-90% of total P should be removed.

In Sweden, the general recommendation has been to construct a soil infiltration system or sand-filter system after the septic tank. However, such systems have often shown poor P removal efficiency. A set of new or upgraded technologies for on-site treatment was recently tested in Sweden, including e.g. package treatment plants, chemical precipitation in combination with large sand filters (Hellström & Jonsson, 2006). All systems installed by the manufacturing companies showed good performance during the project period, partly as a result of regular monitoring and maintenance. Many other different on-site solutions have been launched, such as constructed wetlands and compact filter systems. The latter group includes the Filtralite system, comprising a biofilter consisting of coarse expanded clay aggregates (LWA) and a bed filter with Filtralite P[®]. This technology, developed in Norway, has proven very effective for most treatment parameters except nitrogen and has a long P-retention lifetime (Heistad *et al.*, 2006). The newest generation of Filtralite P has proven interesting for reuse as a P-fertiliser in agriculture, although to date only on the basis of results from pot experiments (Nyholm *et al.*, 2005).

Novel compact filter systems for on-site wastewater treatment, similar to that introduced in Norway, have been developed and launched in Sweden. Reactive filter materials are increasingly used in these systems and such materials are also of interest for producers of other treatment systems, see for example the Swedish website (www.avloppsguiden.se/ent_pro/ent_pro_fil_ter.htm). The filter materials can for instance be used in filter wells as a post-treatment step to reduce excessive effluent P concentrations. On-site treatment is not only of concern for domestic wastewater, but can also be applied for treatment of leachate emanating from landfills or for treatment of urban stormwater (Kietlińska, 2004; Hallberg, 2007). Treatment of these highly polluting wastewaters is becoming mandatory world-wide. Discharge to a municipal sewage treatment plant is often difficult and expensive since the landfill and the sewage plant are not located on the same site. Furthermore stormwater, particu-

larly that from motorways, should not be treated in sewage treatment plants. Solutions for on-site treatment exist but efforts to produce a cleaner and sustainable sludge for recycling will be meaningless as long as leachate and stormwater are mixed with municipal wastewater. Leachate in an untreated form is unsuitable for direct discharge into water courses, as the high metal and ammonia concentrations would have a severe impact on the ecology of the recipient water body. There is a strong argument for the introduction of filter systems using reactive media prepared from natural minerals or from by-products of steel production, such as blast furnace slag. Such filters could be a possible solution for the removal of metals and could be used as a pre-treatment step before leachate handling for N removal in a constructed wetland (Kietlińska, 2004; Kietlińska *et al.*, 2005). Filter materials saturated with heavy metals have to be replaced and stored in a safe way. In addition, the knowledge obtained from research on filter materials is of interest for treatment of drinking water and small industrial effluents. Implementation of the reactive bed filter technology can also be one option to reach the sanitation goals in developing countries. Bed filters using reactive materials may provide an effective, low cost and low maintenance approach for on-site wastewater treatment. Application of this technology can limit the amount of P entering surface water systems and groundwater from wastewater effluents, and may provide significant environmental benefits in rural, un-sewered areas (Heistad *et al.*, 2006).

Sand filter beds, soil infiltration and constructed wetlands (CW) are widely used systems for on-site treatment. All these systems have two main disadvantages from the viewpoint of construction engineering, namely that they are outdoor systems subjected to impacts from precipitation and temperature and that they have large area requirements. The treatment capacity varies and is generally low for P, while P recycling is not possible. During the past 15 years, an increasing number of papers describe the possibility of using materials in filter beds and CWs that are

more efficient in terms of P removal. However, very few of these laboratory investigations of filter materials have been tested in field-scale conditions. Two examples of filter materials that have a decade of full-scale experience are Filtralite P (including previous types) and steel slag (Dobbie *et al.*, 2005; Ádám *et al.*, 2007). The treatment systems designed for these materials use large amounts, implying large area requirements.

Recovering P from domestic wastewater and returning it to arable or other productive land is of major concern. The reason for this is primarily to avoid environmental problems such as eutrophication, which is caused by nutrients from wastewater. However problems associated with P mining, fertiliser production and in the long term the finite amount of minable phosphate minerals are also important. Domestic wastewater contains other elements and substances that are also of interest in recycling such as inorganic N and potassium (K) and organic matter. The prerequisites for P recovery should be good as a result of suggested lower content of contaminants of such plants and their proximity to forest and cultivated land.

However, various structural issues must be clarified, such as the division of responsibility, before recovery can take place. In accordance with the Swedish National Environmental Goals, levels of metal and alien substances in the environment should be close to zero within one generation (SEPA, 2002).

For this purpose it is considered important to define long-term requirements on the quality of wastewater fractions, to which reactive filter materials belong.

The treatment technology

A reactive bed filter (RBF) is designed according to the purpose of treatment, *e.g.* for stormwater, domestic wastewater or leachate water. The construction may be a filter well (Fig. 1, 2) or a CW where the most important component is the reactive medium or sorbent. Different types of artificial adsorbents or ion exchange materials are available as commercial products and most of them are utilised when very high water treatment standards are required. However, these materials are not useful for wastewater treatment because of their high cost. Many different filter materials for wastewater purification have been presented recently (Babel & Kurniawan, 2003; Johansson Westholm, 2006). Mineral-based materials such as Filtralite, Nordkalk Filtra P and Polonite are those most studied by researchers in Scandinavia.

The criteria for selection of a filter material are also related to the purpose of treatment, but usually include the following:

- Availability of material
- Cost
- Physical characteristics; pH, porosity, specific surface area
- Chemical composition
- Sorption capacity

This filter technology is a treatment system where wastewater is allowed to percolate, normally by gravity, through a reactive porous medium that removes the contaminant(s) from the water.

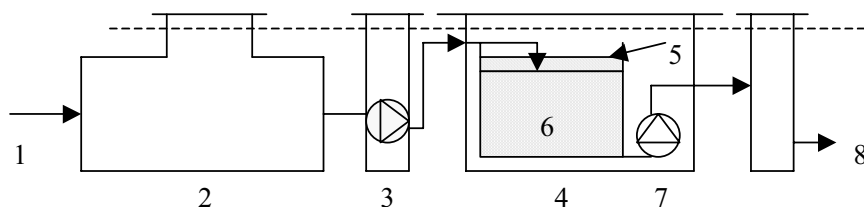


Fig. 1. A filter system layout (not to scale): (1) Inlet of household wastewater, (2) Septic tank, (3) Dosing pump, (4) Filter well, (5) Biofilter, (6) Polonite bed filter, (7) Pump, (8) Sampling well and outlet (Paper VI).



Fig. 2. Filter well for a single house using the material Polonite.

If this type of treatment is successful, the benefit is that a significant mass of the contaminant is accumulated in a finite and accessible volume of material, which allows for future collection and disposal if necessary. The latter is not the case if a natural and large wetland is used for treatment purposes.

Reactive materials can be classified into two distinct groups. One type promotes chemical reactions that destroy the contaminant or transform it to a more benign species (e.g. reductive dehalogenation, denitrification, biodegradation); the second attempts to transfer the contaminant mass from the aqueous phase to the solid phase (e.g. adsorption, ion exchange, precipitation). The latter reactions provide environmental benefits by concentrating the contaminant mass in a finite and known volume of material, which then allows for easier collection and future disposal, or possibly even acceptable rates of release (Baker *et al.*, 1998).

It is believed that the RBF can replace the commonly used soil infiltration of wastewater and other types of on-site treatment technologies, which do not fulfil new environmental requirements and goals.

The RBF technology has several advantages, the most important of which are:

- Purification is achieved by treatment in materials of natural origin or by-products from industry
- Used solid filter materials or sludge from filtration and sedimentation are

replaced regularly and returned to agriculture as P fertilisers and soil amendments

- Minor or no use of electricity, since pumps and other energy-consuming devices are not needed at all or only to a minor extent in the system
- A robust system in terms of function, control and management

Research problem

The advantage of using sorbents or reactive filter materials (RFM) for improving water quality has been proven in several investigations. However, most studies have concentrated on the removal of P and have been performed as batch experiments in the laboratory, while little is known about the success of RFM in removing heavy metals and nitrogen. Furthermore, due to the lack of knowledge of operating systems with RFM over longer time periods, further research is required. Generally, the longevity of filter materials for the removal of metals, N and P is unknown due to lack of long-term studies in of full-scale and column experiments. Furthermore, understanding of the removal and transport processes in the reactive materials is crucial for the control of full-scale operating systems, and for more widespread use in on-site wastewater treatment. In addition, more knowledge is needed about the possibility to recycle the spent materials as P sources and soil amendments in agriculture.

Objectives

The aim of this thesis was to evaluate the removal processes for metal, N and P that take place in reactive bed filter materials, for development of technologies used in on-site wastewater treatment. The overall context is how this technology can contribute to a sustainable flow of P, N and materials in society. This is in agreement with the long-term national aim to return all nutrients in wastewater that can be recovered back to arable soil or other land. For these reasons, the thesis covers a broader spectrum of issues, such as P removal, recycling and engineering application.

The research was performed in close cooperation with small enterprises that work with patent-driven development of small treatment facilities. This approach made it possible to critically test the findings from laboratory experiments in full-scale and real treatment conditions.

The specific objectives of this thesis were to:

- Investigate selected bed filter materials for their removal capacity of phosphorus, nitrogen and metals from wastewater under different treatment conditions (Papers I-VI).
- Cast light on the phosphorus and metal removal mechanisms by means of solubility experiments and geochemical modelling (Papers III, IV).
- Study the used filter materials as soil amendments and phosphorus sources on the effectiveness of plant production (Paper II) and, quantify the content of metals in the filter materials, particularly the Polonite used in small-scale wastewater treatment, and relate that content to statutory limits on metal content in sludge for use in agriculture (Papers I, V).
- Assess the long-term treatment performance and bed filter lifetime for phosphorus removal by Polonite and other filter materials (Paper VI).

STATE OF THE ART

Many recent investigations have shown that the removal efficiency of particular contaminants can be enhanced if a filter medium of high sorption capacity is used in treatment systems such as constructed wetlands for leachate treatment (Mæhlum, 1998) and for domestic wastewater treatment (Zhu, 1998; Arias & Brix, 2005; Vohla *et al.*, 2005; Hedström, 2006). Another approach involving *in situ* CW upgrading with reactive filter media has been developed, where separate filter wells are constructed as a step preceding the CW (Kietlińska, 2004). Besides the filter construction, the most important part is the selection of material or sorbent (Brix *et al.*, 2001). The sorbent is 'reactive' for one or

several contaminants that have to be removed from the wastewater. The term sorbent refers not only to adsorption, but also to processes such as precipitation, ion exchange, complexation and mechanical filtration (McCay, 1996). Sorption depends heavily on conditions such as pH, concentration of pollutants, ligand concentration, competing ions and particle size. Sorbents may consist of natural materials that are available in large quantities and at a low cost, or of by-products from industrial or agricultural operations. Since they are non-expensive, these materials can be disposed of without expensive regeneration, although one must bear in mind that they can contain hazardous substances after use and have to be treated accordingly. Examples of such sorbents are bark and other tannin-rich materials, chitosan and seafood processing wastes, zeolites, clays, fly ash and peat moss (Babel & Kurniawan, 2003). Recent research has identified the use of active filtration through alkaline media for the removal of P from domestic wastewater (Johansson & Gustafsson, 2000; Drizo *et al.*, 2006; Shilton *et al.*, 2006; Ádám *et al.*, 2007). Active filtration belongs to a family of promising techniques for small-scale wastewater treatment, which can be used in combination with other treatments such as wetland treatment systems and source separation/collection (Valsami-Jones, 2001; Shilton *et al.*, 2006; Hedström, 2006).

In the literature, numerous filter materials are described; those removing metals (Bailey *et al.*, 1999), those removing organic compounds (*e.g.* O'Hannesin & Gillham, 1998), those removing N (Ahsan *et al.*, 2001), and those with removal capacities for P (Kløve & Mæhlum, 2000; Johansson Westholm, 2006). Recent studies have focused on filter materials for the removal of P from wastewater, among which are Blast Furnace Slags (BFS), electric arc furnace steel slag (EAF), Filtralite[®], Polonite[®], wollastonite, shell sand, dolomite, red mud, peat and others (Sakadevan & Bavor, 1998; Bailey *et al.*, 1999; Hill *et al.*, 2000; Kløve & Mæhlum, 2000; Brooks *et al.*, 2000; Brown *et al.*, 2000; Heavey, 2003; Brogowski & Renman, 2004; Søvik & Kløve, 2005; Drizo *et al.*, 2006).

Phosphorus usually occurs in wastewater in the form of organic phosphate (e.g. detergents) and inorganic phosphates (ortho- and poly-phosphates). Various techniques have been employed for P removal in wastewater treatment as well as recovery technologies (Morse *et al.*, 1998). The broad categories of P effluent treatment include physical, chemical, biological and crystallisation methods. Chemical removal techniques are the most effective and well-established methods to date, including P precipitation with lime, or aluminium and iron salts. However, the use of metal salts may hinder widespread application of the P resource, as the recovery of P from sludge is difficult (de-Bashan & Bashan, 2004). Consequently, the removal of P compounds through sorption processes onto various filter materials has been tested increasingly during the past decade (e.g. Oguz, 2004; Kostura, 2005; Ganrot *et al.*, 2007).

The possibility of recycling the spent reactive materials or sorbents to agriculture as a fertiliser and soil conditioner has been investigated in some studies (Hylander & Simán, 2001; Kvarnström *et al.*, 2004; Hylander *et al.*, 2006; Cucarella *et al.*, 2008). Their content of P might be low compared with industrial fertilisers but their alkaline properties have positive effects on acid soils (Cucarella *et al.*, 2007; Cucarella *et al.*, 2008). However the benefits of using these materials in agriculture can be outweighed by their content of heavy metals, which can be transferred from soil to crops by plant uptake and become hazardous for man and the environment. Domestic wastewater contains different amounts of metals depending on its source (Moriyama *et al.*, 1989). These metals can accumulate in the filter material during filtration of the wastewater and add to any indigenous content that might be present (Gustafsson *et al.*, 2008). Investigations carried out on treatment of landfill leachate and urban stormwater clearly show the ability of reactive materials to remove metals from the liquid to the solid phase, but leaching from the filter matrix has also been observed (Kietlińska & Renman, 2005; Hallberg & Renman, 2007).

Several mechanisms, such as sorption, complexation and precipitation, can control metal

concentrations in effluent from bed filters employed for wastewater treatment. Divalent metal cations tend to favour sorption on colloidal particles with negatively charged sites, calcite, clay minerals, organics and oxides of Fe, Mn, Al and Si (Trivedi & Axe, 2001). Complexation is the combination of metal ions with non-metallic ligands by covalent bonds. The humic-like substances formed from wastewater decomposition can serve as ligands for metal complexes (Metcalf & Eddy, 2003). Precipitation occurs when a metal species falls out of solution as a solid. Sulphides and carbonates are capable of forming precipitates with Cd, Ni, Zn, Cu and Pb (Kamara *et al.*, 1989; Papadopoulus & Rowell, 1989).

When the aim is to remove metal, N and P by filtration through a reactive filter material, the presence of dissolved and particulate organic matter is of concern. Filtration is the process of passing a liquid through a porous medium, for example sand, either in natural formation or filter constructions with the expectation that the effluent will have a better quality than the influent. High concentrations of dissolved organic matter can result in increased sorption but aqueous complexation with metal ions can also result in a decreased sorption (Düker *et al.*, 1995; Jönsson *et al.*, 2006). Humic substances dominate the total organic content in municipal wastewater (Omoike & Vanloon, 1999). It is therefore expected that organic species can inhibit P sorption mechanisms (Van der Houwen & Valsami-Jones, 2001) and have importance in the removal of wastewater contaminants (Katsoyiannis & Samara, 2007). Organic matter is responsible for different kinds of clogging that can occur in filter constructions. Deposited solids at the particle surface in the pores leads to inner blockage. This volume filtration is the main process of solid removal in most filter beds. Surface filtration may occur if a filter cake develops (Kiely, 1997). The mechanisms by which granular filter materials remove colloidal matter from water are complex and not fully understood. This particularly applies to the bed materials investigated in this thesis (cf. Meyer, 2004).

The P removal potential of a particular filter material can be obtained from batch and/or column studies. The results achieved from column studies are considered more realistic than the maximum P adsorption capacities determined from batch experiments using high P concentrations (Drizo *et al.*, 2002). The main disadvantage of the batch experiment is that particles can break, increasing the specific surface area, which leads to over-estimation of the amount of P removed by the material (Hylander *et al.*, 1999). However, because of the time constraints for long-term column studies, most investigations of P sorption capacities of filter materials have been performed by laboratory batch experiments (Cucarella & Renman, 2008). Phosphorus sorption experiments tend to yield diverging results even with a material of very similar chemical composition (Kostura *et al.*, 2005). The large scatter of results in P sorption on different materials investigated relates to the fact that these materials are not fully and unambiguously defined by their chemical, mineralogical and phase compositions (Kostura *et al.*, 2005). The design capacity for P removal can not either be easily calculated on the sorption results achieved in a batch experiment, as demonstrated on filter beds with sand and oil-shale ash (Vohla *et al.*, 2007).

MATERIALS AND METHODS

This chapter contains a description of materials and methods applied in batch, field and column experiments and a pot experiment, according to the objectives of the study.

Filter materials

Filter materials can be divided into the following classes: Industrial by-products, man-made products and natural materials (Johansson Westholm, 2006). The following materials were used in this thesis and are accordingly described in the following.

Industrial by-products

Three kinds of slag were used in the column experiments: pretreated water-cooled blast furnace slag (WCBFS), crystalline and amorphous blast furnace slag. All slag materials were supplied by Merox AB (Oxelösund, Sweden).

WCBFS is a product from the steel industry and contains amorphous glasses and a small amount of crystalline silicates. It had a particle size of 0-4 mm and was pre-treated with 1% CaO to increase its alkaline reaction. The original composition of WCBFS was as follows (in g/kg dry matter): Ca (216); Si (155); Mg (98); Al (70); and some amounts of K, Mn, Na and Fe. Virgin material had a pH of 9.4. This filter material was tested for phosphorus removal from artificial solution in Paper III.

Blast furnace slag is an industrial by-product resulting from the process of extracting iron from iron ore at steel-works. It had a particle size of 0.25-4 mm; 2-5.6 mm and 2-7 mm and was used in the experiments presented in Paper I, II, IV and V. Blast furnace slag is characterised by high amounts of SiO₂ (36.2%) and CaO (35%). Amount of other components such as MgO and Al₂O₃ were over 13% and 10%, respectively. Pure material had a pH ranging from 9.13 (Paper I) to between 9.4-9.9 (Papers II, IV, V).

Blast furnace slag is produced in large amounts by the steel industry and most of it is reused in a variety of applications such as road construction, liming materials in agriculture and to some extent for wastewater treatment.

Natural materials and man-made products

Opoka belongs to the group of silica-calcite sedimentary rocks, a marine deposit composed of the remains of minute marine organisms from the late Cretaceous period called Mastrych. This formation is found in Poland, Lithuania, Ukraine and Russia. Opoka consist mainly of SiO_2 and CaCO_3 . Depending on the ratio between those compounds, opoka can be classified as light-weight ($> \text{SiO}_2$) or heavy-weight ($> \text{CaCO}_3$). In Polish literature this type of rock can be classified either as geza (synonymous with gaize) when the silica content is high or as opoka when calcite dominates (Brogowski & Renman, 2004). The pH of the opoka used in the study was 8.3 and the particle size was 2-5.6 mm (Papers II, IV, V).

Polonite is the most novel filter material of those used in experiments in this thesis. Polonite® is a product manufactured from the cretaceous rock opoka and is intended for use in wastewater treatment (Brogowski & Renman, 2004). This material is known for its high sorption capacity of soluble phosphorus and usefulness for recycling of nutrients in agriculture.

Limestone was from the Ignaberga quarry, South Sweden. Limestone, a sedimentary rock, is used within several branches of industry such as the steel and concrete industries and the pulp industry. It is also used as a liming agent in agriculture. Due to its high content of calcium, mainly CaCO_3 , limestone has attracted attention as a candidate substrate for P removal. The pH of the limestone used in the study was 8.9 and the particle size was 1-2 mm (Papers II, IV, V).

Peat used in experiments was a manufactured product from Hasselfors Garden AB: a natural *Sphagnum* peat without any additives, moderately decomposed (humification degree H3-H4) and with a density of 70 kg m^{-3} . It had a pH ranging between 3.0-4.0.

Calcium-rich materials can react with the sulphate commonly found in leachate and create gypsum, but by including an organic component this effect can be reduced. Another reason for including peat in the filter matrix was to decrease the saturated hydrau-

lic conductivity since the mineral fractions were coarse. Peat itself can act as an adsorbent of heavy metals but has not been found to be capable of removing metals from landfill leachate to acceptable levels (Ringqvist *et al.*, 2002). Ammonia, on the other hand, can be removed by peat to some extent (Heavey, 2003). Peat was used as an admixture with mineral sorbents in experiments presented in Papers I, III and VI.

Sand was used as inert reference material. The experiment in Paper I used a washed quartz sand produced by Ahlsell AB. Sand had a particle size of 0.2-1.5 mm (Paper II) and 2-5.6 mm (Paper I). The latter was taken from a gravel-pit 20 km SW of Södertälje, Sweden. The main components of sand are SiO_2 (69.3%), Al_2O_3 (13.4%), K_2O (3.4%) and Fe_2O_3 (3.1%). Contents of Cr, Cu, Ni and Zn in the virgin material were 35.8, 20.6, 32.6, 49.4 ppm, respectively (analysed in this study). The pure material before mixing with peat had pH of 6.25 (Paper I).

Wollastonite (CaSiO_3) is a natural calcium meta-silicate. The material used in column experiments was supplied by Minpro AB (Stråssa, Sweden). It had a particle size of 1-3 mm and contained approximately 30% of wollastonite, 11% of diopside, 11% of quartz and 40% of feldspars. This filter material was used to study removal of P from artificial solution in Paper III.

Filtra P (Nordkalk Filtra P) used in column experiments is produced after heating a mixture of limestone, gypsum and Fe oxides. This filter material consists mainly of $\text{Ca}(\text{OH})_2$ (20%), which gives strongly alkaline properties. Filtra P is granulated in a particle size of 2-13 mm. In this study samples of Filtra P were obtained from Nordkalk (Pargas, Finland). This material was used for P removal studies in a column experiment (Paper III).

Column experiments (Papers I-VI)

Three column experiments were performed in this thesis, using three kinds of feed water; landfill leachate, municipal wastewater and synthetic solution, respectively.

Five columns (K0 – K4) made of PVC, each having an overall height of 60 cm and an

internal diameter of 9.8 cm, were used for testing landfill leachate (Paper I). All columns were filled with substrate to a height of 50 cm. The top of each substrate was covered with polyester filter to prevent media scouring and clogging during leachate addition. Peat with a moisture of 77.5% was mixed with the mineral substrates in a ratio of 1:4 by volume. In the column experiment the following substrates were used: sand, Polonite, blast furnace slag (BFS), and peat. Column K0 consisted of sand/peat, columns K1 and K3 were filled with Polonite/peat and columns K2 and K4 with BFS/peat. Peat was intended to prevent clogging because of chemical reactions between sulphur and calcium. Landfill leachate was transported from the Tveta Landfill in Södertälje to the laboratory in eight separate batches during the experimental period. The leachate was stored at a temperature of 4 °C and brought in portions of 25 L to the column test, performed at room temperature. Leachate water was distributed by a peristaltic pump through Teflon tubes to each column with a flow rate of 7 mL min⁻¹, corresponding to a hydraulic loading rate of 1.34 m d⁻¹. The system was operated intermittently for 8 h per day, and each column received approximately 300 L of leachate during the whole experiment. The experiment was run under saturated conditions.

A long-term experiment aimed at overall studies of elements (P, metals, and inorganic forms of N) and their removal by six substrates was carried out indoors (temperature 20 °C) at the Loudden wastewater treatment plant in Stockholm (Papers II, IV, V, VI). The plant receives domestic wastewater and is designed for a flow of 16 000 m³ d⁻¹. The raw wastewater was pumped to a experimental set-up consisting of pretreatment units and columns imitating the conditions of on-site treatment with filter beds (Fig. 3). A two-chamber septic tank was the first step, aimed at removing suspended solids (SS). It was followed by a 2.5 cm thick layer of mineral wool at the top of each column. This wool was exchanged three times during the experimental period. On average, 0.5 L h⁻¹ of wastewater was pumped

and sprinkled equally over the surface area of the column materials every second hour for 67 weeks. The six filter materials and their grain size used were: coarse amorphous furnace slag, 0.25-4 mm (ASC); coarse crystalline furnace slag, 0.25-4 mm (CSC); very coarse crystalline furnace slag, 2-7 mm (CSVC); limestone, 1-2 mm; opoka, 2-5.6 mm; Polonite[®], 2-5.6 mm; and quartz sand, 0.2-1.5 mm. They were filled to a height of 50 cm in 30-cm wide columns (two materials in duplicate) and received wastewater under unsaturated flow conditions. The sand was used as a reference material (Ritter & Eastburn, 1988).

Sampling was performed regularly during 67 weeks with a total number of 40 duplicate samples (100 mL polypropylene bottles) of influent and effluent of each column. The pH and electric conductivity (EC) of the liquids were determined within 1 h, whereafter they were frozen (-18 °C) until time of analysis. Samples were filtered through a 0.45 µm filter (Satorius) before each analysis. The influent and effluent concentrations of P (Papers II, VI) and inorganic forms of N (Paper IV), i.e. ammonium (NH₄-N), nitrate (NO₃-N) and nitrite (NO₂-N), were analysed.

It was not possible to maintain the desired wastewater flow of 6 L day⁻¹ equally to all columns, so the incoming volume was monitored by regular manual measurements and verified by tipping-bucket flow meters connected to a data logger (Campbell CR10X).

In Paper III a column leaching experiment was carried out to provide information on long-term P removal performance of the filter materials. Columns were constructed of PVC tubes of 60 cm length and 10 cm inner diameter and filled with a 50 cm layer of the appropriate filter material. However, the Polonite was sieved for removal of particles less than 2 mm and its composition was changed by addition of 10% (w/w) *Sphagnum* peat. The bottom of the columns was filled with a 2 cm layer of gravel, and with a coarse plastic (HDPE) filter to prevent loss of material from the columns. The experiment was carried out at room temperature (20 °C) under saturated conditions.

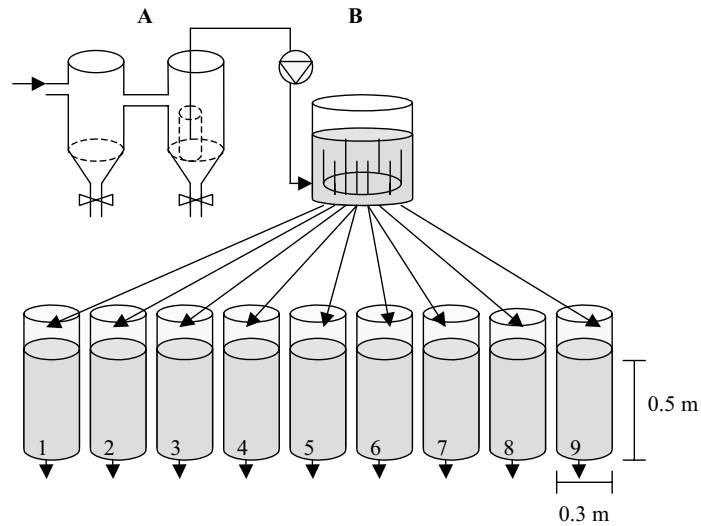


Fig. 3. The experimental set-up with pre-treatment system (A), distribution device (B) and columns (1-9) filled with sand, opoka, Polonite®, limestone and blast furnace slags (Paper IV).

A synthetic solution with $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ concentrations of 5 mg L^{-1} and 30 mg L^{-1} respectively was prepared by adding KH_2PO_4 and NH_4Cl to 200 L of tap water. The solution was stored in a container and pumped automatically to the top of each column three times per day throughout the experimental period of 68 weeks. The loading rate was differentiated so that the pumped volumes were roughly proportional to the pore volume of the particular filter material. Samples were taken from influent and effluent weekly during the first 40 weeks, thereafter biweekly. The pH was analysed directly after collection. The samples were then stored in a freezer at $-18 \text{ }^\circ\text{C}$ until analysis of $\text{PO}_4\text{-P}$. The synthetic solution and the loading schedule were selected to mimic conditions frequently encountered in on-site wastewater treatment using reactive filter media. The concentrations of P and N represent concentrations typically found in wastewater.

Pot experiment (Paper II)

Barley (*Hordeum vulgare*) was grown using the P-enriched filter materials (opoka, sand, Polonite, CSC, ASC, Limestone, CSVS) from the column experiment at the Loudden

wastewater treatment plant as fertilisers in a pot experiment.

Mitscherlich pots were filled (3.6 kg dry soil per pot) with the A-horizon (5-20 cm) of P-depleted soil from agricultural land under permanent cultivation from Bjärröd, Scania, Sweden. This sandy moraine soil is poor in P, rather poor in K, and has an average level of Mg.

Each pot received 1.5 g K_2SO_4 , 1.0 g MgSO_4 and 1.0 g N as NH_4NO_3 as basic fertilisation. The soil was mixed with P in the form of K_2HPO_4 or P sorbed from wastewater to the different filter materials in quantities corresponding to 0.03 g P per pot. Each treatment was performed in triplicate, with filter material from the column layer indicated (generally the surface, 0-5 cm).

Barley was sown and thinned after eight days of growth to 29 blades per pot. The pots were kept outdoors during the period June-September. They were watered once a day or every second day to keep soil moisture between 60% and 80% of maximum water-holding capacity.

At harvest, the blades were cut 10 mm above the soil surface, dried at $55 \text{ }^\circ\text{C}$ and weighed.

Soil pH was determined at sowing in a 1:2.5 (w:V) soil:water suspension.

Batch experiments (Paper III)

Batch experiments were carried out on both unused filter material samples and on samples from the 0-5 cm layer of the used filter materials in a column experiment (Paper III). In brief, 2.00 g material (for wollastonite samples 3.00 g) were suspended in 35 mL solutions of variable composition in polypropylene centrifuge tubes and then equilibrated for 5 d in an end-over-end shaker at 21 °C and at a background ionic strength of 0.1 mol L⁻¹ (NaNO₃ was used as supporting electrolyte). For the used filter materials wet samples were used, which means that the actual liquid to solid (L:S) ratios were larger; 56.6 for Filtra P, 27.7 for Polonite, 27.3 for WCBFS and 12.0 for wollastonite. To produce a range of pH values and PO₄-P concentrations in the suspensions, various amounts of nitric acid (0-10 mmol L⁻¹) were added. To some suspensions with 10 mmol L⁻¹ nitric acid, an additional 5-20 mmol L⁻¹ oxalic acid were added, to further increase the variation in pH values and PO₄-P concentrations. After equilibration, the suspensions were centrifuged, pH was measured (using a Radiometer combination electrode) and they were filtered with 0.2 µm single-use filters (Acrodisc PF). Directly after filtration, the alkalinity of the samples was measured through addition of 0.02 M HCl to pH 5.4.

Modeling approach (Papers III, V)

The speciation of leachates from the batch experiments was processed with Visual MINTEQ (Gustafsson, 2006) using equilibrium constants for aqueous complexes (i.e. CaHCO₃⁺, CaPO₄⁻, CaHPO₄⁰, etc.) from the default Visual MINTEQ database, which mostly relies on the NIST Critical Stability constants, version 7.0 (Smith *et al.*, 2003). Calculated ion activity products were compared with solubility constants given in the literature (Table 3 in Paper III). For ATP, for which few solubility data exist, constants were calculated from raw data given for two amorphous calcium phosphates of varying crystallinity, referred to as ACP1 and ACP2

by the authors (Christoffersen *et al.*, 1990). These thermodynamic data should only be considered as rough estimates, not least because the observed Ca:P ratios in the precipitates were between 1.28 and 1.38, which is slightly less than the ideal ratio of 1.5. The solubility data for OCP were also calculated from experiments conducted by Christoffersen *et al.* (1990).

To investigate whether equilibrium with solid phases might have controlled metal solubility in the materials, Visual MINTEQ ver. 2.53 (Gustafsson, 2007) was applied for speciation of the column effluents (Paper V). In these calculations, complexation with dissolved organic matter (DOM) in the effluents was estimated with the Stockholm Humic Model (Gustafsson, 2001), assuming that 70% of the DOM consisted of fulvic acid. Because measurements of alkalinity and dissolved organic carbon (DOC) were made only for a few samplings, the results should be considered approximate.

Full-scale treatment system experiment (Papers V, VI)

A reactive bed filter system for a one-family house, situated 20 km NE of Uppsala city in Sweden, was used for studies of treatment efficiency. The reactive material used was Polonite mixed with 8% peat (w/w). The system consists of a pre-treatment step with septic tank and biofilter followed by filter well filled with Polonite (volume 800 L, dry weight 560 kg), which receives wastewater intermittently in relation to its production in the household. After 2 years and 3 months of operation, the filter material was removed and exchanged with a new Polonite filter material.

Chemical and physical analyses

The analysis of three forms of nitrogen (NH₄-N, NO₃-N, NO₂-N) and phosphorus as PO₄-P was performed using Flow Injection Analysis (FIA, Aquatec-Tecator autoanalyser) (Paper I-VI). Before analysis, the samples were filtered through a 0.45 µm Micropore filter. The pH and electric conductivity of liquids were measured by the following instruments: Hanna HI 8424 mi-

crocomputer pH meter or Radiometer PHM 82 and Hanna HI 8733 conductivity meter. BOD₇ was determined at the laboratory of Stockholm Water AB, according to Swedish Standards (SS028143-2 mod. and SS-EN 25814-1) (Papers II, IV, V).

The liquids intended for metal analyses were preserved with a few drops of concentrated HNO₃ and kept in a cold-storage room at 4 °C prior to analysis (Papers I, V). The analyses were performed using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) for all elements. Metal concentrations in the virgin materials, in the liquids and in the solids from 0-5, 5-10, 10-20, 20-30, 30-40, and 40-50 cm layers of each column were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) (Paper V).

Carbon and N were determined by dry combustion on a LECO combustion system coupled to an IR-detector (LECO, 1995) (Paper II). Total element contents of carbon, and N in individual layers of the different materials were determined by extraction with conc. HNO₃ in an autoclave (120 °C for 30 minutes, material:solution 1:20; modified from SIS (1986) (Paper II).

Total concentrations of P were determined in three layers (0-5, 5-10, 40-50 cm, Paper III) or in random samples (Paper VI) of the used filter materials using ICP-OES. Samples from different layers (0-5, 5-10, 40-50 cm) in columns studied with synthetic solution were air-dried, gently crushed in a mortar, and then examined by a Perkin-Elmer S2000 Fourier Transform infrared (FTIR) spectrometer. The instrument was run in the attenuated total reflectance (ATR) mode using a Golden-Gate diamond cell. The spectra were compared with those recorded for filter material samples that were not used in the column experiment. Finally, total dissolved Ca, Mg, and Si were determined by plasma emission spectroscopy using a Jobin-Yvon JY24 ICP instrument (Paper III).

Evaluation of treatment performance

The percentage removal efficiencies of P, heavy metals and N by the column substrates were calculated as the difference between

concentrations in influent and effluent water. Mass removal (g kg⁻¹ dry substrate) of each constituent entering and leaving the columns was estimated from water quality and flow data (Papers I-VI).

Fertiliser effectiveness can be summarised as the relative effectiveness (RE%) of P bound to the filter materials (PFM) in increasing barley dry matter production in relation to yield with the standard fertiliser (K₂HPO₄) (Paper II). This was calculated according to the following formula (1):

$$RE\% = \frac{[(Y \text{ with PFM}) - (Y \text{ control})]}{[(Y \text{ with } K_2HPO_4) - (Y \text{ control})]} 100$$

where Y represents the yield.

The percentage removal of inorganic PO₄-P was calculated as the difference between influent and effluent concentrations for the samples collected at the same time. The sorption of PO₄-P to the filter matrix (S_p, mg kg⁻¹) was calculated using the following mass balance equation (Papers II, III, IV):

$$S_p = \frac{(C_i - C_e)V}{m} \quad (2)$$

where C_e is the effluent concentration and C_i is the influent concentration, V is the volume of wastewater treated during the experiment and m the mass (kg) of the filter material.

The removal capacity of the filter materials (R_m, %), i.e. the retention or leaching of dissolved elements during the infiltration of wastewater, was calculated according to the following equation (Paper V):

$$R_m = \left(1 - \frac{C_e}{C_i}\right) 100 \quad (3)$$

where C_e is the effluent concentration and C_i is the influent concentration.

The sorption to, or release of, dissolved elements (mainly metals) from the filter ma-

trix (S_m , mg kg⁻¹) was calculated using the following mass balance equation (Paper V):

$$S_m = \frac{(C_i - C_e)V}{m} \quad (4)$$

where C_e is the effluent concentration and C_i is the influent concentration, V is the volume of wastewater treated during the experiment and m the mass (kg) of the filter material.

The total metal content (mg kg⁻¹) of filter materials in the columns was calculated as the average of the content in each layer. Analyses were performed in duplicate for the 0-5 cm layers (Paper V).

The removal capacity of the filter materials, i.e. loss of organic matter (BOD₅) and of N during the infiltration of wastewater, was calculated according to the following equation (Paper IV):

$$\text{Loss} = \left[1 - \frac{C_e}{C_i} \right] 100 \quad (5)$$

where C_e is the effluent concentration and C_i is the influent concentration.

RESULTS AND DISCUSSION

Phosphate removal and pH development in the columns

Filter materials in the column experiment using synthetic solution were exposed to a high loading rate (> 400 L m⁻²d⁻¹) (Papers III, VI) under saturated conditions. The columns received between 1.1 to 1.8 m³ of solution during 68 weeks. Technical problems with pumping caused less discharge of solution than was intended. The column filled with Filtralite P clogged after 971 pore volumes (pv) and was closed for that reason. Its pore volume also decreased and was found to be 0.45 dm³ less than at the start.

Clear material-specific differences in PO₄-P removal were observed during the course of the experiment. Wollastonite was the least efficient material in terms of PO₄-P removal; on average 51.1% of P was removed. This is partly explained by the low pH in these columns; already after 100 pore volumes, the pH of the effluent was more or less equal to that of the inflow. Water-cooled blast furnace slag (WCBFS) removed more than 95% P during the first 300 pore volumes, but thereafter the P retention efficiency decreased steadily, so for the whole time period the mean P removal was 85.6%.

The two most strongly P-retaining materials were Polonite and Filtra P. Filtra P was slightly more efficient; on average it retained 98.2% P, whereas Polonite retained 96.7%. However, Polonite treated much more solution (1410 pv) than Filtra P. Disintegration of Filtra P was observed, particularly in the beginning of the experiment, as a yellow-brown colour in the effluent. In both cases the pH remained alkaline, particularly so for Filtra P. Before termination of the experiment, there was a tendency for the pH in the Polonite column to decrease, which may suggest that the most reactive CaO phase had dissolved completely.

A column filled with Polonite and run in parallel under intermittent saturated flow conditions had a slightly lower removal (96%). Obviously, the two modes of flow conditions did not have an influence on the removal capacity.

At the end of the experiments the concentration of $\text{PO}_4\text{-P}$ was still very low in the effluent from columns filled with Polonite, both under saturated and intermittent saturated conditions (0.13 and 0.17 mg L^{-1}), respectively). However, the effluent concentration started to increase by the end of the experiment, as did the pH, indicating a beginning of breakthrough (Fig. 4).

Only Polonite showed good $\text{PO}_4\text{-P}$ removal efficiency for the whole experimental period using municipal wastewater as feed solution in columns (Paper II). Effluent from column 3 and 7, filled with Polonite (Fig. 5), had a low mean concentration of P of 0.1 mg L^{-1} throughout the experiment and a simultaneous decrease in pH from 12.8 to 8.9. The P removal capacity decreased successively in the other columns studied and, at the end of the experiment, reached P concentrations in the effluent higher than 2 mg L^{-1} (Fig. 6). An exception was the column filled with sand, which did not remove soluble P at all from the incoming wastewater. The pH in the effluent from the sand column closely matched the influent wastewater pH, while effluent from the other columns had a pH of 8.9-9.2.

The difference in retention capacity between Polonite and opoka was large, more than ten-fold, due to oxidation of CaCO_3 to the more reactive form CaO in Polonite. High temperature thermal pretreatment of opoka also results in sintering and a subsequent large decrease in the surface area of the product Polonite®.

The comparably low sorption capacity of limestone is also explained by its Ca being in the carbonate form. Burning limestone (CaCO_3) to form quick lime (CaO) increases the removal capacity (Hylander & Simán, 2001), but results in a powder with a hydraulic conductivity too low to permit an use in the designed filtration system in its pure form.

In addition to element content and chemical form, the differences in the particle size of the materials can also explain the variations in P sorption that are clearly apparent when comparing the coarse and very coarse crystalline slags. The process of carbonation should also be considered here. In this process, carbonation may occur in a gas-solid-liquid or gas-solid condition (Huijgen *et al.*, 2006).

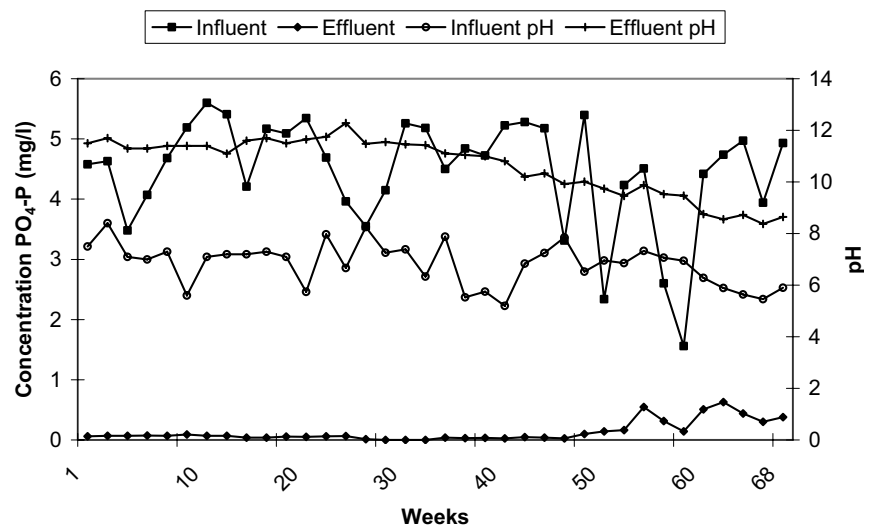


Fig. 4. Changes in pH and influent and effluent concentrations of $\text{PO}_4\text{-P}$ for column run under saturated flow and with artificial solution over a 68-week period.

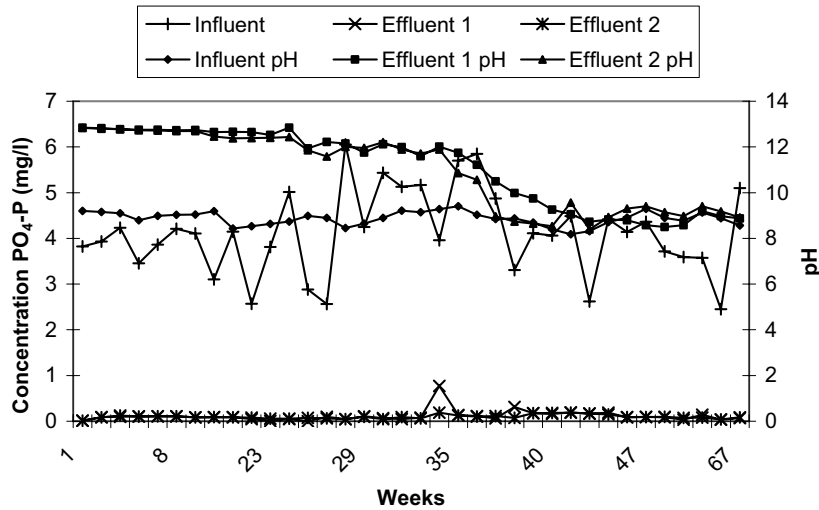


Fig. 5. Changes in pH and influent and effluent concentrations of $PO_4\text{-P}$ for two columns filled with Polonite and fed with municipal wastewater over a 67-week period.

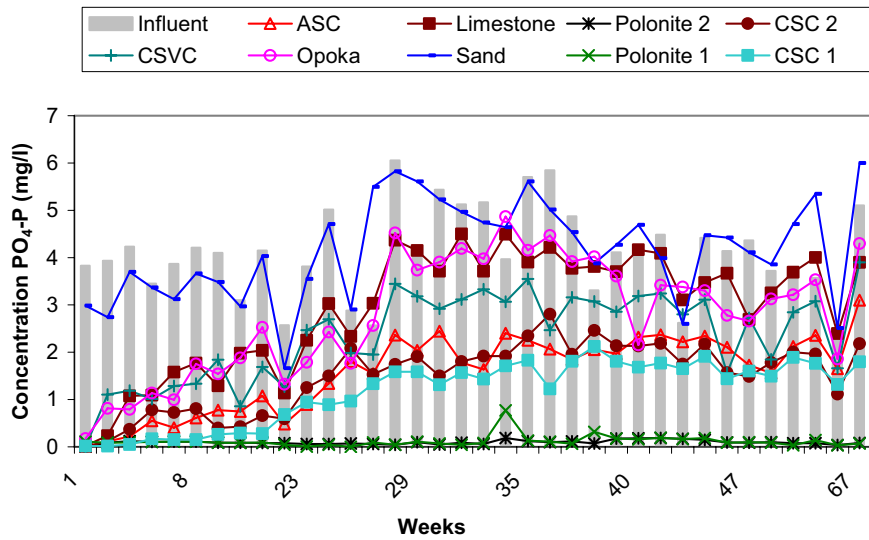


Fig. 6. Long-term development of $PO_4\text{-P}$ concentrations in effluents from nine columns with different filter materials fed by municipal wastewater.

Both processes occur in the surface layer of the filter materials while the aqueous carbonation route appears in the deeper layers, i.e. leaching of Ca, dissolution of CO_2 and subsequent conversion of (bi)carbonate species, followed by nucleation and growth of CaCO_3 .

There were no operational problems such as clogging causing hydraulic failure and overflow in either experiment. Chemical clogging was expected from previous experience (unpublished data) with Polonite and problems with clogging have been observed in many experiments due to formation of precipitates in the outflow system (e.g. Drizo *et al.*, 2006), so a small amount of peat was incorporated to prevent this in the experiment with synthetic solution.

However, the Polonite filters fed with municipal wastewater performed excellently under the particular hydraulic load despite being peat-free.

Phosphate removal and pH development in full-scale bed filter

The full-scale on-site system investigated showed an overall removal of 89% for a period of 92 weeks. The phosphate breakthrough curve for this trial is presented in Fig. 7. After 128 pore volumes had been treated in the bed filter in downflow mode, the C_e/C_i ratio started to rapidly increase, coinciding with the pH drop seen in Fig. 8. After 75% breakthrough, the rate of increase of the breakthrough curve seemed to even out to the end of the experimental period. The effluent $\text{PO}_4\text{-P}$ concentration was 2.49 mg L^{-1} by then. The filter well was operated for an additional 4 months with the same Polonite material after termination of this experiment and analyses of a few samples of the effluent showed that complete breakthrough ($C_e=C_i$) was not achieved in this period. This suggests that $\text{PO}_4\text{-P}$ removal continued, possibly by precipitation and/or biological mechanisms.

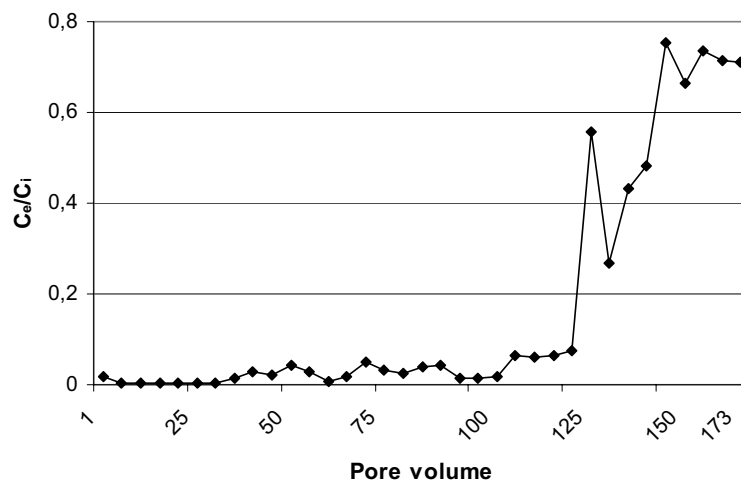


Fig. 7. Phosphate breakthrough curve for Experiment III (part with down-flow feeding of filter).

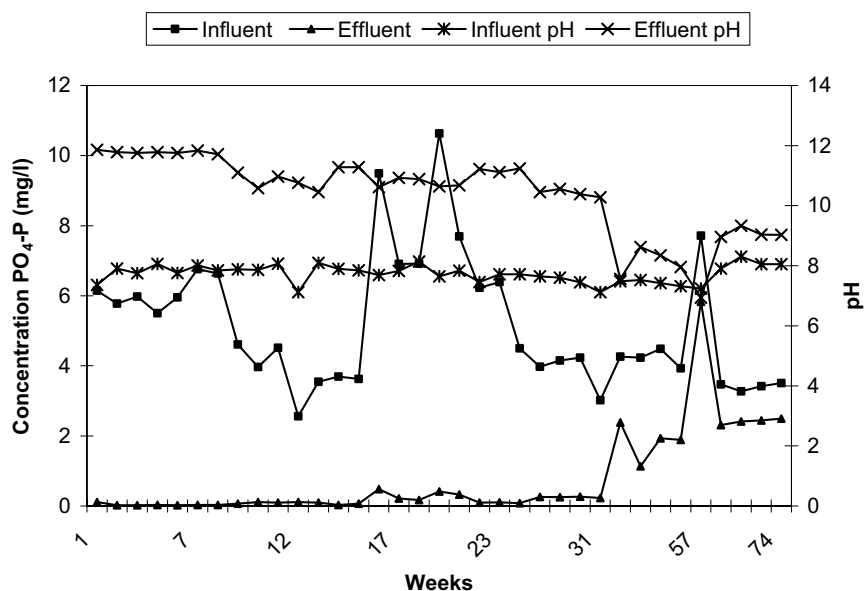


Fig. 8. Changes in pH and influent and effluent concentrations of $PO_4\text{-P}$ in a filter well used for domestic wastewater treatment. The points represent the last 74 weeks of the sampling period (total 92) when the filter was fed in downward flow.

Phosphorus sorption to different materials by layers

The top layer (0-5 cm, 0-10 cm) of each material showed the highest concentration of accumulated P in column and full-scale experiments. The concentration decreased significantly with depth of the columns; this was especially the case in the Filtra P and Polonite materials. The columns fed by municipal wastewater and filled with Polonite increased from an original 0.2 mg g^{-1} to 1.3 mg P g^{-1} dry matter in the top layer. These were followed by sand, which had a higher P content in its surface layer than revealed by its capacity to remove phosphate from percolating wastewater. However, P content decreased significantly in underlying layers of sand, which should not be the case with an effluent rich in phosphate, where the total P content originated mainly from sorbed phosphate. Phosphorus from the wastewater was retained in the surface layer by the sand acting as a filter due to its fine texture and by bacteria living in the surface layer of the column rather than in lower layers (Renman

et al., 2004). Total P content at the surface and in the 5-10 cm layers of the columns filled with Polonite was nearly the same and, due to sorption of phosphate, was more than six times higher than in the bottom layer, which contained only P from the initial material without any P sorbed (Fig. 9). The similar P content in the two upper layers and the continuous decrease in lower layers indicate that only the surface layers were saturated or close to saturated with P. The absence of P retention in the bottom layer and only limited P sorption in the two overlying layers indicate that the column would have been able to efficiently retain P from the wastewater for twice as long a period of time.

In the case of columns operated with synthetic solution, the concentrations also decreased significantly with depth of the column, although not clearly in the column filled with wollastonite (Paper III).

The discharge of liquid was much higher to these columns compared with those using municipal wastewater (approx. 6 times).

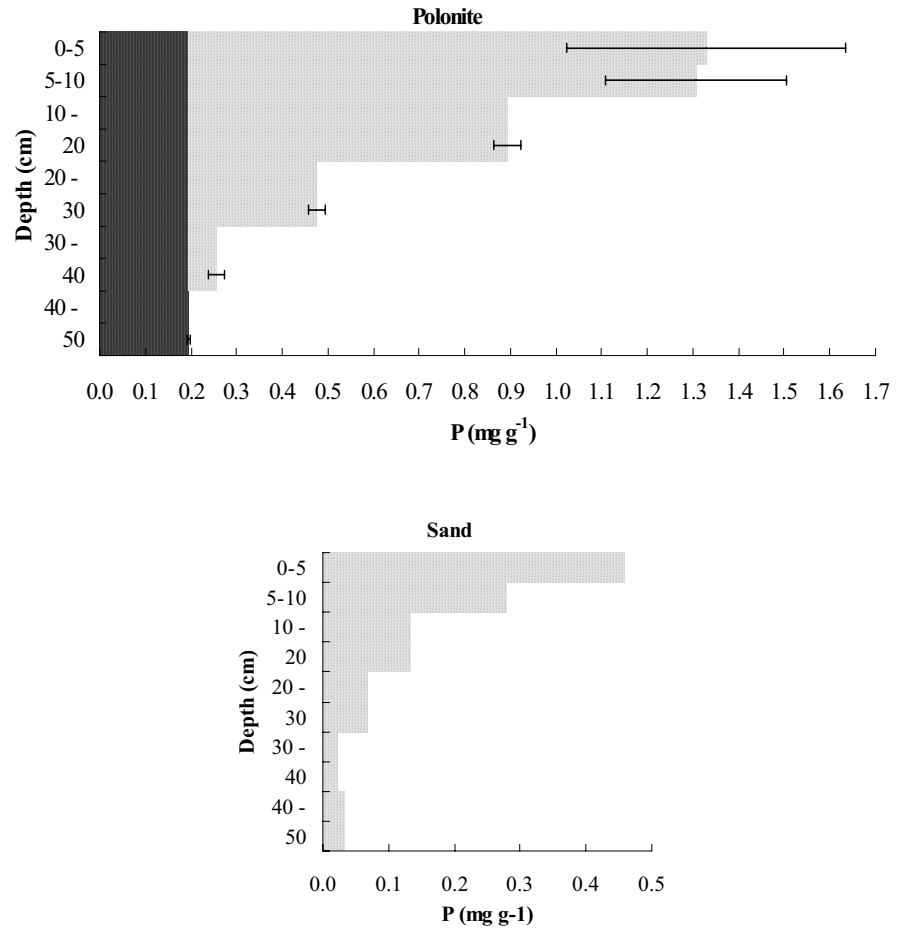


Fig. 9. Initial P content of the Polonite and sand (dark shaded area) and P enriched to different layers (light shaded area) after the column experiment. Bars indicate $\pm SE$ for duplicate columns (Paper II).

The total concentration of P was also much higher, as indicated by Polonite showing a value of 7.39 g kg^{-1} dry matter. The highest concentration of accumulated P was found for Filtra P, approaching 19.4 g kg^{-1} dry matter. However, 12% of the dry matter was lost from the column due to the release of gypsum from the material.

The Polonite used in the filter well showed a P concentration of 1.27 g kg^{-1} dry matter. Significantly lower concentrations were found in other layers of the filter bed.

This can indicate that the wastewater was not evenly distributed in the material, despite the filter bed being operated by a batch-wise filling-up and drainage mode.

Ádám *et al.* (2006) studied the spatial distribution of P in horizontal flow, Filtralite P systems. They concluded with the help of a Br-tracer experiment that preferential flow could appear in the upper parts of the containers used. Drizo *et al.* (2002) showed that when electric arc furnace slag was drained and left to rest for four weeks, it was able to increase its P removal capacity by 74%.

By this regeneration method the P saturation value was increased from 1.35 to 2.35 g of P kg⁻¹. None of the experiments carried out in this thesis used such long resting periods for the materials tested. Completely drained conditions occurred only for hours up to days in the experiments performed in Papers II and VI. More studies are needed on the effects of resting periods and how the contact between solute and solid can be enhanced, as well as how to detect preferential flows. The latter can be performed by using stable isotopes and tracers (Ronkanen & Kløve, 2007).

Transformation and removal of nitrogen

The N dynamics were monitored in the experiment using municipal wastewater for a period of 67 weeks (Paper IV). The removal performance of NH₄-N was over 90% in all columns regardless of filter material. Only two materials (Polonite and CSVC) were able to reduce the total inorganic nitrogen (TIN) content over the whole experimental period, by 17.7% and 9.8% respectively (TIN = Σ NH₄-N, NO₃-N, NO₂-N).

The other filter materials leached NO₃-N and NO₂-N, particularly the amorphous slag. Three filter media (BFS, Polonite, sand) were tested for their ability to remove nitrogen from landfill leachate. As shown in Table 1, TIN was reduced in various amounts by the media used. Polonite achieved the highest removal efficiency (average 18%).

The concentrations of NH₄-N and total inorganic nitrogen in the influent wastewater were on average 26.6 ± 5.5 mg L⁻¹ and 26.9 ± 12.6 mg L⁻¹, respectively. The influent landfill leachate had the corresponding values of 104.5 ± 17 mg L⁻¹ and 105.9 ± 29 mg L⁻¹.

An NH₄-N effluent concentration of below 1 mg L⁻¹ was recorded rather soon after the start of the experiment (Paper IV). The temporal variation in NH₄-N concentration in the effluent of CSVC slag represents the overall pattern found, with the exception of the two Polonite columns (3 and 7). In these latter columns Polonite exhibited a much slower development of NH₄-N transformation and stable, low effluent values as in the other columns were not fully reached.

However NH₄-N was reduced to less than 7 mg L⁻¹ after the wastewater had percolated through the Polonite filter material for a few weeks of operation (Fig. 10). The concentration of NO₂-N in influent wastewater was 55.5 µg L⁻¹ (range 1.8-290.3 µg L⁻¹) and it remained at this low level in effluents from all columns except for those filled with Polonite, where it was 2.93 mg L⁻¹. Nitrate was also quite low in the influent wastewater (0.25 mg L⁻¹, range 0.013-0.49 mg L⁻¹), but on the other hand increased markedly after passing through the materials, resulting generally in concentrations of between 0.03 and 87.6 mg L⁻¹ in the effluents.

The observed decrease in effluent NH₄-N concentration in columns 1, 2, 4, 5, 6 and 8 was obviously attributable to microbial immobilisation and nitrification, i.e. transformation processes rather than removal. At pH values above 9.3, NH₄⁺ can be converted into NH₃. This NH₃ volatilisation could have occurred in the columns with Polonite and amorphous and crystalline slag, i.e. columns 3, 4, 5, 7 and 9.

Table 1. Total inorganic nitrogen (TIN = ΣNH₄-N, NO₃-N, NO₂-N) in influent, and sorption and removal efficiencies by three media (Paper I).

	Influent (mg L ⁻¹)	Sorption (g kg ⁻¹)			Removal (%)		
		Sand	Polonite	BFS	Sand	Polonite	BFS
TIN	105.9±29	0.25	1.9	0.55	4±22	18±15	8±22

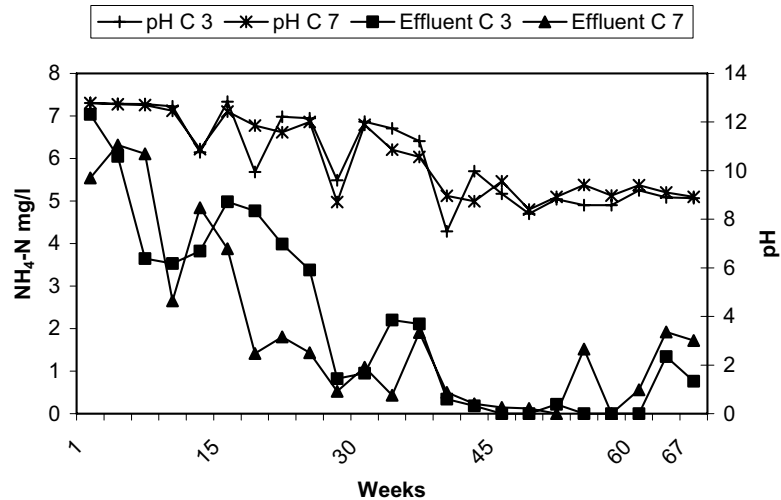


Fig. 10. Temporal variation in the ammonium concentration at the exit of the Polonite columns (C3, C7) and pH of the effluent (influent concentration $26.6 \pm 5.5 \text{ mg L}^{-1}$; influent pH range 8.18-9.28). The samples represent the whole experimental period of 67 weeks (Paper IV).

The total N content was highest in the 0-5-cm layer of all materials, as was found for P too (exemplified in Fig. 11). This was accompanied by a high total carbon (C) content particularly in the surface layers of sand, Polonite and crystalline slag.

The highest C content in the whole filter mass at termination of the experiment was found for opoka. The vertical N distribution differed between materials. The differences were obviously related to particle size distribution and thereby to hydraulic conductivity of each material.

Pell *et al.* (1990) clearly showed a general pattern of decreasing numbers of bacteria with depth in a sand filter, with bacteria constituting a large part of the biomass in the surface layer. This in fact was probably true for all the filter materials studied here but was more accentuated in the most alkaline types.

In the case of Polonite, bacterial activity and mineralisation could have been expected only in the surface layer, where pH was lower. The loss of about 18% TIN from Polonite columns during the experiment with municipal wastewater was caused by volatilisation rather than denitrification.

This was also probably true for the loss observed in the columns feed by landfill leachate. However adsorption and cation exchange are also possible explanations for that removal. A comparison of TIN in the effluent when pH was above and below 9 revealed that the loss was associated with the high pH range. The reactive filter materials obviously create an alkaline environment that inhibits denitrification even in the superficial layer, where the biofilm could create a biologically active part of the filter. Unfavourable conditions for denitrification in sand and limestone were caused by the mode of intermittent discharge of wastewater to the columns and the unsaturated flow. This was intended to create oxygenated conditions in the matrix of each material throughout the whole experimental period.

It is known that the presence of competing ions and organic matter can significantly reduce the removal of $\text{NH}_4\text{-N}$ (Chen *et al.*, 2002) but the role of organic carbon for nitrogen removal in reactive bed filter materials has to be further investigated.

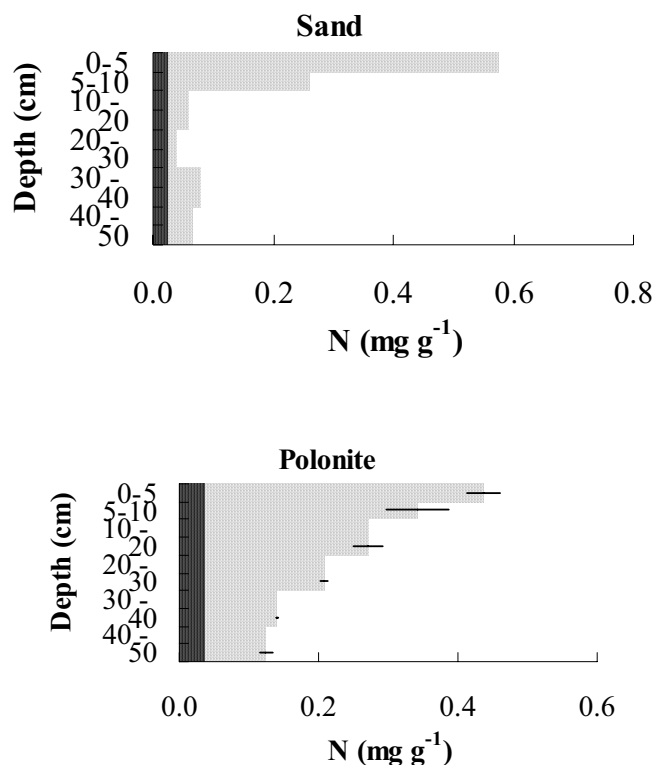


Fig. 11. Initial N content in the sand and Polonite® (dark spotted area) and N enriched to different layers (light spotted area) after 67 weeks of wastewater treatment by infiltration. Bars indicate \pm SE where columns were duplicated (Paper IV).

Metal removal

The metal removal capacity of the filter materials was assessed in two experiments (Papers I, V). In Paper I, the purpose was to test materials able to remove metals from landfill leachate, while Paper II analysed the metal removal by filter materials aimed for P removal and recycling from domestic wastewater.

Polonite, sand and BFS, all of them mixed with peat, were used for treating landfill leachate. The best performance was found for Polonite, where Mn, Fe, Zn and Cu were removed to 99%, 93%, 86% and 67%, respectively. Breakthrough curves are presented in Figs. 12 and 13.

Hydroxide precipitation was suggested as the process for the high removal efficiency of metals by Polonite, forming insoluble precipitates in the bed filter. The precipitation is primarily dependent upon two factors, namely the concentration of the metal and the pH of the water. Chemical treatment plants normally operate at a pH of approximately 9 when multiple metals are present. The superior removal capacity of the Polonite filter is probably a combination of several factors, among which precipitation is the most important. The BFS showed good removal efficiency for Cu (66%), Ni (19%) and Mo (16%). Sand did not demonstrate a promising removal capacity for any of the elements studied with the exception of Cu (25%).

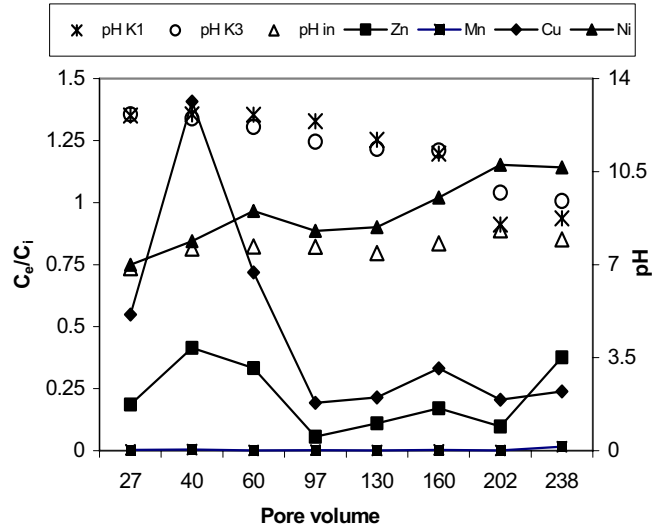


Fig. 12. Breakthrough curves (Zn, Mn, Cu, Ni) and pH data for effluent from columns filled with Polonite. C_e/C_i = ratio for effluent and influent mean concentration (Paper I).

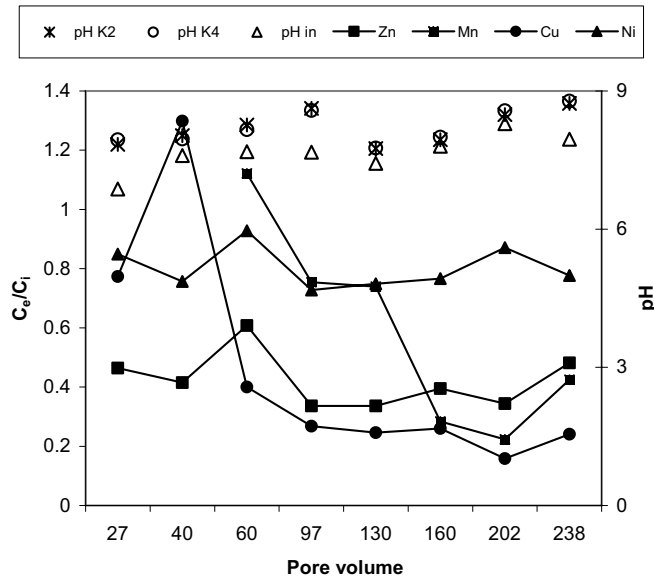


Fig. 13. Breakthrough curves (Zn, Mn, Cu, Ni) and pH data for effluent from columns filled with BFS. C_e/C_i = ratio for effluent and influent mean concentration (Paper I).

Leaching of several elements occurred from the filter media (*e.g.* Mn from BFS). Most pronounced was the release of silica from Polonite and BFS. Calcium was also leached from Polonite but after 60 pore volumes of treated leachate, the release of Ca decreased, while Si release rapidly increased.

The changes in release of Si and Ca versus normalised flow for the Polonite can be related to the weathering of the solid material and the presence of wollastonite. According to other studies, the latter material is efficient for heavy metal removal from aqueous solution (Ni, Pb, Cd) (Sharma *et al.*, 1990; Yadava *et al.*, 1991; Sharma, 1995). The removal of different elements was suggested to be a combination of several factors, *e.g.* precipitation, ion exchange and adsorption.

The apparent propensity for accumulating metals from domestic wastewater followed the order Polonite > ASC > opoka > CSC > limestone > CSVC > sand. All materials removed Fe with an efficiency of around 60%. This element was actually the only one removed by the sand. Zinc was removed by all materials, except the sand, in the range 53-83%. Only the three blast furnace slags (ASC, CSC, CSVC) were able to remove Ni. Polonite removed over 98% of dissolved Mg and Mn in the wastewater, while fairly efficient removal of Cu was demonstrated by the ASC. Analyses of metal concentrations in the leachate (effluent) from columns showed significant ($p < 0.05$) release, *i.e.* an increase in concentration, of some elements from sand, CSC, ASC and CSVC.

Sand released Cu and Zn, while CSC and ASC showed increased concentrations of Mg. The very coarse crystalline slag (CSVC) exhibited a large loss of Mn, although only in the beginning of the experiment.

The wastewater trickles through the filter matrix and colloidal matter can attach to the surface of each mineral particle (Yao *et al.*, 1971). Bacteria create a biofilm where microbial adsorption of heavy metals can occur (Goyal *et al.*, 2003) and where adsorption and precipitation processes can also retain the metals. The increasing concentrations of dissolved metals in the effluent can be the result of leaching from the materials.

The blast furnace slag material, from which Mg and Mn were obviously released, demonstrates this in both experiments.

The presence of peat in the trial with landfill leachate had an effect on the removal of several metals. The sand did not remove metals at all from domestic wastewater.

It is obvious from Table 2 that wide variations occurred in metal concentrations, probably caused by the sources of pollution (Moriyama *et al.*, 1989; Vinnerås *et al.*, 2006).

In fact, metal concentrations in influent were lower than typical effluent discharge limits with the exception of Cu (Metcalf & Eddy, 2003). Thus the wastewater used in the column experiment had very low dissolved metal concentrations, similar to those expected to be found in wastewater from single houses.

Table 2. Influent and column effluent concentrations of elements. The units are $\mu\text{g L}^{-1}$, unless otherwise stated (average, SD).

Element	Influent	Column effluent						
		Sand	Opoka	Polonite**	CSC**	ASC	CSVC	Limestone
Ba	62.2±21.3	68.4±12.6	39.7±12.3	90.4±24.7	34.7±8.9	45.3±9.9	32.6±7.6	53.7±26.9
Cr	1.71±0.52	2.71±3.52	1.51±0.34	26.8±32.6	1.68±0.53	1.55±0.5	1.75±0.52	1.72±0.59
Cu	16.2±10.8	26.4±9.6	18.1±6.4	13.6±7.4	15.01±14.1	11.6±4.8	15.7±5.5	15.0±8.6
Mg*	6.26±0.66	6.88±1.86	7.68±1.25	0.09±0.06	32.1±5.99	28.4±10.3	7.26±0.86	26.3±7.03
Mn	10.9±3.1	31.2±32.2	4.21±4.0	0.24±0.19	29.3±65.3	1.77±2.15	82.6±203.1	6.04±6.7
Ni	4.64±1.6	10.1±5.7	5.52±1.58	6.37±4.15	3.26±0.77	3.11±0.49	3.48±1.34	5.79±5.01
Zn	37.5±11.8	221.3±164.5	11.8±5.5	14.2±10.2	6.57±1.96	7.47±1.63	9.54±2.86	17.36±23.5

** Average and SD for duplicate materials

The treatment preceding the filtration through the column materials probably removed the majority of metal species. These can be trapped by gravity settling of suspended solids in a primary clarifier, e.g. septic tank (Artola *et al.*, 1997; Wang *et al.*, 2006).

Removal mechanisms- heavy metals and phosphorus

The studies on removal mechanisms for metals and P are presented and discussed in the following.

Heavy metals

The filter materials used in the experiment with municipal wastewater removed heavy metals (Paper V). According to speciation calculations with Visual MINTEQ, a very large fraction of dissolved copper in the column leachates was bound to DOM (the median value was 99.99%). The corresponding figures for Cr(III) (assuming that all dissolved Cr existed as trivalent chromium), Zn and Ni were 93, 59 and 24% respectively. Other ions such as Mn, Ca and Ba were less strongly bound to DOM. Dissolved chromium was in most cases slightly lower than predicted by equilibrium with Cr(III) hydroxide. For copper, the results suggest that CuO or a similar phase in the Polonite columns, but not in the other columns, might have controlled the dissolved Cu. Dissolved Zn was very much undersaturated with respect to any Zn mineral phase, suggesting that the processes controlling Zn are likely to involve adsorption/desorption and weathering processes. Lead was far from equilibrium with any mineral phase. Magnesium was close to equilibrium with brucite in the Polonite columns early in the sampling period, suggesting that Mg removal by Polonite involved the precipitation of this mineral. However in the latter part of the experiment there was undersaturation also in the Polonite leachates, despite a continued very strong Mg removal in these columns (> 95% throughout the experiment).

The mechanisms involved in metal retention by blast furnace slag are thought to be ion exchange with calcium on particle surfaces and precipitation on $\text{Al}(\text{OH})_3$ and SiO_2 (Dimitrova & Mehandgiev, 2000). Sorp-

tion/precipitation to sulphuric compounds in blast furnace slag may also be important. However, sulphur was leached in great amounts from blast furnace slag columns in the beginning of the experiment with municipal wastewater (Paper V), as previously observed in the column experiment with landfill leachate (Paper I).

The dissolution of alkaline minerals, particularly in the case of Polonite, can increase the pH of the percolating wastewater above solubility point, which causes metals to precipitate, probably as metal oxides and metal carbonates (Petrovic *et al.*, 1999).

The organic ligands present in wastewater can bring about either enhanced, suppressed or unaffected adsorption of metal ions on clay minerals (Abollino *et al.*, 2008); at low pH an enhanced effect is often seen, whereas at neutral to high pH (as in the present investigation) DOM is likely to suppress metal sorption, especially for Cu. Jönsson *et al.* (2006) studied the sorption processes in the goethite system and found that the presence of Cu(II) resulted in an increased adsorption of DOM at high pH.

Phosphorus

Unused and spent filter materials (Filtration P, Polonite, WCBFS, wollastonite) were characterised using ATR-FTIR (Paper III). All four unused samples contained peaks at ~ 1420 and 870 cm^{-1} , characteristic of the carbonate anion in calcite (Fig. 14).

The presence of wollastonite ($\beta\text{-CaSiO}_3$) in both Polonite and natural wollastonite was indicated by peaks near 1056, 960, 902 and 680 cm^{-1} (Atalay *et al.*, 2001). The observation that wollastonite is an important constituent of Polonite is in agreement with earlier studies employing chemical dissolution techniques and X-ray diffraction (Eveborn, 2003; Brogowski & Renman, 2004).

The unused Filtra P sample was dominated by a number of peaks related to sulphate minerals such as gypsum and ettringite. These minerals were present in large amounts in the unused sample but had disappeared completely in the sample that was in prolonged contact with the synthetic solution.

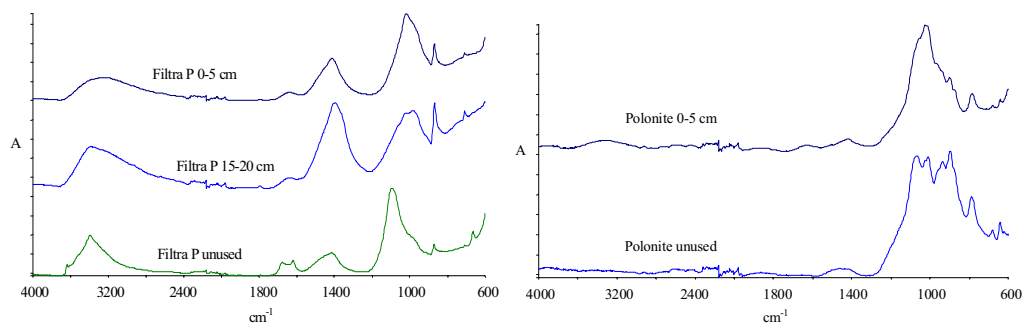


Fig. 14. ATR-FTIR spectra of used and unused Filtra P and Polonite.

Other calcium phosphate compounds were not indicated with the exception of amorphous tricalcium phosphate, which appeared as a single peak near 1025-1030 cm^{-1} .

In an earlier study with other filter materials in which equilibrium was obtained only from supersaturation, it was hypothesised that hydroxyapatite (HAp) was formed (Johansson & Gustafsson, 2000). However, the data presented here are not in agreement with this hypothesis, because $\text{PO}_4\text{-P}$ in the used filter materials was more soluble than would be expected from this equilibrium. Most of the samples were supersaturated with respect to HAp. Two other candidates in controlling PO_4 solubility are DCPD (dibasic calcium phosphate dihydrate; $\text{CaHPO}_4 \times 2\text{H}_2\text{O}$) and DCP (dibasic calcium phosphate, CaHPO_4). However, most samples were undersaturated with respect to these phases, although the most acid Filtra P samples seemed to be in equilibrium with DCP or DCPD. At high pH, however, the samples were far from equilibrium, indicating that the results could not be resolved easily in terms of equilibrium with respect to DCP or DCPD. Many of the samples were relatively close to the solubility line of OCP (octacalcium phosphate, $\text{Ca}_4\text{H}(\text{PO}_4)_3$), indicating that OCP might be involved in determining $\text{PO}_4\text{-P}$ solubility.

Finally ATCP, with stoichiometric composition $\text{Ca}_3(\text{PO}_4)_2$, may also control $\text{PO}_4\text{-P}$ solubility.

As shown in Fig. 15, many samples were close to equilibrium with the less non-crystalline ATCP termed ACP2 (Christoffersen *et al.*, 1990). Moreover, the pH dependence of the ion activity products was in better agreement with ACP2 than with OCP, which suggested that solubility control by ACP2 (or ATCP) was slightly more likely although a prominent role for OCP could not be ruled out from these observations only.

The observation that a soluble Ca-P phase, probably ATCP, had accumulated in the filter materials suggests that at least part of the $\text{PO}_4\text{-P}$ is readily available to plants. However, only between 3.5 and 18% of the accumulated $\text{PO}_4\text{-P}$ was readily dissolved in the batch experiments. There may be several reasons for this, but one possibility is that part of the $\text{PO}_4\text{-P}$ had crystallised to a slightly less soluble phase (such as HAp). Thus more detailed spectroscopic studies need to be performed to fully elucidate the solid-phase speciation and reactivity of the accumulated phosphates.

Recycling of filter materials back to agriculture

The possibility of recycling used filter materials together with their accumulated contents of P and N back to agriculture as fertilisers and soil amendments was of interest in several of the studies (Papers II, III, IV, VI).

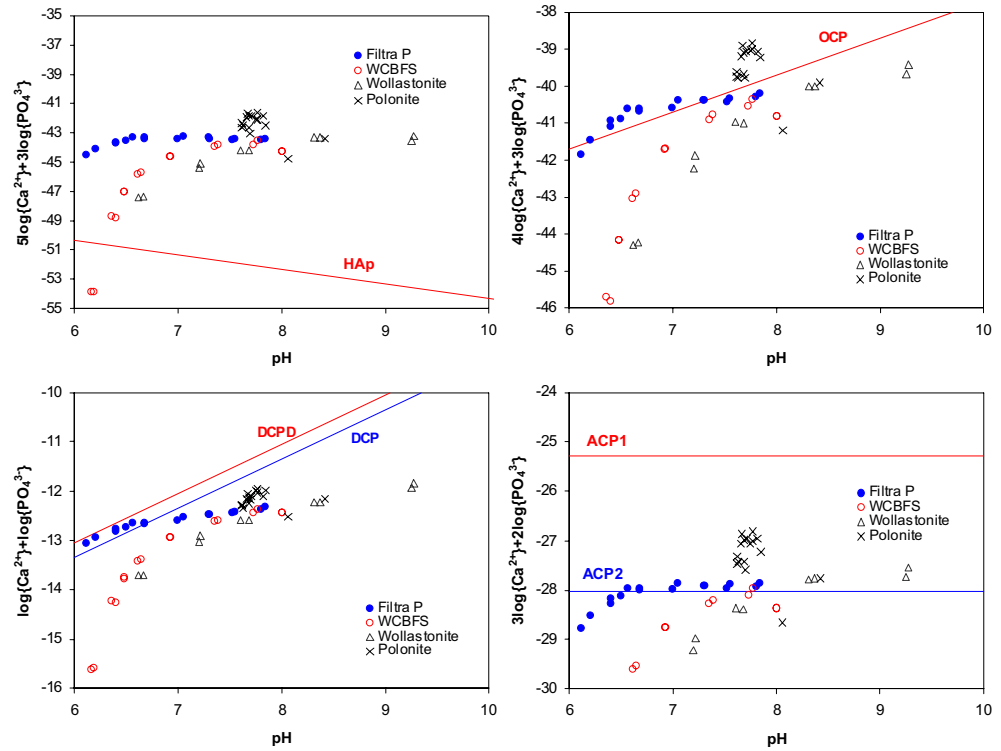


Fig. 15. Solubility diagrams for the 0-5 cm layer of the used filter materials. The points represent the calculated solution activities in the batch experiment extracts. Data points above the lines indicate supersaturation.

A particular column experiment was designed for testing the capacity of materials for use as fertilisers (Paper II). After termination of the experiment, the P-enriched filter materials were tested for their fertiliser effectiveness in a pot experiment where barley (*Hordeum vulgare* L.) was cultivated. The application of 0.03 g P per pot as K_2HPO_4 produced the highest yield, closely followed by P sorbed to slags from the wastewater filters (Fig. 16). This can be attributed to a fast release of loosely bound P from the amorphous and crystalline slags used in our experiment. Yields from treatments with P sorbed to Polonite were significantly lower. Yields with P sorbed to opoka were even lower, despite the application of K_2HPO_4 , but higher from soils that had not had fertiliser added (Fig. 16).

This indicates that P sorbed to opoka can be utilised by barley, although not as readily as P sorbed to slag or P in chemical fertiliser. The low diffusion of P, as previously reported for P transport in soils (*e.g.* Hylander & Ae, 1999), may explain the reduced availability of P in opoka compared with slag. In this regard, Polonite represents a condition somewhere between opoka and slag.

This is because it originates from opoka and has been thermally treated to change its physico-chemical properties, thereby activating its sorption capacity (Brogowski & Renman, 2004).

In the sand filter, the fertiliser effectiveness of accumulated P was also lower when compared with P applied as K_2HPO_4 . The sand was a washed quartz sand, which is inert.

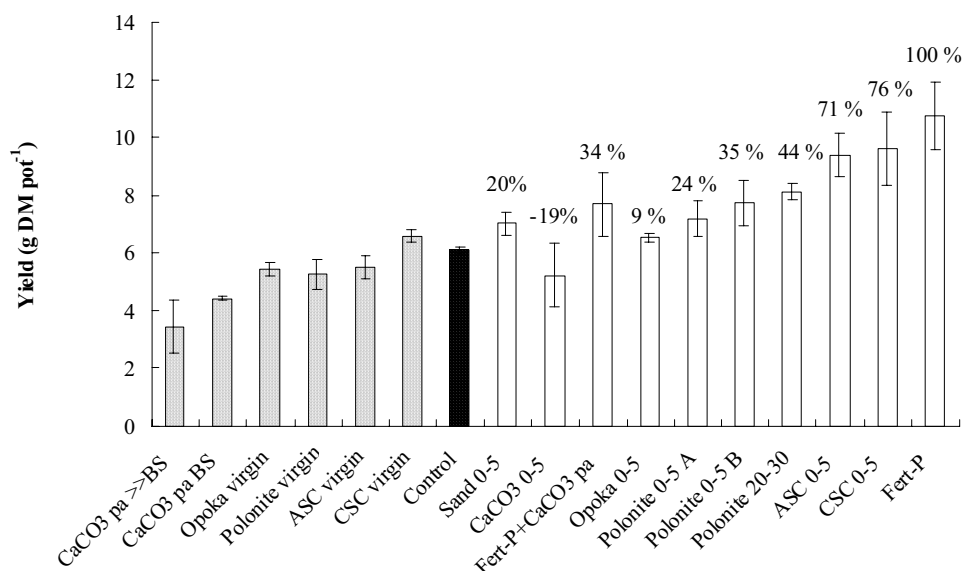


Fig. 16. Yields (average and 95% confidence interval) of barley grown in soil treated with different filter materials containing P (white stacks) or with materials without P (gray stacks). P fertiliser effectiveness (%) in relation to standard P fertiliser is indicated by figures above the stacks (Paper II).

Therefore the P in the sand filter, retained because of the physical filtering capacity of sand, was expected to be mainly in organic form. This filtering was confirmed by increased contents of C and N in the surface layer (Fig. 17). Compared with inorganic orthophosphate, organic P had a significantly lower plant availability in the short term (i.e. days to weeks) when applied to the studied soil.

This can also explain the difference in fertiliser effectiveness between the surface layer and deep layer Polonite (Fig. 16).

Despite the fact that P content in the surface layer was twice that of other horizons, yield and fertiliser effectiveness were higher for barley grown in the deep layer material. All filter media probably retained organic P at the surface. The pH of the material from the surface layer was lower than that from deeper layers. Plant production can be affected by the pH of filter materials as shown by Cucarella *et al.* (2007).

As demonstrated in Figure 16, relative effectiveness was negative or low for P sorbed by limestone and opoka. This was caused by the alkaline characteristics of these materials and the large amounts needed to adsorb sufficient P, as previously explained. Therefore limestone and opoka should only be considered as filter materials if they are to be used in soils with extremely low soil pH after being saturated with P. Slag materials, however, are suitable to use in moderately acidic soils, where their relative effectiveness can be assumed to be at least 70% of commercial P fertiliser during the first year, and possibly more in subsequent years.

The observation that a soluble Ca-P phase, probably ATCP, had accumulated in the filter materials suggests that at least part of the P is readily available to plants (Paper III).

With this evidence from pot and batch experiments, it seems likely that used filter materials from wastewater treatment may contain readily soluble Ca phosphates such as ATCP and DCP.

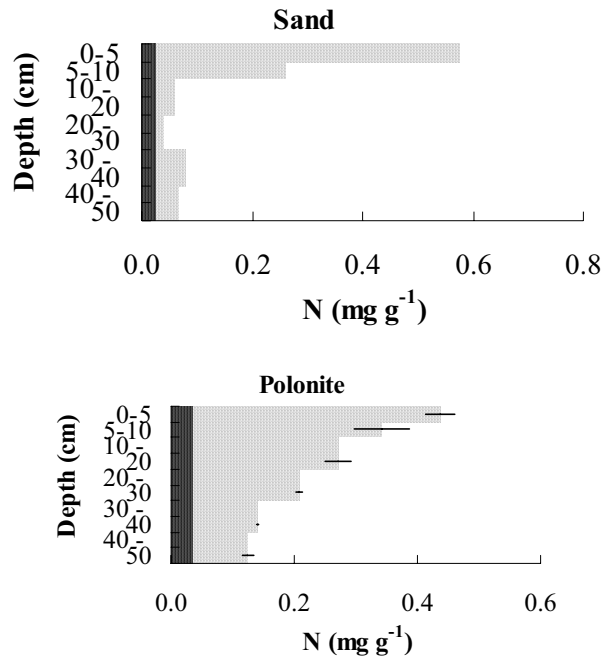


Fig. 17. Initial N content in the sand and Polonite (dark spotted area) and N enriched to different layers (light spotted area) after 67 weeks of wastewater treatment by infiltration. Bars indicate $\pm SE$ where columns were duplicated (Paper IV).

This is supported by results from plant uptake experiments showing that the retained P in similar filter materials is easily accessible (Hylander & Simán, 2001; Kvarnström *et al.*, 2004). However, filter materials cannot be expected to replace industrial P fertilisers, at least not in the short-term, because of their low contents of P.

The alkaline properties and the content of micro-elements, such as in the Polonite, are still of interest for the recycling of materials as soil amendments (Cucarella *et al.*, 2008). The Polonite material used in both on-site wastewater treatment and the column experiment showed heavy metal concentrations that are much lower than the European limits for sludge disposal. Hence the low content of heavy metals in the filter materials will not interfere with their use as a fertiliser or soil amendment. However it must be pointed out that the wastewater used in the experiments had very low dissolved metal concentrations.

Bed filter lifetime for P removal

The Polonite used in the full-scale filter well in a volume of 800 L (560 kg) was a sufficient amount for treating approximately 70 m³ of domestic wastewater, i.e. 11 L (8 kg) were required per cubic metre (Paper IV). These results can be compared with the expected lifetime of the Filtralite P material as calculated by Heistad *et al.* (2006), where a total filter volume of 6 m³ was expected to meet the required effluent limit of 1.0 mg P L⁻¹ for 5 years. Based on the data given by Heistad *et al.* (2006), it can be calculated that 1 m³ of wastewater could be treated by filtration through approximately 5 L of Filtralite P. This is half the amount required for treatment to approximately the same effluent limit by Polonite. A comparison of expected maximum P sorption capacity has revealed that Polonite has a much higher capacity than Filtralite P (Brogowski & Renman, 2004; Ádám *et al.*, 2006; Cucarella & Renman, 2008).

Hence Polonite could be expected to have shown better removal capacity in the full-scale treatment system tested. There are several possible explanations for the observed lowered capacity.

The properties of the material can vary depending on the manufacturing process. The Polonite used in the experiment had a starting pH of 11.9, compared with the normal pH of 12.5 for this product.

Polonite is normally produced in the particle size range 2-5.6 mm but it was observed that the material used in the filter well contained coarser fractions. Finer fractions of Polonite give higher P sorption capacity (unpubl. data). The loading of organic matter to the filter was high during the first 18 weeks of operation because of inadequate pre-treatment in the septic tank. This improved when the wastewater was discharged to the filter through a biofilter but the effect of dissolved organic matter could have persisted, which is suggested to reduce the P sorption capacity of many alkaline filter materials.

Plotting the removal capacity against pH for the filter well experiment revealed a good correlation and a strong relationship between $\text{PO}_4\text{-P}$ removal and pH for Polonite. Other studies of alkaline filter materials have shown the same relationship, although in batch experiments (Ádám *et al.*, 2007).

The pH could be an easy parameter to use for decisions on replacing the filter material in the filter well. Hence a certain pH could correspond to a minimum effluent concentration or removal capacity according to local discharge limits. In Norway (Heistad *et al.*, 2006) and Sweden (www.avloppsguiden.se), the effluent criterion is normally a total P concentration of 1 mg L^{-1} . This value corresponds to a total P reduction of 90%. The data presented here for the full-scale treatment system show that effluent pH cannot indicate when a reactive bed filter has to be exchanged. The filter material Polonite had an extraordinarily high P removal capacity during two-thirds of the operation time, while a gradual breakthrough developed during the last one-third. This could have

been expected for the Nordkalk Filtra P as well, but it clogged and disintegrated during the experiment performed (Paper III). This will limit its practical lifetime in field applications.

For Polonite it is suggested that 1-2 kg would be required as a design volume for treatment of one cubic metre of wastewater. However, other parameters such as nitrogen and BOD have to be considered too and the Polonite material and filter well design, including pre-treatment steps, have to be further improved. Drizo *et al.* (2002) argued that allowing the system to rest for a certain time could enhance the P removal of slag-based systems. Short resting periods were applied in the filter beds studied in the present thesis, although clear advantages for the P removal were not observed. In the case of strong alkaline materials, resting periods can also increase the interference with atmospheric CO_2 , leading to the formation of CaCO_3 (cf. Drizo *et al.*, 2002). The RBF technology studied in this thesis has already been applied for treatment of wastewater in summer cottages and part-time residences. This means that longer resting periods will occur and the question is how these periods will affect the longevity of a filter material such as Polonite. Further studies should be performed on the effect of operating and resting periods, and the integration of drying and wetting periods for optimal removal efficiency.

CONCLUSIONS

The research in this thesis, with a combination of batch, long-term column and experiments with a full-scale treatment system, demonstrated the potential of using reactive filter materials for the treatment of wastewater. The removal of metals and nutrients by different materials was shown to be influenced by many factors, such as pH, chemical composition of material, element and organic matter competition in wastewater. Experiments with wastewater are more difficult to interpret than those performed with aqueous solutions. The differences in the results obtained by investigators of reactive filter materials arise from the fact that wastewater, particularly landfill leachate, has a complex

composition, which can interfere with the adsorption of metals. Hence, this suggests that it is not possible to draw conclusions of a general or fundamental nature on the removal mechanisms involved.

The conclusions of this thesis are as follows:

- Polonite and Nordkalk Filtra P are promising filter materials for removal of $\text{PO}_4\text{-P}$ from household wastewater, maintaining a $\text{PO}_4\text{-P}$ removal efficiency of $>95\%$. Water-cooled blast furnace slag and natural wollastonite were also able to remove $\text{PO}_4\text{-P}$, although less efficiently.
- Investigations of the role of the feed solution applied to the filter material showed that synthetic wastewater loading in small columns led to better long-term P removal capacity than real wastewater in a full-scale, bed filter trial. The Polonite in the column systems examined was still 'active' at the end of the experimental period, showing no clear breakthrough tendency, while this clearly occurred in the full-scale bed filter system.
- Cyclic loading of wastewater to the filters interspersed with periods of saturation/drying did not improve P removal capacity. However, more studies are needed in both column and full-scale experiments.
- None of the six filter materials tested here showed good potential for removing total inorganic nitrogen (TIN). Ammonium-N, a dominant N component in the wastewater, was transformed in the filter beds to $\text{NO}_3\text{-N}$. Polonite removed 17.7% of the influent nitrogen, which was mainly associated with losses through volatilisation. A similar removal capacity was found in the experiment using landfill leachate. Although efficient for P removal, alkaline filter materials cannot be considered suitable bed components for N removal in engineered wetlands and compact filter wells. Instead, dual treatment systems should be developed where e.g. zeolites for $\text{NH}_4\text{-N}$ removal could be included.
- Batch experiments and ATR-FTIR investigations indicate that amorphous tricalcium phosphate (ATCP) forms in the materials. This means that at least part of the accumulated $\text{PO}_4\text{-P}$ is readily available to plants. However, since only up to 18% of the accumulated $\text{PO}_4\text{-P}$ was readily dissolved in the experiments, the possibility cannot be excluded that part of the phosphorus had crystallised to slightly less soluble phases.
- Polonite used in wastewater filters can be recycled as a combined fertiliser for plant production and liming agent on acidic soils. While P retention capacity of blast furnace slag is lower than that of Polonite, it nevertheless shows greater promise in P fertiliser effectiveness. The low content of heavy metals in the filter materials will not interfere with their use as a fertiliser or soil amendment.
- Two long-term column experiments showed that dissolved metals in wastewater (domestic and landfill leachate) were removed in various amounts by the filter materials studied. The kind of blast furnace slag (BFS) used in our investigation did not show good removal efficiency over the whole contaminant spectrum. The reactive medium Polonite did not reach the saturation point of many of the major contaminants. A drawback of the studied reactive media was the release of certain elements, such as Cr, from the BFS and Polonite filter matrix. According to speciation calculations with Visual MINTEQ, a large fraction of dissolved Cu, Cr(III), Zn and Ni in the column leachates were bound to DOM.
- The pH proved not to be a simple parameter for determining when the filter material should be replaced. Instead, the P removal longevity of re-

active filter materials can be estimated from the volume of wastewater treated if a water meter is installed in the house.

- A filter facility designed as a multi-layer unit of several reactive media could be a possible solution for more effective, broad-spectrum removal of pollutants. Prior to full-scale application, matrix selection, filter design and operational procedures must be developed to ensure appropriate hydraulic conditions and to facilitate periodic media replacement and possible recovery.

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I



An evaluation of reactive filter media for treating landfill leachate

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Abstract

A laboratory bench-scale column study was conducted to evaluate permeable reactive filter materials as a new method for removal of heavy metals and inorganic nitrogen from landfill leachate. Mixtures of sand and peat, blast-furnace slag (BFS) and peat, and Polonite® and peat were tested by loading columns with leachate collected from a pond at Tvetaverket Landfill, Sweden. Sand, peat and Polonite® represent natural materials. BFS is a by-product from steel-works. The metal treatment efficiencies of the media were assessed and Polonite® was found to perform best, where Mn, Fe, Zn and Cu concentrations were removed by 99%, 93%, 86% and 67%, respectively. This material was also able to reduce inorganic N by 18%. The BFS showed good removal efficiency for Cu (66%), Zn (62%), Ni (19%) and Mo (16%). The sand–peat mixture did not demonstrate a promising removal capacity for any of the elements studied with the exception of Cu (25%). The removal of different elements was suggested to be a combination of several factors, i.e. precipitation, ion exchange and adsorption. Prior to full-scale application of reactive filters at a landfill site, matrix selection, filter design and operational procedures must be developed.

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Keywords: Filter media; Column experiment; Metal removal; Landfill leachate; Sorption

1. Introduction

Landfilling is a widely used method for the disposal of wastes from households and industries. One of the main problems with landfill management is to find efficient treatments for the large quantities of polluted leachate. Landfill leachate contains high amounts of organic compounds, ammonia and heavy metals and is identified as a potential source of ground and surface water contamination (Christensen et al., 2001).

One method of treating landfill leachate is to establish constructed wetlands for nitrogen removal (Mula-moottil et al., 1999) or hybrid systems for both nitrogen and heavy metal treatment (Mæhlum et al., 1999; Robinson et al., 1999; Sataj et al., 1999; Horne, 2000; Renman and Kietlińska, 2000). Many other methods exist for leachate treatment, but those using large quantities of chemicals and electric energy are not dealt with here. Instead, the focus is on eco-technological treatment methods since landfill operators seek alternatives that can be applied and managed at a low cost, and can be efficient enough to fulfill landfill operation requirements.

Landfills are often located in regions where high levels of pollutant removal are required due to the

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sensitivity of receiving waters. Space constraints may limit the construction of large retention ponds or wetlands, and hence more effective contaminant removal techniques are required. Therefore we argue for the introduction of filter systems using reactive media prepared from natural minerals or from by-products of steel production, such as blast-furnace slag. Such filters could be a possible solution for the removal of metals and could be used as a pre-treatment step before leachate handling for nitrogen removal in a constructed wetland (Kietlińska, 2003). Filter materials saturated with heavy metals have to be replaced and safely stored. An alternative method could be to leach out the metals with acids under controlled conditions and subsequently concentrate the leachate for further work.

Several low-cost filter materials for removal of heavy metals have been investigated (Bailey et al., 1999) and these could be included in systems based on filter-bed techniques (Kängsepp et al., 2003). Laboratory column and batch experiments have been performed with zeolites to assess their sorption of ammonium nitrogen (Papadopoulos et al., 1996; Demir et al., 2002).

In the present study, we tested three filter media for their ability to remove selected elements, such as heavy metals and nitrogen from landfill leachate. Sand, blast-furnace slag (BFS) and Polonite[®] were used in a bench-scale dynamic column experiment. The determination of contaminant saturation potential of a material in a long-term column study is considered to provide a good indicator of its capacity to retain elements and could serve as a parameter for estimating the lifetime of full-scale systems (cf. Ajmal et al., 2001; Drizo et al., 2002). Since leachate pollutants are not associated with particles, at least after pre-treatment in ponds, devices that use physical filtration (e.g. sand filters) are not expected to remove contaminants.

2. Methodology

2.1. Description of materials

Polonite[®] is a product manufactured from the cretaceous rock opoka and intended for use in wastewater treatment (Brogowski and Renman, 2004). This material is known for its high sorption capacity of soluble phosphorus and usefulness for recycling of nutrients in agriculture (Hylander and Simán, 2001; Renman et al., 2003). The major components of Polonite[®] are SiO₂ (39.4%), CaO (42%), Al₂O₃ (4.3%) and Fe₂O₃ (2%) (Brogowski and Renman, 2004). Contents of Cr, Cu, Ni and Zn in the virgin material were 58.6, 13.0, 26.9, 121.3 ppm, respectively. Five samples of this material were analysed by X-ray diffraction, and in all of them, four dominating crystalline phases were found: wollas-

tonite (CaSiO₃), quartz (SiO₂), calcite (CaCO₃) and albite (NaAlSi₃O₈) (results not shown).

BFS is an industrial by-product resulting from the process of extracting iron from iron ore at steelworks. A manufactured product from Merox AB in Oxelösund, Sweden was used in our column experiment. Fast cooling of the melted blast-furnace slag in water results in a light, glassy, granulated product. This slag is characterized by high amounts of SiO₂ (36.2%) and CaO (35%). It includes other components such as MgO (13.4%) and Al₂O₃ (10.6%) (Data from Merox AB). Contents of Cr, Cu, Ni and Zn in the virgin material were 46.4, 10.5, 26.3, 87.1 ppm, respectively.

Sand used in the experiment was taken from a gravel-pit 20 km SW of Södertälje, Sweden. The main components of the sand were SiO₂ (69.3%), Al₂O₃ (13.4%), K₂O (3.4%) and Fe₂O₃ (3.1%). Contents of Cr, Cu, Ni and Zn in the virgin material were 35.8, 20.6, 32.6, 49.4 ppm, respectively (analysed in this study). The peat used was a manufactured product from Hasselfors Garden AB: a natural *Sphagnum* peat without any additives, moderately decomposed (humification degree H3-H4) and with a density of 70 kg m⁻³.

The particle size of the filter materials was 2–5.6 mm. The pure materials Polonite[®], BFS, sand and peat had a pH of 12.62, 9.13, 6.25 and 3.0–4.0, respectively.

2.2. Column experiment

Five columns (K0–K4) made of PVC, each having an overall height of 60 cm and an internal diameter of 9.8 cm, were used for the experiment. All columns were filled with filter material to a height of 50 cm. Polyester texture was used to cover the material in each column so as to prevent media scouring and clogging during leachate addition. Peat, with moisture content of 77.5%, was mixed with the mineral substrates in a ratio of 1:4 by volume. Ca-rich materials can react with the sulphate commonly found in leachate and create gypsum, but by including an organic component this effect can be reduced. Another reason for including peat in the filter matrix was to decrease the saturated hydraulic conductivity since the mineral fractions were coarse. Peat itself can act as an adsorbent of heavy metals but has not been found to be capable of removing metals from landfill leachate to acceptable levels (Ringqvist et al., 2002). Ammonia, on the other hand, can be removed by peat to some extent (Heavey, 2003).

Column K0 consisted of sand, columns K1 and K3 were filled with Polonite[®], and columns K2 and K4 with BFS. The pH of the filter media was determined in a 1:2.5 (w:V) media:distilled water suspension and the following values were obtained at start-up of the experiment: K0 = 4.51; K1 and K3 = 12.42; and K2 and

K4 = 8.29. Landfill leachate was transported from the Tveta Landfill in Södertälje to the laboratory in eight separate batches during the experimental period. The main characteristic of the leachate is a high content of organic compounds, indicated by a TOC content of $115 \pm 21 \text{ mg l}^{-1}$ (data from 2002, monitoring by Telge Återvinning). The leachate was stored in 251 tanks at a temperature of 4°C and brought one by one to the column test, which was performed at room temperature. Leachate water was distributed by a peristaltic pump through Teflon tubes to each column with a flow rate of 7 ml min^{-1} , corresponding to a hydraulic loading rate of 1.34 m d^{-1} . The system was operated 8 h d^{-1} . This treatment in portions aimed to minimise effects of leachate breakdown in the storage tank. Each column received approximately 300 l of leachate during the whole experiment. Gravimetric measurements were made during set-up of the experiment to enable estimation of the column porosity. One pore volume (pv) was defined as nV_t , where n is the effective transport porosity and V_t is the total volume of the column. The percentage removal efficiencies of elements by the column media were calculated as the difference between concentrations in influent and effluent samples. Mass removals (g kg^{-1} dry weight) of each constituent entering and leaving the columns were estimated from concentrations and flow data. More data for operational parameters are shown in Table 1.

The experiment was run under saturated conditions and effective saturation was indicated by near-steady flow rates. Column influent and effluent samples were collected in 100 ml acid-washed plastic vessels three times per week. The samples were filtered through a $0.45 \mu\text{m}$ micropore filter (Sartorius), conserved with a few drops of concentrated HNO_3 and kept in a cold-storage room at 4°C prior to analysis. Separate samples were transferred to bottles for pH and electric conductivity determination. The analyses were performed using ICP-AES (inductively coupled plasma atomic emission spectrometry) for elements, and flow injection analysis (Fia, Aquatec-Tecator autoanalyser) for nitrogen compounds ($\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$).

3. Results and discussion

The experiment performed well without any hydraulic problems during discharge of the landfill leachate. The addition of peat probably helped to avoid chemical clogging by forming CaSO_4 , i.e. gypsum, in the columns filled with Polonite[®] and BFS. When the filter media were removed from the columns at the end of the experiment, it was observed that the material had solidified at certain levels in column K3. The role of peat as a releaser of humic substances for sorption processes in mixed media filter systems must be investigated, but was not considered in this study.

3.1. pH and electrical conductivity measurements

A variation in pH from 6.87 to 8.95 of the leachate influent was observed. Approximately the same values were obtained for effluent from column K0 filled with sand. A decrease in pH from 12.65 to 8.50 with increasing pore volumes percolating through the Polonite[®] medium was found (Fig. 1). Effluent from the BFS medium showed more stable pH conditions, following the changes in pH of the influent leachate (Fig. 2). After the experiment, the contents of the columns were removed and the pH was determined for each extract at varying levels (Table 2). The results revealed an increasing pH with depth in columns filled with Polonite[®]. The pH of the bottom layer was slightly more than one unit lower compared to that of the virgin material. In contrast to the former material, the BFS columns showed more stable pH values at all depths. The sand column started with acid conditions and was equalised with the higher pH of the leachate during discharge.

The conductivity of the landfill leachate influent was in the range of $2.25\text{--}8.48 \text{ mS cm}^{-1}$ during the experiment, reflecting the complex ion composition of this kind of wastewater. The effluent from the Polonite[®] columns first showed an increase in conductivity up to 97 pv, possibly due to the initial fast release of calcium, and thereafter a slow decline. Leachate treated by the BFS columns showed varying conductivity in the

Table 1
Operating parameters for columns K0–K4 and their filter substrates

Parameter	Column				
	K0 sand	K1 Polonite	K2 BFS	K3 Polonite	K4 BFS
Bulk density (g cm^{-3})	1.42	0.77	1.22	0.85	1.26
Porosity (%)	39.8	31.8	30.5	34.5	35.8
LOI (%) ^a	6.2	9.4	7.3	9.7	7.3
Permeability (m d^{-1})	97.2	15	191.8	15	191.8
Pore volume (pv) (cm^3)	1500	1200	1150	1300	1350
Normalized flow rate (pv d^{-1})	6.72	8.40	8.77	7.75	7.47

^a Loss of ignition, 550°C , expressing the ash content of each material.

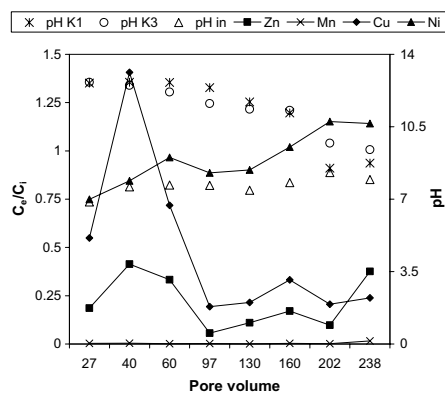


Fig. 1. Breakthrough curves (Zn, Mn, Cu, Ni) and pH data for effluent from columns filled with Polonite[®]. C_e/C_i = ratio for effluent and influent mean concentration.

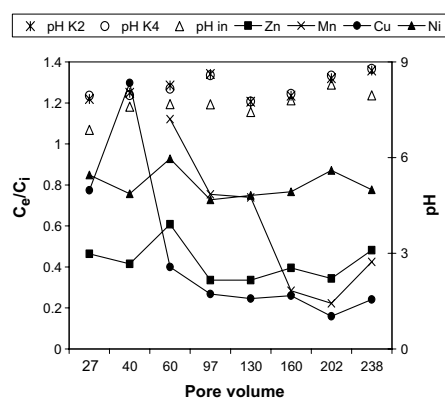


Fig. 2. Breakthrough curves (Zn, Mn, Cu, Ni) and pH data for effluent from columns filled with BFS (Note: Two values of Mn have been excluded from the figure—values 5.2 at pv 27 and 40).

beginning of the experiment. After 97 pv had discharged, the conductivity values decreased compared to that of the influent.

3.2. Removal of the heavy metals

The screening with ICP-AES encompassed in total 32 elements. Influent concentrations of arsenic (As), lead (Pb), cadmium (Cd), beryllium (Be), scandium (Sc) and lanthanum (La) were very low, i.e. below the detection limit of the instrument. Thus, those elements played a rather less competitive role in the removal mechanisms. The influent (untreated) concentrations of 13 selected elements are presented in Table 3. It is clear from the data that a large variation occurred in concentrations of many elements.

The filter media differed in their contaminant removal performance (Table 3). The efficiency of removal was in the order of $Mn > Fe > Zn > Cu > Co > Ni > Mo$ for Polonite[®], $Cu > Zn > Co > Fe > Ni > Mo$ for BFS, and $Cu > Mo$ for sand. The Polonite[®]–peat mixture was the most effective matrix for removal of Mn (99%), Fe (93%), Zn (86%) and Co (30%). However, the BFS–peat mixture showed higher removal efficiency than the previous media for elements such as Ni and Mo (19% and 16%). Copper (Cu) was removed with an efficiency of over 65% from the landfill leachate after passing through the columns filled with Polonite[®] and BFS. Column K0, which was filled with sand and peat, showed 25% removal of Cu and approximately 14% removal of Mo, but no significant removal of the other metals studied.

All filter materials, except the sand, exhibited a good contaminant removal performance over time, although with some exceptions (Figs. 1 and 2). A trend from uptake to release of Ni was observed for the Polonite[®] and Mn was released from the BFS columns during percolation of the initial 40 pv. Explanations could be that Ni sorption decreases with pH and that the surface charge on Polonite[®] is affected by pH. The Mn release was obviously due to leaching from the slag. Hydroxide precipitation is suggested as the process responsible for the high removal efficiency of metals by Polonite[®], forming insoluble precipitates in the bed filter. The precipitation

Table 2
pH of reactive media at different levels of the columns after the experiment (pH of virgin materials are shown in brackets)

Depth in column (cm)	Column number and pH				
	K0 (4.51)	K1 (12.42)	K2 (8.29)	K3 (12.42)	K4 (8.29)
0–10	7.35	8.77	8.31	8.76	8.32
10–20	5.81	8.73	8.47	8.92	8.52
20–30	6.21	8.98	8.68	9.17	8.63
30–40	7.78	9.06	8.67	9.33	8.61
40–50	6.55	10.94	8.55	11.06	8.44

Table 3
Concentrations of selected elements in leachate distributed to the columns (influent), and values for sorption and removal efficiencies by three media

Element	Influent (mg l ⁻¹)	Sorption (mg kg ⁻¹)			Removal (%)		
		Sand	Polonite	BFS	Sand	Polonite	BFS
Mg	101 ± 33	120	8450	-20	2 ± 6.5	89 ± 16	0
S	124 ± 34	137	434	-27	2 ± 3.6	4 ± 8	0
Mn	0.57 ± 0.33	-3.2	52	-38	0	99 ± 0.6	0
Fe	0.61 ± 0.66	-261	42	6	0	93 ± 17	20 ± 33
Zn	0.08 ± 0.08	-108	8	3.6	0	86 ± 21	62 ± 30
Zr	0.003 ± 0.001	-21	0.31	0.2	0	86 ± 13	63 ± 14
Ba	0.19 ± 0.06	-9	16	3.9	0	85 ± 12	31 ± 15
Cu	0.03 ± 0.01	0.4	1.8	1.2	25 ± 36	67 ± 31	66 ± 32
Ti	0.002 ± 0.001	-275	0.11	-1643	0	77 ± 30	0
Y	0.001 ± 0.0003	-2226	0.04	-18	0	60 ± 15	0
Co	0.004 ± 0.001	-265	0.1	0.1	0	30 ± 21	33 ± 16
Ni	0.02 ± 0.002	-36	0.03	0.2	0	2 ± 10	19 ± 9
Mo	0.02 ± 0.001	0.2	-10	0.2	15 ± 22	0	16 ± 23

Values are shown as mean ± SD. Negative sorption value indicates a release of a particular element.

is primarily dependent upon two factors: the concentration of the metal and the pH of the water. Chemical treatment plants normally operate at a pH of approximately 9 when multiple metals are present. The superior removal capacity of the Polonite[®] filter is probably a combination of several factors, i.e. precipitation, ion exchange and adsorption. Thermally activated clay marl, which has a similar chemical composition to Polonite[®], has been reported as a suitable material for the removal of metal cations in the order Pb²⁺ > Cu²⁺ > Zn²⁺ from aqueous solutions (Stefanova, 2001). Stefanova observed a sharp increase in sorption at pH ~ 5–6 due to the formation of various hydroxy species. Nevertheless, it was difficult to distinguish whether surface complexation or surface precipitation was the main removal mechanism at high pH, results that agree well with the work of Rao et al. (2002). Frost and Griffin (1977) and Lin and Yang (2002) found that the adsorption of metals was attributable to competition for cation exchange sites by the high levels of other components present in leachate. It was observed that the complex composition of landfill leachate interfered with the adsorption of pollutants compared to adsorption from the pure salt solutions in the presence of different adsorbents.

In the present study, the adsorption of Cu was significant for BFS and Polonite[®] (Table 3), which could possibly be attributed to the added organic matter, i.e. peat. The removal of Cu and Mo by the sand was similarly caused by the presence of peat. Many authors report efficient removal of Cu by different adsorbents when mixed with humic or organic substances (Calace et al., 2001; Kabata-Pendias and Pendias, 2001; Yabe and de Oliveira, 2003). Addition of inorganic substances can also enhance the removal capacity of a filter media. Tsai

and Vesilind (1999) showed that addition of lime enhances the ability of the filter media zeolite (montmorillonite) to adsorb Zn at low initial Zn concentrations. The BFS exceeded the Polonite[®] in removal efficiency for elements such as Ni and Mo (Table 3). Dimitrova (1996) found that the high sorption capacity for Cu, Zn and Ni of the blast-furnace slag is related to the formation of scarcely soluble compounds (silicates) on the adsorbent surface. Ćurković et al. (2001) investigated electric furnace slag and found efficient removal capacity for lead and copper from artificial solutions. Ni sorption on Fe and Mn oxides is especially pH dependent (Kabata-Pendias and Pendias, 2001), with predominantly insoluble nickel hydroxides existing at pH values >6.7 (Merian, 1991). Sharma et al. (1990) assumed that SiO₂ and/or CaO had removed Ni species in wollastonite. Muhammad et al. (1998) found from Langmuir and Freundlich isotherms that a slow sand filter (filtration rates ranging from 0.1 to 0.2 m h⁻¹) had the highest adsorption capacity at neutral pH for Pb, followed by Cu, Cr and Cd. We conclude from our results that sand filters would be more suitable for treating surface run-off from landfill sites, since metals are particle-bound at that stage.

3.3. Removal of nitrogen

As shown in Table 5, total inorganic nitrogen was reduced in various amounts by the media used. The columns filled with Polonite[®] (K1 and K3) achieved the highest removal efficiency (16% and 20%, respectively). The other columns tested had values below 10%. The removal observed by K1 and K3 has minor connection with biological processes since the high pH of the medium does not allow microbial growth (Renman

et al., 2003). Instead, nitrogen transformation and uptake is related to volatilisation, adsorption and cation exchange. The initial high pH of Polonite® may cause a release of NH_3 . However, most of the $\text{NH}_4\text{-N}$ is transformed to $\text{NO}_3\text{-N}$ or adsorbed to wollastonite, which occurs in Polonite® (Kietlińska and Renman, unpubl. data). Lind et al. (2000) described the excellent adsorption qualities of wollastonite for removal of $\text{NH}_4\text{-N}$.

Different kinds of zeolite are known to be excellent materials for ammonium-nitrogen removal. Cation exchange is considered as a main process for that removal (Sposito, 1989; Ahn et al., 2002). According to Liu and Lo (2001), the presence of competitive ions such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} in landfill leachate can reduce the ammonium adsorption capacity of the zeolite. However, experimental results indicate that ammonia can be removed by 84% from leachate using clinoptilolite as an ion exchanger (Papadopoulos et al., 1996). Rožić et al. (2000) tested a natural zeolite (clinoptilolite) at the lowest concentration of $100 \text{ mg NH}_4\text{-N l}^{-1}$ and achieved a removal of up to 61.1%.

3.4. Leaching of elements

Several elements were released in different amounts from the studied media (Table 3). Five of these released elements were common to all filter media during the column experiment (Table 4). Different chemical reactions with the strong landfill leachate, e.g. ion exchange and mineralisation of organic material, can contribute to such release. Calcium leached from the Polonite® filter in amounts of up to almost twice the leachate influent mass of Ca. Silica behaved in the same way, and the BFS column released almost three times more by mass.

Table 4
Leaching of elements from column media

Element/unit	Influent mass	Effluent mass		
		Sand	Polonite	BFS
Ca (g)	70.5	68.1	133.2	0
Si (g)	3.4	3.5	7.6	9.3
Al (mg)	14.7	550.4	18	212.9
Cr (mg)	2.5	3.1	5.9	6.7
V (mg)	1.1	1.2	4.5	2.2

Total mass in influent landfill leachate is compared with total mass in treated, effluent leachate.

Table 5
Total inorganic nitrogen ($\text{TIN} = \sum \text{NH}_4\text{-N}, \text{NO}_3\text{-N}, \text{NO}_2\text{-N}$) in influent, and sorption and removal efficiencies by three media

	Influent (mg l^{-1})	Sorption (g kg^{-1})			Removal (%)		
		Sand	Polonite	BFS	Sand	Polonite	BFS
TIN	105.9 ± 29	0.25	1.9	0.55	4 ± 22	18 ± 15	8 ± 22

Values are shown as mean \pm SD.

A considerable mass of Al was released from the sand and BFS columns. Elevated amounts of Cr and V in the effluent leachate were also found. These elements are natural constituents of the bedrock that is used for production of Polonite®. Vanadium is used in the process of iron production and becomes a contaminant in the slag.

Breakthrough curves for Si and Ca are presented in Figs. 3 and 4. It can be seen that changes appeared after

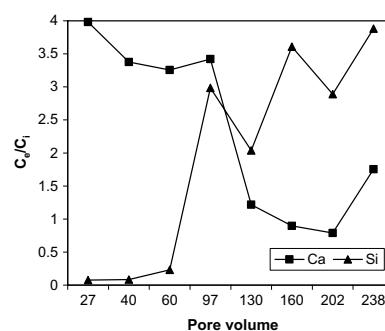


Fig. 3. Breakthrough curves (Ca, Si) for columns filled with Polonite® (cf. Fig. 1 for pH data).

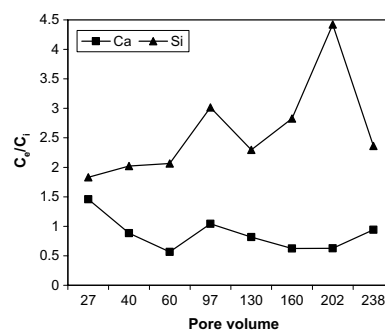


Fig. 4. Breakthrough curves (calcium, silica) for columns filled with BFS (cf. Fig. 2 for pH data).

97 pv of leachate discharge, i.e. at the same time as some changes in metal removal were observed (Figs. 1 and 2). However, an initial removal of Ca was observed for the BFS material. The changes in release of Si and Ca versus flow for the Polonite® can be related to the weathering of the solid material and the presence of wollastonite. According to other studies, the latter material is efficient for heavy metal removal (Sharma et al., 1990; Stefanova, 2001).

Dimitrova and Mehandgiev (1998) considered that in a solution with initial pH ranging from 3 to 7, a release of calcium took place from the granulated blast-furnace slag into the artificial prepared solution, and thereby the sites for sorption of metals (Pb) were freed. In the present study, the results were the opposite, i.e. calcium was adsorbed over a certain period of time by the slag. Ouki and Kavannagh (1997) studied the effect of Ca on metal removal by chabazite and clinoptilolite. Their results showed that Ca was a major competing cation for ion exchange for both zeolites at high Ca concentrations. Such mechanisms could be responsible for the lower removal of metals by BFS, especially in the light of the high content of calcium, up to 400 mg l^{-1} , in the landfill leachate used in our study.

4. Conclusions

Dominating heavy metals in landfill leachate were efficiently removed by a filter medium composed of Polonite® and peat. The kind of blast-furnace slag (BFS) used in our investigation did not show good removal efficiency over the whole contaminant spectra. Sand filters are not recommended for treatment of leachate originating from older landfills. The reactive medium Polonite® did not reach the saturation point of many of the major contaminants. Future studies should aim to identify the breakthrough point for target pollutants, i.e. when effluent concentrations equal influent concentrations. A drawback of the studied reactive media was the release of certain elements, such as Cr, from the BFS and Polonite® filter matrix.

This paper showed that removal of metals by different media is influenced by many factors, such as pH, chemical composition of material, and element competition in leachate water. Experiments with landfill leachate are more difficult to interpret than those performed with aqueous solutions. The differences in the results obtained by investigators of reactive filter media arise from the fact that the leachate has a complex composition, which can interfere with the adsorption of metals. Hence, this suggests that it is not possible to draw conclusions of a general or fundamental nature on the removal mechanisms involved.

A filter facility designed as a multi-layer unit of several reactive media could be a possible solution for more

effective, broad-spectrum metal removal. Prior to full-scale application at a landfill site, matrix selection, filter design and operational procedures must be developed to ensure appropriate hydraulic conditions and to facilitate periodic media replacement and possible recovery.

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II



Phosphorus retention in filter materials for wastewater treatment and its subsequent suitability for plant production

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Abstract

Constructed sand filter beds are advantageous for the treatment of wastewater in areas with a low population density. Phosphorus-sorbing materials with additional beneficial characteristics may be used instead of sand. This study aimed at determining and comparing phosphorus (P) retention capacities of amorphous and crystalline blast furnace slags, limestone, opoka, Polonite® and sand, for filtering domestic wastewater through columns over a period of 67 weeks. The P-enriched filter materials were subsequently tested for their fertilizer effectiveness in a pot experiment where barley was cultivated. Polonite®, i.e. calcinated bedrock opoka, was most effective in removing P. This occurred at a relatively high hydraulic conductivity that reduced the risk of clogging. Barley grown in two types of slag, with a grain size of 0.25–4 mm, was most effective in dry matter production followed by Polonite®. Fine-grained slags and Polonite® were suggested as most suited of the investigated materials to recycle P back to agriculture. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Barley; Blast furnace slag; Fertiliser; Polonite®; Phosphorus recycling

1. Introduction

Phosphorus (P) in municipal wastewater can be a source of pollution as well as a resource (Swedish Environmental Protection Agency and Ministry of Foreign Affairs, 1998; Vymazal et al., 1998). The release of wastewater into water bodies can accelerate eutrophication significantly (Pretty et al., 2003). Phosphorus is an essential macro-nutrient for crop growth and should therefore be recycled, especially since raw materials for manufacturing P fertilizers are limited and non-renewable. Precipitation of P by chemicals and subsequent sludge storage in landfills does not solve the pollution problem, rather it postpones it (Günther, 1999). Correctly designed filter beds or constructed wetlands are

advantageous for the treatment of wastewater in areas with a low population density. Using the P from wastewater as a fertilizer would turn P into a valuable resource, thereby eliminating pollution problems (Hylander et al., 1999; Hylander and Simán, 2001). Phosphorus could be separated by trapping it in soil infiltration beds, constructed filter wells—where the commonly used sand and gravel is substituted for a material with a large P-retention capacity—or in constructed wetlands (Zhu et al., 1997; Baker et al., 1998; Sakadevan and Bavor, 1998; Brooks et al., 2000; Hill et al., 2000; Drizo et al., 2002; Cameron et al., 2003).

Several recently conducted investigations on different materials show that P can be trapped efficiently (e.g. Johansson, 1999; Roseth, 2000; Kvarnström, 2001; Agyei et al., 2002). The mechanisms of P retention by these materials are not known in detail, but adsorption to particle surfaces is one of them. The term “sorption”

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is generally used as a synonym for retention, which covers physical, chemical and biological processes in which P is immobilised (see e.g. Zhu et al., 1997). The material that is enriched with P can be used as a fertilizer, provided that P is available to the plants, and contents of toxic compounds and pathogens do not restrict such use. Most of the materials are characterised by high pH values (9–12), which create an unfavourable environment for bacteria (Renman et al., 2004). Phosphorus-sorbing materials with additional beneficial characteristics may be used. For example, lime can be used to counteract acidification to improve soil structure (Rex, 2000). Potential availability of P to plants can be estimated using test P methods, such as chemical extraction with acetic acid/ammonium-lactate and 2 M HCl, and can be determined both in terms of the crops response in pot experiments and measuring the crops uptake of P (Hylander and Simán, 2001).

The objectives of this study were (i) to determine and compare the capacities of different filter materials to remove P from domestic wastewater and (ii) to study the effectiveness in dry matter production when growing barley in soils mixed with those filter materials.

2. Methods

2.1. Column experiment

Six inorganic materials, one of which had two different grain sizes, were filled to a height of 50 cm in nine, 30-cm wide columns (two of the material filled columns were duplicated; Fig. 1, Table 1). The materials and their grain size used were: amorphous steel-works furnace slag, 0.25–4 mm (ASC); crystalline steel-works furnace slag, 0.25–4 mm (CSC) and 2–7 mm (CSVC);

limestone from Ignaberga, South Sweden, 1–2 mm; opoka, a bedrock from Poland, rich in CaCO_3 and SiO_2 that was formed from marine sediments (Brogowski and Renman, 2004), 2–5.6 mm; calcinated opoka (Polonite[®]), 2–5.6 mm; and quartz sand washed with tap water, 0.2–1.5 mm, used as an inert reference material. The columns were placed indoors (20 °C) at Louden wastewater treatment plant, Stockholm, where on average 0.5 L of wastewater was pumped to each column every second hour for a period of 67 weeks. Before being supplied to the columns, the wastewater was kept in a two-chamber septic tank with an average storage time of 22 h, so that coarse, suspended mineral and organic particles would settle as sludge. From the second chamber of the septic tank, wastewater was pumped through a filter made of high density polyethylene material (HDPE, pore diameter 100 μm) to a distribution tank, which distributed equal subsamples of wastewater to all columns. The average concentration of P (as PO_4^{3-}) in the wastewater distributed to the columns was 4.2 mg l^{-1} . Columns, tanks and the tubing were made of polyvinyl chloride (PVC) plastics. The filter material was lined with a 2.5 cm thick layer of mineral wool at the top of each column, thereby acting as a barrier and preventing any further clogging at the surface. This mineral wool also had the function to distribute the wastewater equally over the filter media. Throughout the duration of the experiment, the mineral wool was exchanged in all columns three times because of clogging and preferential flow tendencies.

The P analyses of influent and effluent wastewater were performed using Flow Injection Analysis (FIA, Aquatec-Tecator autoanalyser). A Radiometer PHM 82 Standard pH-meter was used for determining pH.

At the end of the column experiment, the materials were sampled in 0–5, 5–10, 10–20, 20–30, 30–40, and

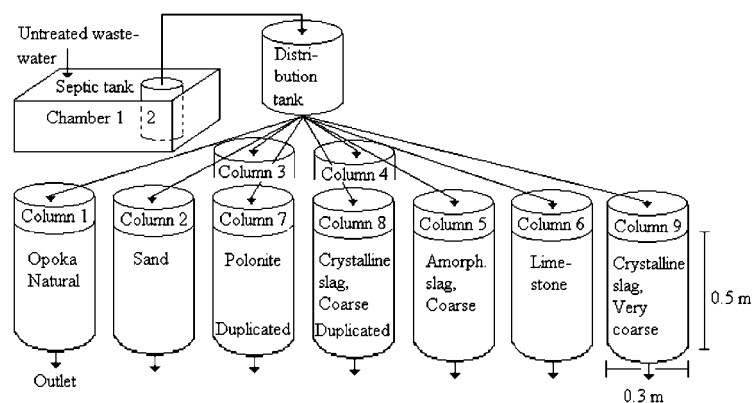


Fig. 1. Schematic design of research set-up for studies of wastewater treatment materials. Each column's material was covered with a 2.5-cm layer of mineral wool (Rockwool[®]).

Table 1
Physical parameters and pH of sorption materials at start of column experiment

Sorption material ^a	Particle size (mm)	Surface area (m ² g ⁻¹)	Hydraulic conductivity (mday ⁻¹)	Column porosity (%)	pH _{H₂O} (1:2.5)
ASC	0.25–4	0.43	40.6	46.7	9.9
CSC	0.25–4	0.50	15.9	45.5	9.6
CSVC	2–7	0.37	1950	50.9	9.4
Limestone	1–2	0.57	238.5	46.4	8.9
Polonite [®]	2–5.6	0.70	800	47.7	12.5
Opoka	2–5.6	50.85	1481	50.2	8.3
Sand	0.2–2	0.09	200	43.7	6.5

^a ASC = amorphous slag, coarse; CSC = crystalline slag, coarse; CSVC = crystalline slag, very coarse.

40–50 cm layers and dried at room temperature (20–25 °C). Duplicated subsamples of virgin material and material from each layer were finely crushed in a mortar. After extraction with concentrated HNO₃ in an autoclave (120 °C for 30 min, material:solution 1:20; modified from SIS, 1986), the total element contents of P and of the elements Al, Ca, Fe, Mg, and Mn (Table 2) were determined on Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Perkin Elmer, 1993). Initial P content was also analysed in the virgin material. The additional five elements measured were potentially important for binding phosphate ions in the sorbing materials and were also capable of influencing results from the pot experiment.

2.2. Pot experiment

Barley was grown using the P-enriched filter materials as fertilizers in a pot experiment. Mitscherlich pots were filled (3.6 kg dry soil per pot) with the A-horizon (5–20 cm) of P-depleted soil from agricultural land under permanent cultivation from Bjärröd, Scania, Sweden (55°42'N, 13°43'E, alt. 105 m a.s.l.). The soil, classified as a mesic Oxiaquic Hapludoll according to the Soil Taxonomy, is a sandy moraine with 14% clay and a pH_{H₂O} of 6.3 (Slänberg and Hylander, 2004). It has acetic acid/ammonium-lactate extractable P, K, and Mg (Egnér et al., 1960) of 9, 50, and 66 µg g⁻¹ dry soil, respectively, corresponding to 0.29, 1.28 and 2.72 µmol g⁻¹ dry soil.

This indicates a soil poor in P, rather poor in K, and has an average level of Mg.

Each pot received 1.5 g K₂SO₄, 1.0 g MgSO₄, and 1.0 g N as NH₄NO₃ as basic fertilisation. The soil was mixed with P in the form of K₂HPO₄ or as P sorbed from wastewater to the different filter materials in quantities corresponding to 0.03 g P per pot (Table 3). Each treatment was in triplicate with filter material from the indicated column layer (generally the surface, 0–5 cm).

Barley, *Hordeum vulgare* L. c.v. Filippa, was sown and thinned after eight days of growth to 29 blades per pot. The pots were kept outdoors (June to September) under a shelter so as to experience natural light conditions, but protected from rain and from damage by birds. They were watered once a day or every second day depending on the rate of evapotranspiration, so that soil moisture was kept between 60% and 80% of maximum water-holding capacity. During the 70-day growth period, the average air temperature was 14.6 °C and the accumulated insolation was 887 MJ m⁻² (Meteorologiska observationer vid Ultuna N 59°49' E 17°39', 2001). All pots were re-randomised weekly. The barley was sprayed to prevent grey speck disease with a manganese solution (2.4 g l⁻¹) and leaf fungi diseases with prokloraz (Sportak EW, 5 ml l⁻¹) on the 21st of August and 12th of September.

At harvest, the blades were cut 10 mm above soil surface, dried at 55 °C, and weighed. Soil pH was determined at sowing in a 1:2.5 (w:V) soil:water suspension.

Table 2
Nitric acid extractable element concentrations of virgin sorption materials

Sorption material ^a	Al (mg g ⁻¹)	Ca (mg g ⁻¹)	Fe (mg g ⁻¹)	Mg (mg g ⁻¹)	Mn (mg g ⁻¹)	Si (mg g ⁻¹) ^b
ASC	59.1 ± 8.8	210.8 ± 28.4	1.13 ± 0.15	108.0 ± 15.5	3.03 ± 0.22	166
CSC	39.6 ± 2.1	183.0 ± 7.4	1.81 ± 0.32	81.4 ± 5.2	3.65 ± 0.15	164
CSVC	33.3 ± 2.8	142.7 ± 11.4	1.10 ± 0.04	57.8 ± 6.4	2.35 ± 0.29	163
Limestone	0.09 ± 0.01	363.5 ± 14.9	0.53 ± 0.01	2.86 ± 0.11	0.45 ± 0.02	n.a. ^c
Polonite [®]	14.8 ± 1.0	159.3 ± 9.1	7.79 ± 0.46	3.67 ± 0.63	0.08 ± 0.01	280
Opoka	3.67 ± 0.50	280.1 ± 27.2	8.18 ± 0.99	2.48 ± 0.23	0.11 ± 0.01	160
Sand	<0.01	<0.01	0.78 ± 0.07	<0.01	<0.01	466

Average ± SD.

^a ASC = amorphous slag, coarse; CSC = crystalline slag, coarse; CSVC = crystalline slag, very coarse.

^b Data on Si from Johansson and Hylander (1998).

^c Not analysed.

Fertiliser effectiveness can be summarised as the relative effectiveness (RE%) of P bound to the filter materials (PFM) in increasing barley dry matter production in relation to yield with the standard fertilizer (K_2HPO_4). This has been calculated according to the following formula:

$$RE\% = \left\{ \frac{[(\text{yield with PFM}) - (\text{yield control})]}{[(\text{yield with } K_2HPO_4) - (\text{yield control})]} \right\} * 100$$

Data were subjected to analysis of variance (Statistix for Windows, 1996).

3. Results and discussion

3.1. Phosphorus sorption to different materials by layers

Total P content in the surface layer was highest in the 0–5 cm layer of Polonite[®], where the P content had increased from 0.2 mg g^{-1} originally to 1.3 mg g^{-1} (Fig. 2). It was followed by sand (Fig. 2), which had a higher P content in its surface layer than revealed by its capacity to remove phosphate from percolating wastewater (Renman et al., 2004). However, P content decreased significantly in underlying layers of sand, which should not be the case with an effluent rich in phosphate, where the total P content originated mainly from sorbed phosphate. Phosphorus from the wastewater was retained in the surface layer by the sand, when acting as a filter, due to its fine texture and by bacteria more than likely living in the surface layer of the column rather than in lower layers (Renman et al., 2004). Total P content at the surface and in the 5–10 cm layers of the columns filled with Polonite[®] were nearly the same and, due to sorption of phosphate, were more than six times higher than in the bottom layer, which contained only P from the initial material without any P sorbed (Fig. 2). The similar P content in the two upper layers and the continuous decrease in lower layers indicate that only the surface layers were saturated or close to saturated with P. The absence of P retention in the bottom layer and only limited P sorption in the two overlying layers indicate that the column would have been able to retain P from the wastewater efficiently for a period of time twice as long as that used in the experiment. Effluents from columns three and seven, filled with Polonite (see Fig. 1), had a low mean concentration of P of 0.1 mg l^{-1} throughout the experiment and the pH decreased from 12.8 to 8.9. The P removal capacity decreased successively in the other columns studied and, at the end of the experiment, reached P concentrations in the effluent higher than 2 mg l^{-1} . An exception was the column filled with sand, which did not remove soluble P at all from the incoming wastewater. The pH in the effluent from the

sand column closely matched the influent wastewater pH, while effluent from the other columns had a pH of 8.9–9.2.

The difference in retention capacity between Polonite[®] and opoka was large, more than ten-fold, due to oxidation of $CaCO_3$ to the more reactive form CaO in Polonite[®]. High temperature thermal pretreatment of opoka also results in sintering and a subsequent large decrease of the surface area in the product Polonite[®] (Table 1). The comparably low sorption capacity of limestone is also explained by its Ca being in the carbonate form. Burning limestone ($CaCO_3$) to form quick lime (CaO) increased the removal capacity (Hylander and Simán, 2001), but resulted in a powder with a hydraulic conductivity too low to permit any use in the designed filtration system in its pure form. In addition to element content (Table 2) and chemical form, the differences in the materials' grain size can also explain observed variations in P sorption, clearly shown when comparing the coarse and very coarse crystalline slags (Table 1, Fig. 2).

3.2. Barley dry matter production in soil fertilized with different filter materials

The poor P status of the soil was demonstrated by a significantly increased dry matter yield when P was added, with the exception of the application of P sorbed to limestone (Fig. 3). This was probably caused by the large amounts of limestone (72.2 g) that had to be applied (0.03 g P per pot), because of the poor sorption capacity of limestone in the wastewater filter. Hence, the soil was possibly over-saturated with Ca during the course of the experiment. This was not demonstrated by soil pH when the barley was sown (Table 3), due to the comparably coarse texture of the limestone (1–2 mm) used in the filter. The laboratory grade $CaCO_3$ used in parallel treatments reacted faster in the soil because of its finer structure (<0.02 mm) and produced a pH above 7 when the barley was sown (Table 3). Base saturation exceeding 100% resulted in large yield reductions, especially when P was not applied, since less soil P was made available to the barley (Fig. 3). In addition, the application of the other virgin materials, except for coarse crystalline slag, reduced the yield, probably through a combination of increasing soil pH and P uptake from the soil solution (Fig. 3).

The application of 0.03 g P per pot as K_2HPO_4 produced the highest yield, closely followed by P sorbed to slags from the wastewater filters (Fig. 3). The availability of P sorbed to slag to the barley was also observed in an earlier experiment (Hylander and Simán, 2001). It may be attributed to a fast release of loosely bound P from the amorphous and crystalline slags used in the present experiment. Yields from treatments with P sorbed to Polonite[®] were significantly lower. Yields with

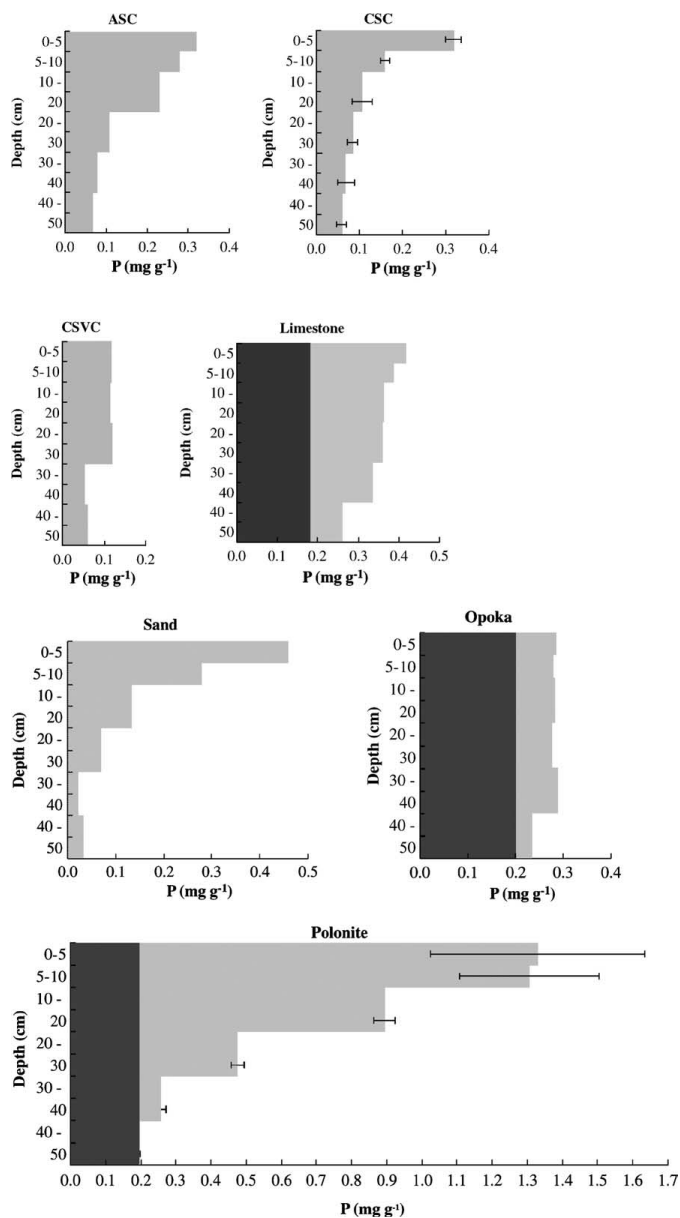


Fig. 2. Initial P content of the filter materials (dark shaded area) and P enriched to different layers (light shaded area) after the column experiment. Bars indicate \pm SE for duplicated columns. ASC = amorphous slag, coarse; CSC = crystalline slag, coarse; CSVC = crystalline slag, very coarse.

P sorbed to opoka were even lower despite the application of K_2HPO_4 , but higher than those with soils that had not had fertilizer added (Fig. 3). This indicates that

P sorbed to opoka can be utilised by barley, although not as readily as P sorbed to slag or P in chemical fertilizer. The low diffusion of P, as previously reported for P trans-

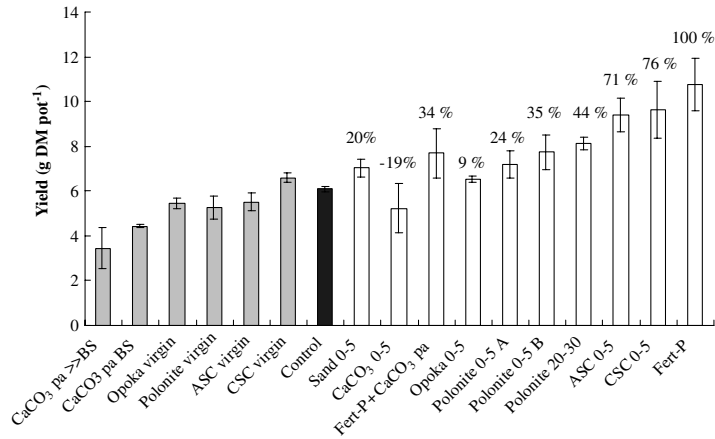


Fig. 3. Yields (average and 95% confidence interval) of barley grown in soil treated with different filter materials containing P (white stacks) or with materials without P (gray stacks). P fertilizer effectiveness (%) in relation to standard P fertilizer indicated by figures above the stacks. See Table 3 for further explanation.

Table 3
Type and amount of sorption material added to the pot treatments and soil pH at sowing

Treatment name	Description	Material (g pot ⁻¹)	P (g pot ⁻¹)	pH _{H₂O} (1:2.5)	SE
CaCO ₃ pa >>BS	Laboratory grade chemical, 4 times larger quantity applied than needed to reach 100% base saturation	42.8	0	7.21	0.03
CaCO ₃ pa BS	Laboratory grade chemical, applied quantity estimated to give 100% base saturation	10.7	0	7.24	0.17
Opoka virgin	Natural opoka	98.1	0	5.84	0.19
Polonite [®] virgin	Calcinated opoka	63.2	0	6.55	0.05
ASC virgin	Amorphous slag 0.25–4 mm	117.6	0	5.78	0.06
CSC virgin	Crystalline slag 0.25–4 mm	100.0	0	6.01	0.06
Control	Untreated original soil	–	0	5.30	0.01
Sand 0–5	Inert sand from filter, 0–5 cm layer	65.4	0.03	5.33	0.01
Limestone 0–5	From filter, 0–5 cm layer	72.2	0.03	6.38	0.01
Fert-P + CaCO ₃ pa	Laboratory grade chemicals, P as K ₂ HPO ₄	11.0	0.03	7.16	0.02
Opoka 0–5	From filter, 0–5 cm layer	98.1	0.03	6.00	0.07
Polonite [®] 0–5 A	From filter, 0–5 cm layer, column A	29.3	0.03	5.59	0.09
Polonite [®] 0–5 B	From filter, 0–5 cm layer, column B	18.3	0.03	5.41	0.04
Polonite [®] 20–30	From filter, 20–30 cm layer	63.2	0.03	5.98	0.06
ASC 0–5	From filter, 0–5 cm layer	117.6	0.03	5.49	0.03
CSC 0–5	From filter, 0–5 cm layer	100.0	0.03	5.72	0.01
Fert-P	K ₂ HPO ₄ , laboratory grade chemical	–	0.03	5.32	0.01

port in soils (e.g. Hylander and Ae, 1999), may explain the reduced availability of P in opoka compared to slag. In this regard, Polonite[®] represents a condition somewhere between opoka and slag. This is because it originates from opoka and has been thermally treated to change its physico-chemical properties, thereby activating its sorption capacity (Brogowski and Renman, 2004).

In the sand filter, the fertilizer effectiveness of accumulated P was also lower when compared to P applied as K₂HPO₄. The sand was a washed quartz sand, which is inert. Therefore the P in the sand filter, retained because of the physical filtering capacity of sand, was ex-

pected to be mainly in organic form. This filtering was confirmed by increased contents of C and N in the surface layer (Fig. 4). Compared to inorganic orthophosphate, organic P has a significantly lower plant availability in the short term (i.e. days to weeks) when applied to the studied soil. This can also explain the difference in fertilizer effectiveness between the surface layer and deep layer Polonite[®] (Fig. 3). Despite the fact that P content in the surface layer was twice that of other horizons, yield and fertilizer effectiveness were higher for barley grown in the deep layer material. All filter media probably retained organic P at the surface.

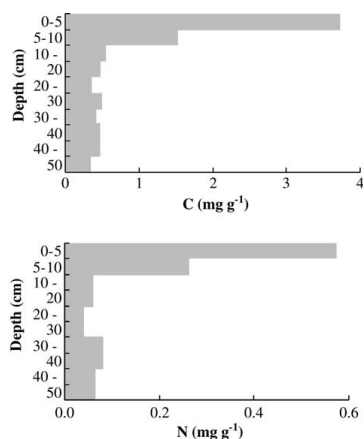


Fig. 4. Carbon and nitrogen contents in different layers of sand.

As demonstrated in Fig. 3, relative effectiveness was negative or low for P sorbed by limestone and opoka. This was caused by the alkaline characteristics of these materials and the large amounts needed to adsorb enough P, as previously explained. Therefore limestone and opoka should only be considered as filter materials if they will be used in soils with extremely low soil pH after being saturated with P. Slag materials, however, are suitable for use in moderately acidic soils, where their relative effectiveness can be assumed to be at least 70% that of commercial P fertilizer during the first year, and possibly more in subsequent years.

4. Conclusion

The present use of sand in wastewater infiltration plants cannot be recommended because of the poor P binding capacity. Of all the studied materials, Polonite[®] had the largest sorption capacity for P. Polonite[®] used in wastewater filters can be recycled as a combined fertilizer for plant production and liming agent on acidic soils. While P retention capacity of blast furnace slag is lower than that of Polonite[®], it does, however, show greater promise in P fertilizer effectiveness.

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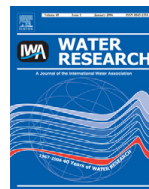
water treatment plant, MSc Bertil Nilsson at the Department of Land and Water Resources Engineering, KTH, and the staff at the Division of Plant Nutrition, Swedish University of Agricultural Sciences.

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Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment

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Wollastonite

ABSTRACT

The mineral-based sorbents Filtra P, Polonite[®], natural wollastonite and water-cooled blast furnace slag (WCBFS) were studied in terms of their PO₄ removal performance. Results from a long-term column experiment showed that both Filtra P and Polonite[®] removed >95% of PO₄ from the applied synthetic solution, and that the used filter materials had accumulated several (1.9–19) g kg⁻¹ P. Phosphorus was removed also by natural wollastonite and WCBFS, but these materials were less efficient. Batch experiments on the used materials showed that the solubility PO₄ was considerably larger than the one expected for crystalline Ca phosphates such as hydroxyapatite, and results from investigations with attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR) on the Filtra P material showed that the formed P phase was not crystalline. These evidence suggest that a soluble amorphous tricalcium phosphate (ATCP) was formed in the mineral-based sorbents; the apparent solubility constant on dissolution was estimated to $\log K_s = -27.94 (\pm 0.31)$ at 21 °C. However, since only up to 18% of the accumulated PO₄ was readily dissolved in the experiments, it cannot be excluded that part of the phosphorus had crystallized to slightly less soluble phases. In conclusion, Filtra P and Polonite are two promising mineral-based sorbents for phosphorus removal, and at least part of the accumulated phosphorus is present in a soluble form, readily available to plants.

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1. Introduction

Recent research has identified the use of active filtration through alkaline media for the removal of phosphorus from domestic wastewater (Johansson and Gustafsson, 2000; Drizo et al., 2006; Shilton et al., 2006; Ádám et al., 2007). Active filtration belongs to a family of promising techniques for small-scale wastewater treatment, which can be used in combination with other treatments such as wetland treatment systems and source separation/collection (Johansson, 1998; Valsami-Jones, 2001; Shilton et al., 2006). An attractive feature of the filter technique is that the nutrient-loaded filter media can be used in agriculture as P fertilizer and soil conditioner (Hylander et al., 2006). This would be of help in rural areas around the world since many houses are devoid of or use private wastewater treatment systems that are not

acceptable from sanitary and environmental point of view. However, many aspects of these techniques remain unclear. Most crucial perhaps is the lifetime of the filters and the risk of unacceptable contamination due to metal accumulation in the filters.

Examples of filter materials include metallurgical slags (Johansson and Gustafsson, 2000; Shilton et al., 2006) and various products that contain lime and/or alkaline Ca silicates such as Polonite (Brogowski and Renman, 2004) and Filtralite P (Kvarnström et al., 2004).

These filter materials generally have pH values above 9 and they release Ca to the water phase, which causes subsequent removal of P. The formation of Ca phosphates explains the observed P removal. An obvious candidate is precipitation of hydroxyapatite (HAp) (Johansson and Gustafsson, 2000; Drizo et al., 2006).

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A large supersaturation is required to form HAP within a short time. In many filter media, it is likely that the supersaturation is sufficient and that HAP is formed. Formation of HAP in filter media has recently been shown by some researchers, who identified HAP by the use of X-ray diffraction techniques (Khadhraoui et al., 2002; Drizo et al., 2006). Once formed, phosphate bound as HAP would not be easily released in a short time due to the low solubility of HAP. However, other more soluble Ca phosphates may also be formed at least initially (Valsami-Jones, 2001). For example, Kim et al. (2006) were able to identify both amorphous tricalcium phosphate (ATCP, $\text{Ca}_3(\text{PO}_4)_2$) and dibasic calcium phosphate (DCP, CaHPO_4), as well as HAP, in converter slag used as seed material for phosphorus crystallization. Similarly, by means of XANES (X-ray absorption near-edge structure) spectroscopy Sato et al. (2005) found that ATCP and DCP were important phases in poultry manure. No octacalcium phosphate (OCP, $\text{Ca}_8\text{H}(\text{PO}_4)_3$) or HAP was found, although both these more crystalline phases are common in soils (Beauchemin et al., 2003). With this evidence in hand, it seems likely that used filter materials from wastewater treatment may contain readily soluble Ca phosphates such as ATCP and DCP. This is supported by the results from the plant uptake experiments that show that the retained P in both slags and Filtralite P is easily accessible (Hylander and Simán, 2001; Kvarnström et al., 2004; Hylander et al., 2006).

The purpose of this study was to evaluate the performance of four different filter materials for their ability to remove phosphate by means of a column experiment mimicking a filter system in the field, and to cast light on the P removal mechanisms by means of solubility experiments and infrared spectroscopic investigations on the used filter materials. To our knowledge, this paper is the first to report the solubility of P in used alkaline filter materials.

2. Materials and methods

2.1. Filter materials

The elemental composition of the four filter materials is shown in Table 1. Polonite[®] is manufactured from siliceous sedimentary Opoka rock in Poland that is heated to 900 °C (Brogowski and Renman, 2004). Samples of Polonite[®] were supplied by Bioptech AB (Hallstavik, Sweden). The filter material is available in different fractions and the 2–5.6 mm particle size was used in our experiment. The material consists mainly of reactive lime and wollastonite phases, which contribute to the strongly alkaline conditions. This material has earlier proved to be successful for P removal (Hylander et al., 2006). Filtra P is produced after heating a mixture of limestone, gypsum and Fe oxides. The product, which is strongly alkaline because of its content of $\text{Ca}(\text{OH})_2$ (about 20%), is granulated in a particle size of 2–13 mm for use as a filter material in wastewater treatment. Samples of Filtra P were obtained from Nordkalk Oyj Abp (Pargas, Finland). Water-cooled blast furnace slag (WCBFS) is a by-product from the steel industry and contains amorphous glasses and a small amount of crystalline silicates of the åkermanite/gehlenite type. The particular WCBFS sample used in this study was supplied by Mercox AB (Oxelösund, Sweden). It had a particle size

Table 1 – Original elemental composition of the four filter materials

	Filtra P	Polonite	WCBFS	Wollastonite
Si	14.6	241	155	276
Al	11.1	27	69.7	54.6
Ca	312	245	216	151
Fe	41.3	16.5	3.11	21.5
K	4.89	9.15	6.18	26.2
Mg	4.68	4.4	97.6	13.3
Mn	0.317	0.121	4.69	0.894
Na	1.46	1.46	4.28	12.3
P	1.44	0.34	<0.1	<0.1
LOI (% TS)	20.9	5.1	0.8	1

The unit is g kg^{-1} dry matter, unless otherwise stated.

of 0–4 mm and was pretreated with 1% CaO to increase its alkaline reaction. Natural wollastonite has been shown to be able to remove ammonium from urine (Lind et al., 2000). Because of its high pH (which can be explained by the dissolution of wollastonite) and because of its mineralogical similarity to Polonite, we decided to investigate also its ability to remove phosphorus. The sample used in this investigation was supplied by Minpro AB (Stråssa, Sweden). It had a particle size of 1–3 mm and contained 27.3% wollastonite, as revealed by quantitative X-ray diffraction. The remainder consisted mostly of feldspars (39.9%), diopside (10.8%) and quartz (10.4%).

2.2. Column leaching experiment

To provide information on the long-term P removal performance of the filter materials, a column leaching experiment was carried out. Columns were constructed of PVC tubes of 60 cm length and 10 cm inner diameter and filled with a 50 cm layer of the appropriate filter material. However, the Polonite was sieved for removal of particles less than 2 mm and its composition was changed by the addition of 10% (w/w) *Sphagnum* peat. The bottom of the columns was filled with a 2 cm layer of gravel and with a coarse plastic (HDPE) filter to prevent loss of material from the columns. The experiment was carried out in room temperature (20 °C) under water-saturated conditions. A synthetic solution with $\text{PO}_4\text{-P}$ (orthophosphate ions quantified as P) and $\text{NH}_4\text{-N}$ (ammonium ions quantified as N) concentrations of 5 and 30 mg dm^{-3} , respectively, was prepared by adding KH_2PO_4 and NH_4Cl to 200 dm^{-3} of tap water. These concentrations are within the range normally found in wastewater (see, e.g., Vymazal, 2007). The solution was stored in a container and pumped automatically to the top of each column three times per day (08.00, 13.00, 17.00) throughout the experimental period of 68 weeks. The loading rate was differentiated so that the pumped volumes were roughly proportional to the pore volume (pv) of the particular filter material (Table 2). One pv was defined as nV_t , where n is the effective transport porosity and V_t is the total volume of the filled column.

Samples were taken from influent and effluent weekly during the first 40 weeks, thereafter biweekly. The pH was analyzed

Table 2 – Pore volumes of the columns and daily load of NP (nitrogen–phosphorus) solution

Material	Pore volume (dm ³)	Pore volume (% of bulk material)	Daily load (dm ³ m ⁻²)	No. of pore volumes of water applied during 68 weeks
Filtra P	1.39	34.4	710	971 ^a
Polonite	1.40	35.6	530	1410
WCBFS	0.80	20.8	340	1590
Wollastonite	1.34	35.0	610	1700

^a The Filtra P column was shut down after 35 weeks because of clogging.

directly after collection. The samples were then stored in a freezer at -18°C until analysis of $\text{PO}_4\text{-P}$. Before analysis, the samples were filtered through a $0.45\ \mu\text{m}$ Micropore filter. Inorganic $\text{PO}_4\text{-P}$ was determined colorimetrically (acid molybdate method) using flow injection analysis (Aquatec-Tecator autoanalyzer). The percentage removal of P was calculated as the difference between influent and effluent concentrations at the same sampling occasion. On the basis of all removal rates for the entire period, the mean P removal percentages were determined. Apart from $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$ was also quantified and nitrogen removal rates calculated; however, these results will be dealt with in a later publication. However, there was no evidence for precipitation of ammonium-containing phosphates in the experiments; all solutions were consistently undersaturated with respect to struvite (a solubility constant of $10^{-12.6}$ was used; Doyle and Parsons, 2002).

The synthetic solution and the loading schedule were selected to mimic conditions frequently encountered in onsite wastewater treatment using reactive filter media. The concentrations of P and N represent concentrations typically found in wastewaters.

After termination of the column experiment, the columns were divided into 5-cm sections and sampled. Part of the samples from the uppermost layers (0–5 cm) and from the 15–20 cm layer of the Filtra P columns were air dried, gently crushed in a mortar, and then examined by a Perkin-Elmer S2000 Fourier transform infrared (FTIR) spectrometer. The instrument was run in the attenuated total reflectance (ATR) mode using a Golden-Gate diamond cell. The spectra were compared to those recorded for filter material samples that were not used in the column experiment.

Total concentrations of P were determined in three layers (0–5, 5–10, 40–50 cm) of the used filter materials using ICP-OES. Representative samples were dried and melted with LiBO_2 and thereafter dissolved in HNO_3 before analysis.

2.3. Solubility studies

To cast light on the mechanisms that control the solubility of PO_4 in the materials, batch experiments were carried out on both unused samples and on samples from the 0–5 cm layer of the used filter materials. Including both unused and used samples in the study provided a means to approach the equilibrium state from both supersaturation and undersaturation. Briefly, 2.00 g material (for wollastonite samples 3.00 g) was suspended in $35\ \text{cm}^3$ solutions of variable composition in polypropylene

centrifuge tubes and then equilibrated for 5 days in an end-over-end shaker at 21°C and at a background ionic strength of $0.1\ \text{mol dm}^{-3}$ (NaNO_3 was used as supporting electrolyte). For the used filter materials wet samples were used, which means that the actual liquid-to-solid (L:S) ratios were larger; 56.6 for Filtra P, 27.7 for Polonite, 27.3 for WCBFS and 12.0 for wollastonite. To produce a range of pH values and $\text{PO}_4\text{-P}$ concentrations in the suspensions, various amounts of nitric acid ($0\text{--}10\ \text{mmol dm}^{-3}$) were added. To some suspensions with $10\ \text{mmol dm}^{-3}$ nitric acid, an additional $5\text{--}20\ \text{mmol dm}^{-3}$ oxalic acid was added, to further increase the variation in pH values and $\text{PO}_4\text{-P}$ concentrations. After equilibration, the suspensions were centrifuged, their pHs were measured (using a Radiometer combination electrode) and they were filtered with $0.2\ \mu\text{m}$ single-use filters (Acrodisc PF). Directly after filtration, the alkalinity of the samples was measured through addition of $0.02\ \text{M HCl}$ to pH 5.4. Samples were analyzed for inorganic $\text{PO}_4\text{-P}$ with the acid molybdate method. Finally, total dissolved Ca, Mg and Si were determined by plasma emission spectroscopy using a Jobin Yvon JY24 ICP instrument.

The speciation of leachates from the batch experiments were processed with Visual MINTEQ (Gustafsson, 2006) using equilibrium constants for aqueous complexes (i.e. CaHCO_3^+ , CaPO_4 , CaHPO_4 , etc.) from the default Visual MINTEQ database, which mostly relies on the NIST Critical Stability constants, version 7.0 (Smith et al., 2003). Calculated ion activity products were compared to solubility constants given in the literature (Table 3). For ATCP, for which few solubility data exist, constants were calculated from raw data given for two amorphous calcium phosphates of varying crystallinities, referred to as ACP1 and ACP2 by the authors (Christoffersen et al., 1990). These thermodynamic data should only be considered as rough estimates, not least because the observed Ca:P ratios in the precipitates were between 1.28 and 1.38, which is slightly less than the ideal ratio of 1.5. The solubility data for OCP were also calculated from experiments conducted by Christoffersen et al. (1990).

3. Results

3.1. Long-term phosphate removal and pH development in columns

The columns received between 1.1 and $1.8\ \text{m}^3$ of synthetic solution during the experiment (Table 2). Technical problems with pumping caused less discharge of solution than that was intended. The column filled with Filtra P clogged after 971 pv

Table 3 – Solubility constants and heats of reaction for Ca phosphates used in the calculations

Reaction	log K _s (25 °C) ^a	ΔH _r (kJ mol ⁻¹) ^a
HAP: Ca ₅ (PO ₄) ₃ OH(s)+H ⁺ ⇌ 5Ca ²⁺ +3PO ₄ ³⁻ +H ₂ O	-44.3 ^b	0
OCP: Ca ₄ H(PO ₄) ₃ (s) ⇌ 4Ca ²⁺ +3PO ₄ ³⁻ +H ⁺	-47.95 ^c	-105 ^c
DCP: CaHPO ₄ (s) ⇌ Ca ²⁺ +PO ₄ ³⁻ +H ⁺	-19.28	31
DCPD: CaHPO ₄ × 2H ₂ O(s) ⇌ Ca ²⁺ +PO ₄ ³⁻ +H ⁺ +2H ₂ O	-19.00	23
ACP2: Ca ₃ (PO ₄) ₂ (s) ⇌ 3Ca ²⁺ +2PO ₄ ³⁻	-28.25 ^c	-87 ^c
ACPI: Ca ₃ (PO ₄) ₂ (s) ⇌ 3Ca ²⁺ +2PO ₄ ³⁻	-25.5 ^c	-94 ^c

^a Unless otherwise stated, the values are from Smith et al. (2003).

^b Solubility of HAP at 21 °C (McDowell et al., 1977).

^c Calculated from raw data given by Christoffersen et al. (1990).

and was closed for that reason. Its pv decreased and was found to be 0.45 dm³ less than that at the start.

The PO₄-P concentration in the influent was not constant; it averaged 4.5 (±0.9) mg dm⁻³. The variation probably resulted from biological activity in the container where the solution was stored.

Clear material-specific differences in PO₄-P removal were observed during the course of the experiment. Wollastonite was the least efficient material in terms of PO₄-P removal; on average 51.1% of P was removed. This is partly explained by the low pH in these columns; already after 100 pvs (134 dm⁻³), the pH of the effluent was more or less equal to that of the inflow (around pH 8). WCBFS removed more than 95% P during the first 300 pvs (240 dm⁻³), and afterwards the P retention efficiency decreased steadily; averaged over the whole time period, the P removal was 85.6%. The pH of the column effluent decreased from 11.4 at the start of the experiment to 8.8 at the end.

The two most strongly P-retaining materials were Polonite and Filtra P. Filtra P was slightly more efficient; on an average it retained 98.2% P, whereas Polonite retained 96.7%. Disintegration of Filtra P was observed, particularly in the beginning of the experiment, as a yellow-brown colour in the effluent. In both cases, the pH remained alkaline, particularly so for Filtra P, for which the column effluent pH decreased from 12.9 to 11.6 during the experiment (the corresponding pH values for Polonite was 11.7 and 9.5).

The top layer (0–5 cm) of each material showed the highest concentration of accumulated P (Table 4). The concentration decreased significantly with depth of the columns; this was especially the case in the Filtra P and Polonite materials.

3.2. Characterization of unused and used filter materials with ATR-FTIR

All four unused samples contained peaks at ~1420 and 870 cm⁻¹, characteristic for the carbonate anion in calcite (Fig. 1). Another common constituent was water with characteristic absorption peaks near 3500 and 1640 cm⁻¹.

Table 4 – Total concentration of P (g kg⁻¹ dry matter) in selected layers of the filter materials after termination of the column experiment

Layer (cm)	Filtra P	Polonite	WCBFS	Wollastonite
0–5	19.4	7.39	3.11	0.467
5–10	13.7	5.31	2.25	1.80
40–50	2.47	1.87	1.00	0.589

Other peaks in the spectra represent material-specific peaks. For example, the presence of wollastonite (β-CaSiO₃) in both Polonite and natural wollastonite was indicated by peaks near 1056, 960, 902 and 680 cm⁻¹ (Atalay et al., 2001). The observation that wollastonite was an important constituent of Polonite is in agreement with earlier studies employing chemical dissolution techniques and X-ray diffraction (Eveborn, 2003; Brogowski and Renman, 2004). The unused Filtra P sample was dominated by a number of peaks related to sulphate minerals such as gypsum, i.e. the broad sulphate peak near 1100 cm⁻¹. The split of the H₂O peak near 1640 cm⁻¹ to two peaks is characteristic for gypsum. Furthermore, the OH-stretching peak at 3640 cm⁻¹ may indicate the presence of ettringite. The presence of a small amount of ettringite was supported by the product data sheet supplied by the manufacturer (Nordkalk Oyj Abp, unpublished).

The used filter materials resembled the original samples except that the intensity and position of the carbonate peaks changed somewhat, and that a new peak appeared near 1025 cm⁻¹, which likely corresponds to the ν₃ band of the phosphate anion (Fig. 1). This peak was seen most clearly in the Filtra P and Polonite samples. In the Filtra P 0–5 cm sample, the peak position was slightly lower probably because of overlap with a silicate peak near 980 cm⁻¹, which is visible as a shoulder in the original Filtra P sample and also in the Filtra P 10–25 cm sample. Gypsum, which was present in large amounts in the unused sample, had disappeared completely. In the wollastonite sample the phosphate peak was visible as a weak shoulder, whereas in the WCBFS sample there was no clear evidence at all for a phosphate peak, probably because of overlap with neighbouring silicate peaks. In the Filtra P 0–5 cm sample, where the phosphate peak was a dominant one, there was no indication of a second high-wave-number ν₃ component at around 1050–1070 cm⁻¹, which would be typical for crystalline HAP (Soejoko and Tjia, 2003). Similarly, OCP and DCPs (DCP and dibasic calcium phosphate dihydrate (DCPD)) are not very likely candidates since these compounds are expected to possess two or more well resolved peaks in the ν₃ region (Fowler et al., 1993; Sivakumar et al., 1998). Hence, the results for the Filtra P sample indicate that the formed phosphate phase was poorly crystalline in nature. The presence of a single peak near 1025–1030 cm⁻¹ is in general agreement with ATCP (Gee and Deitz, 1954), but the peak can also be attributed to the presence of other poorly crystalline phosphate minerals (e.g., Al and Fe phosphates) as well as to adsorbed phosphate.

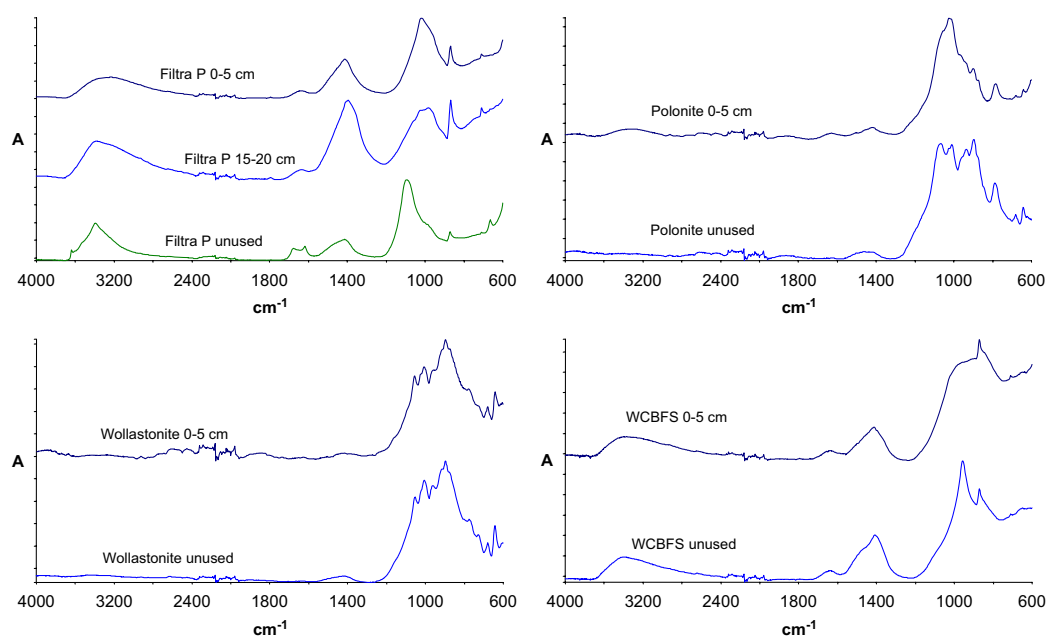


Fig. 1 – ATR-FTIR spectra of used and unused filter materials.

3.3. Solubility of phosphate in the filter materials

All $\text{PO}_4\text{-P}$ that was added to unused WCBFS, Filtra P and Polonite was removed by 100% in batch experiments. This can be explained by the very high initial pH ($= 11\text{--}13$) and dissolved Ca in these samples, which caused PO_4 to precipitate quantitatively as calcium phosphates. Addition of $\text{PO}_4\text{-P}$ as NaH_2PO_4 did not cause a sufficiently high pH reduction to increase $\text{PO}_4\text{-P}$ to detectable levels. By contrast, no added $\text{PO}_4\text{-P}$ was bound to natural wollastonite, for which pH and dissolved Ca was lower. Therefore, the batch experiments on unused filter materials provided little useful information about solubility-controlling mechanisms.

Batch experiments performed on the surface layer (0–5 cm) of the spent filter materials revealed that the pH had decreased considerably as a result of the column experiment. For example, in the Filtra P sample, the pH was only 7.8 compared with 12.6 before the experiment. The release of $\text{PO}_4\text{-P}$ from the samples was also rather high. On further acidification of the sample, the soluble $\text{PO}_4\text{-P}$ concentration of the Filtra P sample increased further, which would be expected if a Ca phosphate controls the P solubility (Fig. 2). At the lowest pH almost 2 mM $\text{PO}_4\text{-P}$ was dissolved, which was equivalent to 3.5 g P kg⁻¹ dry matter, or 18% of the total amount of accumulated P (see Table 4). The same trend, although much weaker, was observed for wollastonite. For WCBFS, the dissolved $\text{PO}_4\text{-P}$ concentration increased with increasing acid additions until pH 6.9, at which point 5.6% of the total accumulated P had dissolved. Further pH reduction

caused decreasing $\text{PO}_4\text{-P}$ concentrations. A possible explanation is adsorption of $\text{PO}_4\text{-P}$ to an oxide phase (Fe or Al oxide) at low pH in the slag. Interestingly, Pratt et al. (2007) showed that most of the retained P in a melter slag filter was associated with Fe and Al after 5 years of operation; the pH in their filter was reported to range from 6.7 to 7.4. For Polonite, the results are less clear because pH could not be decreased below 7.6, when not more than 3.5% of the accumulated P was dissolved. Results from ICP measurements indicate that the wollastonite matrix is dissolved near this pH (data not shown), which would prevent Ca phosphates from dissolving.

In an earlier study with other filter materials in which equilibrium was obtained only from supersaturation, it was hypothesized that HAp was formed (Johansson and Gustafsson, 2000); this was based on the observed slope between pH and $5\log[\text{Ca}^{2+}] + 3\log[\text{PO}_4^{3-}]$. However, the data we present here are not in agreement with this hypothesis, because $\text{PO}_4\text{-P}$ in the used filter materials was more soluble than would be expected from this equilibrium. Most of the samples were supersaturated with respect to HAp (Fig. 3). Two other candidates to control PO_4 solubility are DCPD ($\text{CaHPO}_4 \times 2\text{H}_2\text{O}$) and DCP. However, most samples were undersaturated with respect to these phases, although the most acid Filtra P samples seemed to be in equilibrium with DCP or DCPD. At high pH however, the samples were far from equilibrium indicating that the results could not be resolved easily in terms of equilibrium with respect to DCP or DCPD. Many of the samples were relatively close to the solubility line of OCP (Fig. 3), indicating that OCP might be involved in determining $\text{PO}_4\text{-P}$ solubility.

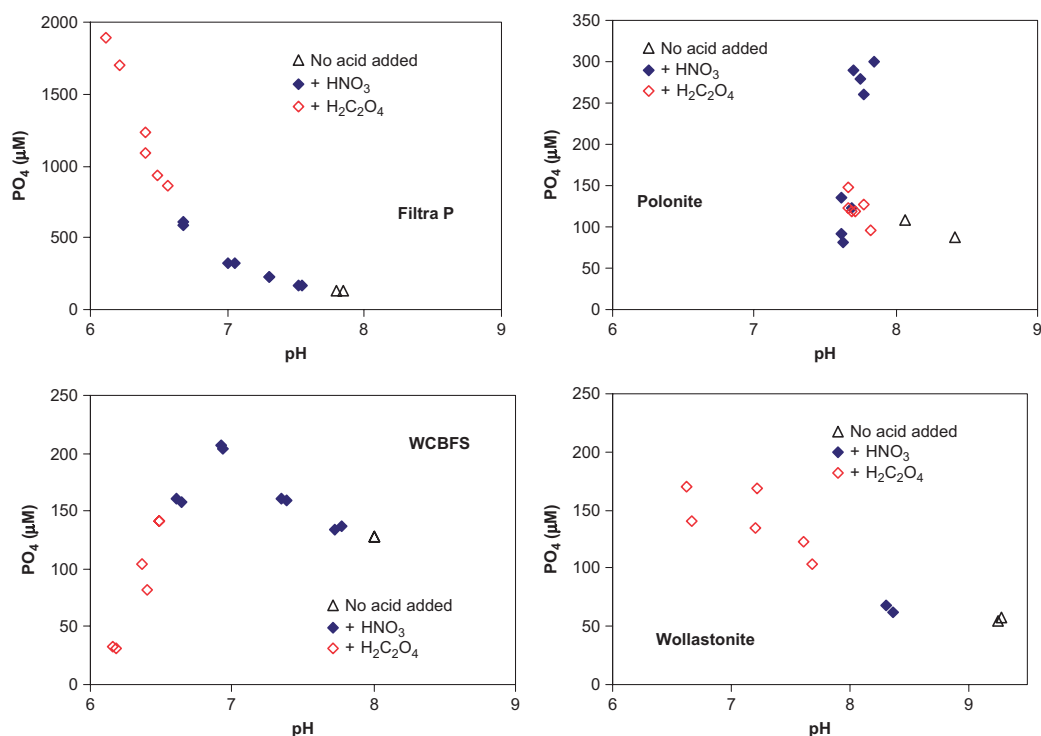


Fig. 2 – Dissolved PO_4 ($\mu\text{mol dm}^{-3}$) from the 0–5 cm layers of the used filter materials as a function of pH, as recorded in batch experiments with varying amounts of acid.

Finally ATCP, with the stoichiometric composition $\text{Ca}_3(\text{PO}_4)_2$, may also control PO_4 -P solubility. As shown in Fig. 3, many samples were close to equilibrium with the less non-crystalline ATCP termed ACP2 (Christoffersen et al., 1990). Moreover, the pH dependence of the ion activity products were in better agreement with ACP2 than with OCP, which suggested that solubility control by ACP2 (or ATCP) was slightly more likely although a prominent role for OCP could not be ruled out from these observations only.

4. Discussion

Both Filtra P and Polonite had a remarkable potential to remove PO_4 -P from solution, as evidenced by the results shown in Table 4. This suggests that they can be applied for a relatively long time in the field before saturation of phosphate occurs; this would be attractive from a sustainability perspective. In practice however, the lifetime of these materials is likely to be limited by their technical performance (i.e., clogging). In the column experiment, it was noted that severe clogging occurred for the Filtra P column and it was consequently shut down after 971 pvs. This seemed to be related to structural degradation of the material because of

matrix dissolution and subsequent precipitation of secondary phases. In the field with real wastewater, the lifetime is likely to be shorter for both materials because of inflow of particulate and colloidal matter.

As can be seen in Fig. 3, PO_4 -P was slightly more soluble in the Polonite samples than in the Filtra P samples. The reason seems to be connected to the different response to the acid additions. For Filtra P, increasing acid additions led to decreasing ion activity products for ATCP (Fig. 4), probably because dissolved PO_4 -P reached equilibrium with respect to DCP or DCPD. For Polonite, the ion activity products for ATCP increased with increasing acid additions (Fig. 4). A possible explanation is that the acid addition initially released PO_4 -P, which was then re-precipitated as ATCP during the batch experiment when pH was increased because of wollastonite dissolution. At the same time, equilibrium with DCP/DCPD was not reached, allowing the ion activity products for ATCP to rise. Thus in many of the Polonite samples, equilibrium may have been approached from supersaturation rather than from undersaturation.

It is of interest to compare the batch experiment results on PO_4 -P solubility with those from the previous study (Johansson and Gustafsson, 2000), in which equilibrium was approached from supersaturation for a series of blast furnace

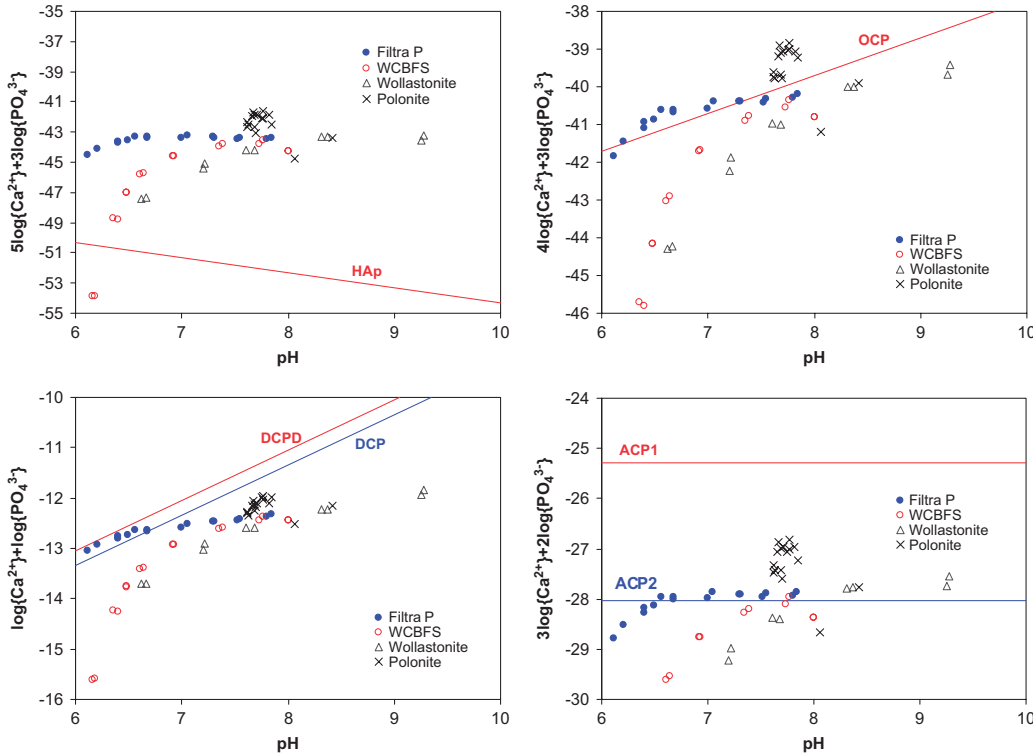


Fig. 3 – Solubility diagrams for the 0–5 cm layer of the used filter materials. The points represent the calculated solution activities in the batch experiment extracts. The solubility lines are calculated from the data given in Table 3. Data points above the lines indicate supersaturation.

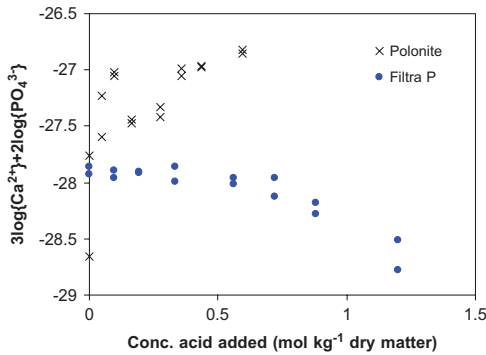


Fig. 4 – The logarithm of the ion activity product of ATCP, $3 \log(\text{Ca}^{2+}) + 2 \log(\text{PO}_4^{3-})$, as a function of the concentration of added acid for the 0–5 cm layers of Filtra P and Polonite.

slags (similar to WCBFS of the present study). Not surprisingly, the PO_4 solubility of these slag samples was slightly larger (Fig. 5). Below pH 10.5, the deviation between the two

series of data was comparably large, which may suggest that equilibration from supersaturation is slow at low pH. At higher pH, the ion activity products were in better agreement. These observations, together with the ATR-FTIR evidence, provide support for the formation of ATCP as a reactive surface phase on the filter materials. An estimate of the apparent solubility constant for ATCP was made by averaging the logarithms of the ion activity products for samples for which no acid additions had been made. This resulted in $\log K_s = -27.94 \pm 0.31 (1\sigma, n = 7)$. As is seen in Fig. 5, the solubility line is close to the observed values for many samples, particularly at pH 6.6 and higher.

The observation that a soluble Ca–P phase, probably ATCP, had accumulated in the filter materials suggests that at least part of the $\text{PO}_4\text{-P}$ is easily available to plants. However, only between 3.5% and 18% of the accumulated $\text{PO}_4\text{-P}$ was readily dissolved from the used filter materials in the batch experiments. There may be several reasons for this, partial crystallization to slightly less soluble phases (such as HAp) or adsorption of $\text{PO}_4\text{-P}$ to Fe/Al oxide components are two possibilities. Thus, more detailed spectroscopic studies need to be performed to fully elucidate the solid-phase speciation and reactivity of the accumulated phosphates.

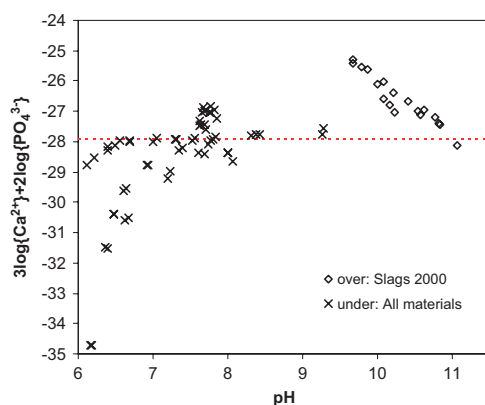


Fig. 5 – Solubility diagram for (a) slag samples in which equilibrium was approached from supersaturation (Johansson and Gustafsson, 2000) and (b) the materials from the present study, in which equilibrium was approached from undersaturation. The dotted line indicates the suggested solubility constant ($= 10^{-27.94}$ at 21 °C) for the ATCP phase formed.

5. Conclusions

Polonite[®] and Filtra P are two promising filter materials for the removal of PO₄-P from households. In column experiments using synthetic solutions, these materials were able to accumulate between 1.9 and 19 g kg⁻¹ PO₄-P, maintaining a PO₄-P removal efficiency of >95%. However, Filtra P is susceptible to clogging because of structural degradation; this will limit its practical lifetime in field applications. Water-cooled blast furnace slag and natural wollastonite were also able to remove PO₄-P, although less efficiently. Batch experiments on used filter materials indicated that amorphous tricalcium phosphate (ATCP) had formed. This means that at least part of the accumulated PO₄-P is readily available to plants.

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IV

Transformation and removal of nitrogen in reactive bed filter materials designed for on-site wastewater treatment

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Abstract

Nitrogen (N) and phosphorus (P) should be removed and recycled from wastewater in order to reduce the nutrient load to recipient waters, avoid contamination of groundwater and conserve resources. Nitrogen removal and transformation were studied in domestic wastewater percolating in unsaturated conditions through 0.5 m long columns containing potential filter materials. Six materials (three types of slag, limestone, opoka, Polonite[®] and sand) were compared at a design loading rate of 85 L m⁻² d⁻¹ during 67 weeks. All materials transformed ammonium efficiently to nitrate (>98%). Apparent removal of inorganic N was shown only by the coarsest slag and by Polonite[®], possibly due to losses through volatilisation. All other filter materials leached nitrate at the column effluent. Total N content was highest in the surface layer of the column material, with decreasing values with depth. In contrast, carbon (C) was more evenly distributed throughout the column. This indicates that mineralisation and biological activity primarily took place close to the surface of the filter material. It was concluded that the alkaline filter materials studied were not suitable media for combined nitrogen and phosphorus removal in engineered wetlands and compact filter wells.

Key words: ammonium removal, blast furnace slag, column experiment, nitrification, Polonite[®]

1. Introduction

Nitrogen (N) and phosphorus (P) in wastewater flows from single houses and small hamlets in rural areas are an important source of pollution of surface water and groundwater (Jacks et al., 2000; Camargo and Alonso, 2006). It has long been recognised that nitrogen species such as nitrate (NO₃-N) can pollute groundwater when wastewater is treated by soil infiltration systems (Yates, 1985). NO₃-N is highly mobile and poses a health risk to people using drinking water from polluted wells. Removal of nitrogen can be accomplished through the use of air stripping, breakpoint chlorination, ion exchange and biological nitrification-

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denitrification (Metcalf and Eddy, 2003). However, these advanced technologies are rarely found in decentralised wastewater treatment systems, where on-site systems such as soil infiltration, constructed wetlands and filter beds are more often employed (Vymazal et al., 1998; Jantrania and Gross, 2006). Good performance in N and organic matter removal (measured as Biological Oxygen Demand, BOD) has been reported for various types of on-site systems (Arias et al., 2005; Vymazal, 2007). The efficiency of P removal in such systems has been questioned and it has been suggested that the commonly used sand, gravel and peat should be replaced by materials with a higher capacity for P removal, such as expanded lightweight clay aggregates (LWA), Filtralite™, shale, slag, shell sand, Filtra P and Polonite® (Drizo et al., 1997; Zhu et al., 1997; Roseth, 2000; Jenssen and Krogstad, 2002; Søvik and Kløve, 2005; Gustafsson et al., 2008). It could also be possible to recycle such materials together with the P removed back to agriculture as fertilisers and soil amendments (Hylander and Simán, 2001; Hylander et al., 2006; Cucarella et al., 2007). The capacity of these materials to recycle N has not yet been studied.

The use of reactive filter materials with a pH around or above 10 when treating wastewater is suggested to change the prerequisites for biological N removal. However limited studies exist to support this assumption. A compact filter system developed in Norway using the alkaline material Filtralite™ demonstrated 30-40% N removal (Jenssen et al., 2005; Heistad et al. 2006). The relatively low removal rate was suggested by Heistad et al. (2006) to be the result of inhibition of microbial denitrification due to the high pH of the filter material used.

A mineral-based filter material that is well-known for its excellent N removal capacity and that could be useful in constructed wetlands and compact filter systems is zeolite. Extensive investigations have been performed on different types of zeolite (clinoptilolite, mordenite) during the past three decades but most of these examined N removal under laboratory conditions (e.g. Klieve and Semmens, 1980; Baykal and Guven, 1997; Sarioglu, 2005; Ji et al., 2007). Zeolites should be tested in full-scale treatment systems where their N removal capacities could be studied together with the effect of biological activity and the presence of organic matter (cf. McVeigh and Weatherley, 1999).

This paper examines the performance of fixed bed 0.5 m long columns of filter materials for treating domestic wastewater on-site under unsaturated, intermittent flow conditions. The study forms part of a long-term experiment, with P retention and the subsequent use of the filter materials as fertilisers presented in a previous publication (Hylander et al., 2006). Six materials were compared in the present study: two types of slag, limestone, opoka, Polonite® and sand. The by-product blast furnace slag used here is similar to that applied previously in constructed wetlands (Gruneberg and Kern, 2001) and slag filters (Shilton et al., 2006). The natural materials (limestone, opoka, sand) are commonly used or intended for use in bed filters or constructed wetlands (e.g. Pell, 1991; Coombes and Collet, 1995; Brogowski and Renman, 2004). Polonite® was included as it is a novel filter material, not previously evaluated for domestic wastewater. Based on the content of CaO, the materials can be classified on a scale from chemically highly reactive to non-reactive. The slags and Polonite belong to the highly reactive group, while sand is non-reactive and limestone and opoka are intermediate.

The removal capacity regarding inorganic N of the six materials was investigated by examining N transformations following the downflow unsaturated mode of the treatment system and by determining the content and vertical distribution of carbon and nitrogen in the filter columns.

2. Materials and methods

The experiment was carried out indoors (temperature 20 °C) at the Loudden wastewater treatment plant in Stockholm. The plant receives domestic wastewater and is designed for a flow of 16 000 m³ d⁻¹. The raw wastewater was pumped to a experimental set-up consisting of pretreatment units and columns imitating the conditions of on-site treatment with filter beds (Fig. 1). A two-chamber septic tank was the first step, aimed to remove suspended solids (SS). It was followed by a 2.5 cm thick layer of mineral wool at the top of each column. This wool was exchanged three times during the experimental period. On average, 0.5 L h⁻¹ of wastewater was pumped and sprinkled equally over the surface area of the column materials every second hour for 67 weeks. The wastewater distributed to the filters had the following characteristics according to data received from the owner of the wastewater treatment plant (mg L⁻¹, n=5): SS 130 ±11, BOD₇ 85 ±15, Tot-P 4.9 ±0.5, Tot-N 32 ±3.1. The six filter materials coarse amorphous slag (ASC), crystalline slag, coarse (CSC) and very coarse (CSV), limestone, opoka, Polonite[®] and sand were filled to a height of 50 cm in 30-cm wide columns (two materials in duplicate) and received wastewater under unsaturated flow conditions. Data on the materials used and their physical properties are shown in Table 1. The sand was used as a reference material because of its known N removal capacity (Ritter and Eastburn, 1988).

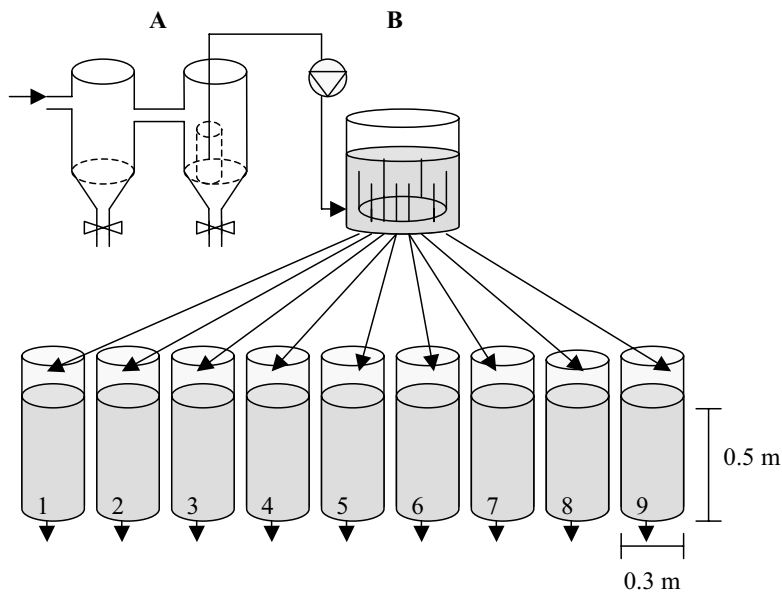


Figure 1. The experimental set-up with pre-treatment system (A), distribution device (B) and columns (1-9) filled with sand, opoka, Polonite[®], limestone and blast furnace slags.

Table 1. Physical parameters of filter materials at the start of the experiment

Column No.	Filter material ^a	pH _{H₂O} (1:2.5)	Particle size (mm)	Specific surface area (m ² g ⁻¹)	Hydraulic conductivity (m day ⁻¹)	Column porosity (%)	Column pore vol. (l)
1	Opoka	8.3	2-5.6	50.85	1481	50.2	17.7
2	Sand	6.5	0-2	0.09	200	43.7	15.4
3,7	Polonite	12.5	2-5.6	0.70	800	47.7, 50.8	15.7, 17.9
4,8	CSC	9.6	0.25-4	0.50	15.9	45.5, 44.5	16.4, 15.7
5	ASC	9.9	0.25-4	0.43	40.6	46.7	16.5
6	Limestone	8.9	1-2	0.57	238.5	46.4	16.4
9	CSVC	9.4	2-7	0.37	1950	50.9	18

^a ASC = amorphous slag, coarse; CSC = crystalline slag, coarse; CSVC = crystalline slag, very coarse.

The blast furnace slags were donated by the steel producer SSAB Merox, Oxelösund, Sweden; the limestone was obtained from Ignaberga quarry in southern Sweden; and the sand was a manufactured washed quartz sand. Polonite, which is processed from opoka, a bedrock found in the south-eastern part of Europe (Brogowski and Renman, 2004), was donated by NCC AB, Sweden.

Sampling was performed regularly during 67 weeks with a total number of 40 duplicated samples (100 mL polypropylene bottles) of influent and effluent of each column. The pH and electric conductivity (EC) of the liquids were determined within 1 h, whereafter they were frozen (-18 °C) until time of analysis. Samples were filtered through a 0.45 µm filter (Satorius) before each analysis. Inorganic forms of nitrogen, i.e. ammonium (NH₄-N), nitrate (NO₃-N) and nitrite (NO₂-N) were analysed using Flow Injection Analysis (FIA, Aquatec-Tecator autoanalyser). The pH of liquids was determined by a Radiometer PHM 82 Standard pH-meter. BOD₇ was measured at the laboratory of Stockholm Water AB, according to Swedish Standards (SS028143-2 mod. and SS-EN 25814-1).

It was not possible to maintain the desired wastewater flow of 6 L day⁻¹ equally to all columns, so the incoming volume was followed by regular manual measurements and verified by tipping-bucket flow meters connected to a data logger (Campbell CR10X).

The removal capacity of the filter materials, i.e. loss of organic matter (BOD₇) and of N during the infiltration of wastewater, was calculated according to the equation:

$$\text{Loss} = \left[1 - \frac{C_e}{C_i} \right] 100 \quad (1)$$

where C_e is the effluent concentration and C_i is the influent concentration.

When the column experiment was completed, the columns were divided into the layers 0-5, 5-10, 10-20, 20-30, 30-40, and 40-50 cm depth from the surface and sampled. Samples were dried at room temperature (20-30 °C). Duplicate subsamples of materials used for analyses were finely crushed in a mortar. Total element contents in individual sections of the different materials were determined by extraction with conc. HNO₃ in an autoclave (120 °C for 30 minutes, material:solution 1:20; modified from SIS (1986). Carbon and N were determined by dry combustion on a LECO combustion system coupled to an IR-detektor (LECO, 1995).

Data were subjected to analysis of variance (Statistix for Windows, 1996).

3. Results and discussion

3.1. pH, electrical conductivity and volume of wastewater treated

The pretreated wastewater distributed to the columns maintained a pH between 8.18 and 9.28 during the course of the experiment, while the EC was between 0.32 and 0.63 mS cm⁻¹. The volume of treated wastewater in each column varied only slightly (Table 2). Column effluents had a larger variation in both pH and EC, specific for each material (Table 2). High pH and EC values appeared at the start in the effluents of the columns filled with Polonite and decreased towards the end of the experiment. The slags showed a similar pattern but the range of the time-dependent decrease was markedly smaller. The column effluents from sand and to some extent limestone mainly followed the pH and EC values of the incoming wastewater.

The column experiment was closed periodically for maintenance. The wastewater distribution system with tubes and pumps had to be cleaned and the sludge had to be removed from the septic tank. For that reason, the expected volume of about 2 800 litres to be treated was not reached. The differences between volumes treated in individual columns (Table 2) were related to sporadic failures of the distribution system.

An even distribution of liquid over the bed filter surface is crucial for the treatment performance and is likely to become an engineering problem of the future when unsaturated flow systems are used. The filter material was inspected carefully during excavation and sampling of the solid phase. We could not find any evidence that uneven distribution and preferential flows had occurred, which otherwise could have had significance for interpretation of the results.

Table 2. Range of pH and electrical conductivity (EC) in column effluents and measured volumes of treated wastewater during the experiment

Column, filter material	Effluent pH	Effluent EC (mS cm ⁻¹)	Treated wastewater volume (L)
1 Opoka	8.29-9.95	0.44-1.53	2 734
2 Sand	6.05-9.27	0.43-0.74	2 617
3, 7 Polonite	8.23-12.84	0.35-6.64	2 528, 2 551
4, 8 CSC	8.09-9.88	0.57-1.83	2 303, 2 378
5 ASC	8.93-9.73	0.55-1.08	2 387
6 Limestone	7.63-9.81	0.45-0.96	2 448
9 CSVC	8.49-9.75	0.52-1.49	2 790

3.2. Inorganic nitrogen transformations and removal

The concentrations of NH₄-N and total inorganic nitrogen (TIN = Σ NH₄-N, NO₃-N, NO₂-N) in the influent wastewater were on average 26.6 ±5.5 mg L⁻¹ and 26.9 ±12.6 mg L⁻¹, respectively. An effluent concentration of NH₄-N below 1 mg L⁻¹ was recorded rather soon after the start of the experiment. The temporal variation in NH₄-N concentration in the effluent of CSVC slag (Fig. 2) represents the overall pattern found, with the exception of the two Polonite columns (3 and 7). In these latter columns Polonite exhibited a much slower development of NH₄-N transformation and stable, low effluent values as in the other columns were not fully reached. However NH₄-N was reduced to less than 7 mg L⁻¹ after the wastewater had percolated through the Polonite filter material for a few weeks of operation (Fig. 3).

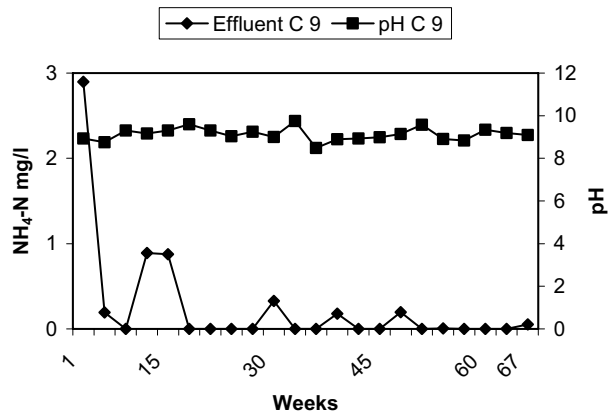


Figure 2. Temporal variation in the ammonium concentration at the exit of the CSVC column (C9) and pH of the effluent (influent concentration $26.6 \pm 5.5 \text{ mg L}^{-1}$; influent pH range 8.18-9.28).

The concentration of $\text{NO}_2\text{-N}$ in influent wastewater was $55.5 \mu\text{g L}^{-1}$ (range 1.8 - $90.3 \mu\text{g L}^{-1}$) and it remained at this low level in effluents from all columns except for those filled with Polonite, where it was 2.93 mg L^{-1} . Nitrate was also quite low in the influent wastewater (0.25 mg L^{-1} , range 0.013 - 0.49 mg L^{-1} , but on the other hand increased markedly after passing through the materials, resulting generally in concentrations of between 0.03 and 87.6 mg L^{-1} in the effluents.

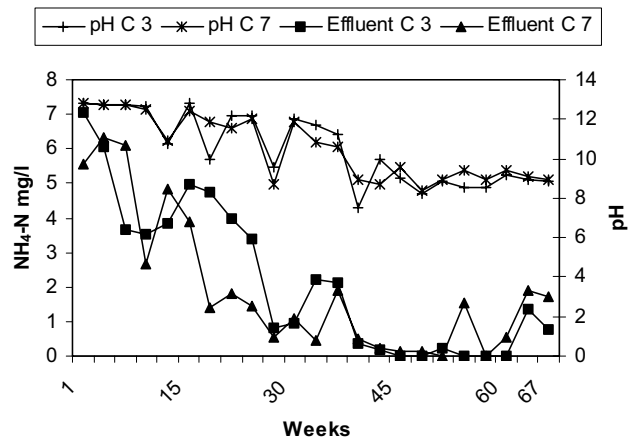


Figure 3. Temporal variation in the ammonium concentration at the exit of the Polonite columns (C3, C7) and pH of the effluent (influent concentration $26.6 \pm 5.5 \text{ mg L}^{-1}$; influent pH range 8.18-9.28).

The removal performance of NH₄-N was over 90% in all columns regardless of filter material (Table 3). Only two materials (Polonite and CSVC) were able to reduce the total inorganic nitrogen (TIN) content over the whole experimental period, by 17.7% and 9.8% respectively. The other filter materials leached NO₃-N and NO₂-N, particularly the amorphous slag.

Effluent pH remained high in Polonite and CSVC columns at the end of the experiment (Figs. 2,3). Oxygen was not measured but the coarser materials such as these two were most likely more aerated than the finer materials due to a higher diffusion rate. However opoka (column 1) had the same particle size distribution and similar porosity, although not high pH, and did not remove TIN. Ammonium nitrogen may be present in ionised (NH₄⁺) and non-ionised (NH₃) forms and the equilibrium of both species depends on pH values according to the equation (Thornton et al., 2007):



The nitrification process converts ammonium to nitrate. Nitrification is a two-step process mainly associated with the chemo-autotrophic bacteria, which consume oxygen. In the first step the strictly aerobic nitrifiers derive their C largely from CO₂ or carbonates. The oxidation of nitrite to nitrate is the second step, where bacteria also need organic compounds for the process.

Table 3. Nitrogen removal capacity of the filter materials studied and the column effluent concentration of NH₄-N and NO₃-N (mean ± SD) for the study period

Column, filter material	Treatment capacity (%)		Effluent concentration (mg L ⁻¹)	
	NH ₄ -N	TIN	NH ₄ -N	NO ₃ -N
1 Opoka	98.8 ±1.54	0*	0.33 ±0.44	30.44 ±13.37
2 Sand	98.6 ±3.30	0*	0.25 ±0.55	31.69 ±7.26
3,7 Polonite	90.8 ±10.80	17.7	2.17 ±2.86	17.12 ±12.85
4,8 CSC	99.3 ±1.96	0*	0.17 ±0.51	26.99 ±7.13
5 ASC	99.5 ±1.31	0*	0.11 ±0.32	33.94 ±13.99
6 Limestone	99.6 ±1.39	0*	0.10 ±0.34	27.08 ±6.11
9 CSVC	98.8 ±2.59	9.8	0.31 ±0.66	23.59 ±8.38

TIN= Σ NH₄-N, NO₃-N, NO₂-N. Leaching indicated by *

The observed decrease in effluent NH₄-N concentration in columns 1, 2, 4, 5, 6 and 8 was obviously attributable to microbial immobilisation and nitrification, i.e. transformation processes rather than removal. At pH values above 9.3, NH₄⁺ can be converted into NH₃. This NH₃ volatilisation could have occurred in the columns with Polonite and amorphous and crystalline slag, i.e. columns 3, 4, 5, 7 and 9.

In contrast to the zeolites, which have been frequently studied in terms of nitrogen removal, NH₄-N ion exchange is most likely a process that does not occur in the reactive filter materials studied here due to their chemical structure and content. In reactive filter materials, CaO is dominant and the high Ca²⁺ ion activity and high pH can decrease the capacity of NH₄-N removal by ion exchange (Sarioglu, 2005; Thornton et al., 2007). Wollastonite (CaSiO₃) is one of the mineral phases identified in Polonite (Brogowski and Renman, 2004). According to Lind et al. (2000) wollastonite can remove 50% of ammonium in human urine through direct contact and a similar process could to some extent be possible in Polonite.

3.3 Carbon and nitrogen content and distribution in the materials

The total N content was highest in the 0-5-cm layer of all materials (Fig. 4). This was accompanied by a high total C content particularly in the surface layers of sand, Polonite and crystalline slag (Table 4). The highest C content in the whole filter mass at termination of the experiment was found for opoka. The vertical N distribution differed between materials, as can be seen in Figure 4. The differences were obviously related to particle size distribution and thereby to hydraulic conductivity of each material (cf. Table 1).

It is of interest to compare the two slags CSC and CSVC, which are chemically identical products with different particle size distributions. The fine fraction of CSC was able to create a dense covering in the surface layer where organic matter was retained and bacteria populations developed. The very coarse CSVC, on the other hand, allowed solute transport downwards and retention of organic matter and bacteria growth in the whole filter matrix. As a matter of fact in both these slag materials total contents of C and N were roughly the same, although differently distributed. The clear difference in content and distribution of C and N between opoka and Polonite, which is manufactured from opoka by heating, had several causes. Polonite in the desired fraction of 2-5.6 mm always contains a tail of very fine particles and its CaO reacts with wastewater forming a solid, but not impermeable, surface layer. For that reason percolation is slower than in opoka and a superficial layer of organic matter and bacteria can develop, as is also the case for sand, CSC and ASC.

Pell et al. (1990) clearly showed a general pattern of decreasing numbers of bacteria with depth in a sand filter, with bacteria constituting a large part of the biomass in the surface layer. This in fact was probably true for all the filter materials studied here but was more accentuated in the most alkaline types. In the case of Polonite, bacterial activity and mineralisation could have been expected only in the surface layer, where pH was lower. The mineral wool used to protect the filter matrix from entry of particulate matter also served as a biomat. Support for these observations is provided in a paper by Renman et al. (2004), who studied the occurrence of bacteria in filter material (0-5 cm) and effluent from four columns of the same experiment as presented here (sand, coarse slag, Polonite and opoka). After 58 weeks of operation, high removal efficiency of bacteria was found, particularly in the Polonite material where a high percentage of the bacteria in effluent comprised spore-forming bacteria, mostly belonging to *Bacillus* spp. Sand reduced bacteria much better than opoka, which was most likely related to the finer particle size of the sand used.

Contrary to what has been observed in other investigations, the column filled with sand in this study did not show good removal of TIN. Aslan and Cakici (2007) observed NO₃-N removal at the upper layer of a slow sand filter bed, while Nakhla and Farooq (2003) demonstrated that simultaneous nitrification-denitrification processes can occur. Bahgat et al. (1999) observed that the ammonia oxidising bacteria (*Nitrosomonas*) were more abundant and better distributed than the nitrite oxidisers (*Nitrobacter*) throughout the depth of a sand filter. However the reactive materials used in our study were not promising in terms of TIN removal capacity. The loss of about 18% TIN from Polonite columns during the experiment was probably caused by volatilisation. A comparison of TIN in the effluent when pH was above and below 9 revealed that the loss was associated with the high pH range. The role of wollastonite in the observed loss is unclear but assumed to be minor considering its low content in the filter material. The reactive filter materials obviously create an alkaline environment that inhibits denitrification even in the superficial layer, where the biofilm could create a biologically active part of the filter. Unfavourable conditions for denitrification in sand and limestone too were caused by the mode of intermittent discharge of wastewater to the columns and the unsaturated flow. This was intended to create oxygenated conditions in the matrix of each material throughout the whole experimental period. It is known that the

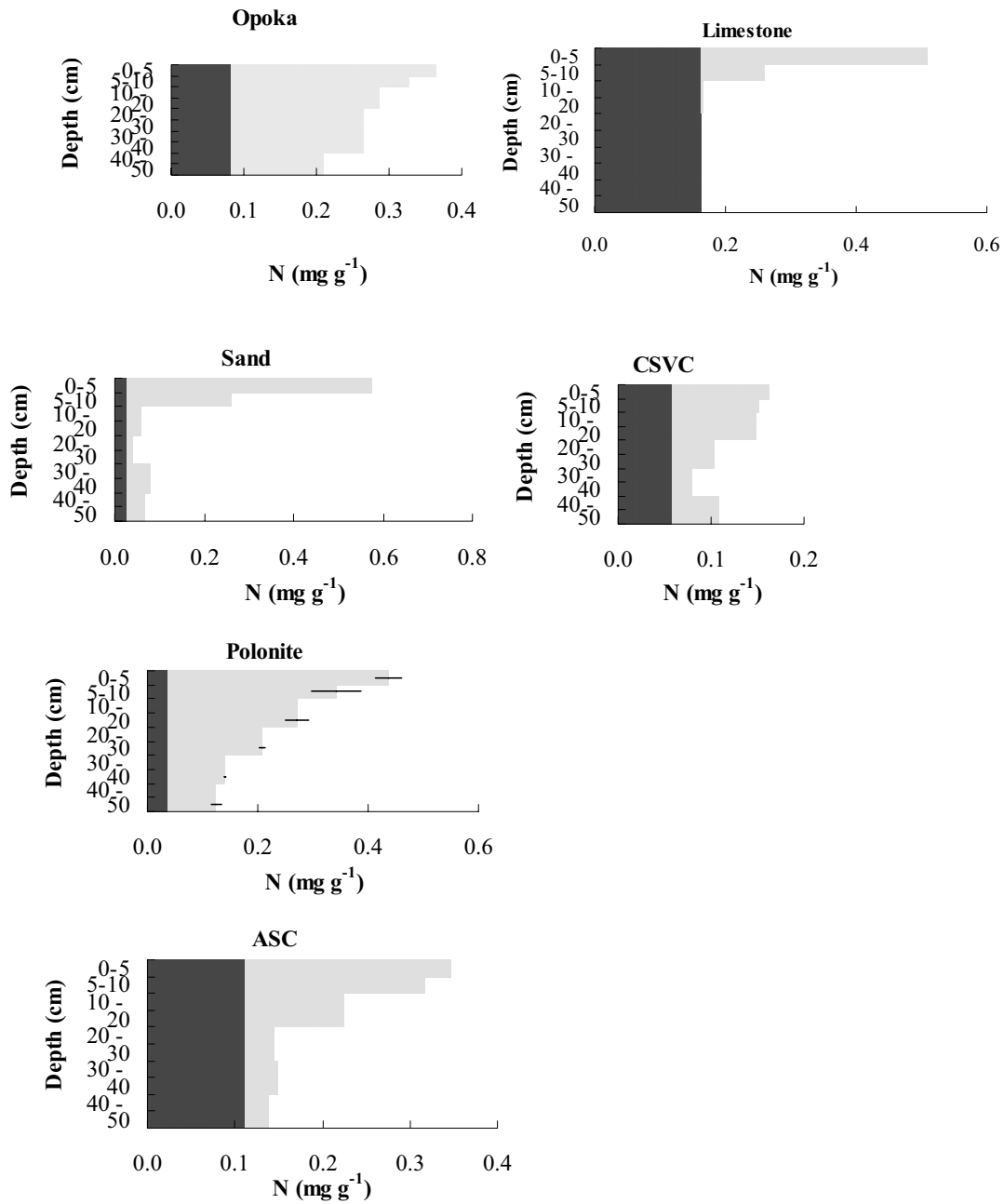


Figure 4. Initial N content in the materials (dark spotted area) and N enriched to different layers (light spotted area) after 67 weeks of wastewater treatment by infiltration. Bars indicate ±SE where columns were duplicated.

Table 4. Total C concentration in different layers of the filter materials (average and SD given for duplicate columns).

Column Filter material ^a	Back- ground	Additionally accumulated C at layer (cm)					
		0-5	5-10	10-20	20-30	30-40	40-50
(mg g ⁻¹)							
1 Opoka	19.4	44.2	46.9	47.6	53.2	54.5	47.1
2 Sand	0.4	3.0	1.2	0.12	0.02	0.04	<0.01
3, 7 Polonite	21.3	6.4	3.2	4.8	0.81	1.1	<0.01
4, 8 CSC	2.6	1.4	0.25	0.17	0.15	0.19	<0.01
5 ASC	1.7	0.16	0.27	0.34	0.03	0.35	0.65
6 Limestone	104.8	1.6	<0.01	3.3	4.3	6.5	6.6
9 CSVC	1.9	<0.01	0.15	0.47	0.69	0.53	0.94

^a ASC = amorphous slag, coarse; CSC = crystalline slag, coarse; CSVC = crystalline slag, very coarse

presence of competing ions and organic matter can significantly reduce the removal of NH₄-N (Chen et al., 2002) but the role of organic carbon for nitrogen removal in reactive bed filter materials has to be further investigated.

The loss of TIN from the very coarse slag is more difficult to explain. Its pH over 9 possibly caused some losses by volatilisation that could have been enhanced due to the coarse and well-aerated material.

The effluent BOD values were investigated after 45, 50 and 58 weeks of operation of the column system. The organic matter removal appeared to be excellent in all filters (mean 97.7% ±0.76, n=3 for each column). The relatively low content of total carbon in the filter mass and the similar BOD removal rate in all columns seem to be partly related to efficient pretreatment by the mineral wool placed on the surface of the filter materials, which prevented the occurrence of filter bed clogging. Clogging of the reactive material by organic matter accumulation and/or structural degradation with CaCO₃ precipitation can otherwise cause problems in constructed wetlands (Ádám et al., 2005) and compact filter systems (Ádám et al., 2007; Gustafsson et al., 2008). The present study indicates that efficient N and P removal within the same filter material is difficult to obtain. For this purpose dual or multiple systems of reactive materials have to be applied to achieve strictly applied effluent criteria.

4. Conclusions

None of the six filter materials tested here showed good potential for removing total inorganic nitrogen (TIN). Ammonium-N, a dominant N component in the wastewater, was transformed in the filter beds to NO₃-N. In addition, effective mineralisation of organic matter occurred in the surface layers of all columns, which was indicated by leaching of TIN and reduced BOD values. Ammonium-N removal within the column filter systems was apparent from the beginning of the experiment and reached equilibrium after about 2-3 weeks of operation of all columns except those filled with Polonite. This strongly alkaline material removed 17.7% of the influent nitrogen, which was mainly associated with losses through volatilisation. The content and distribution of carbon and nitrogen in the 0.5-m deep filter columns was related to the particle size distributions of the materials studied. Sand and Polonite exhibited the most visible accumulation of C and N in their surface layers (0-5 cm) in contrast to opoka, the matrix of which had the same C and N content independent of filter depth. Although efficient

for P removal, alkaline filter materials cannot be considered suitable bed components for N removal in engineered wetlands and compact filter wells. Instead, dual treatment systems should be developed where e.g. zeolites for NH₄-N removal could be included.

Acknowledgements

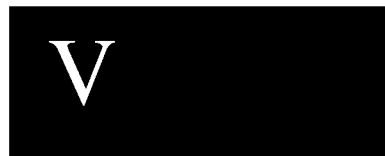
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Metal removal by bed filter materials used in domestic wastewater treatment

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Abstract

Bed filters using reactive materials are an emerging technology for on-site wastewater treatment. Used materials, which are enriched with phosphorus, can be used as a fertiliser or soil amendment. However the materials can also be enriched with metals from the wastewater. Six materials (opoka, sand, Polonite[®], limestone, two types of blast furnace slag) exposed to long-term wastewater loading in columns and in a compact filter well filled with Polonite were investigated for metal removal and accumulation. Wastewater applied to the columns had low heavy metal concentrations in the order Zn > Cu > Mn > Ni > Cr. All columns removed Zn (53-83%) except sand. Polonite demonstrated high removal of Mn (> 98%), while only the slags removed Ni. All materials showed increased Cu, Cr(III), Mn, Pb and Zn content after filtration. Speciation calculations showed that the high concentrations of dissolved organic matter might have prevented efficient metal removal, particularly in the case of Cu. The low content of toxic heavy metals in the filter materials studied would probably not restrict their use as a fertiliser or soil amendment.

Key words: column experiment; contamination; blast furnace slag; soil amendment; Polonite[®]

1. Introduction

On-site systems are considered a legitimate form of wastewater treatment in rural areas and in such cases a septic tank system combined with unsaturated soil adsorption bed is the most common disposal design. However other treatment systems have been developed during recent decades, among which constructed wetlands are the most widely applied [1]. A new alternative on-site system that provides treatment prior to soil disposal or to a receiving water body comprises a self-contained flow-through unit where a reactive mixture (also referred to as substrate, medium, material, sorbent) is incorporated [2]. This system has the advantage of being very efficient in the removal of phosphorus (P) [3, 4, 5]. However, a problem with the use of these materials is that they also may sorb heavy metals from the wastewater. This poses a

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risk of soil contamination when the spent materials are used in agriculture as a fertiliser or soil amendment [6, 7].

Blast furnace slag is one example of a sorbent industrial by-product suggested as being suitable for metal removal from wastewater [8]. Slag and similar materials produced from the steel-making industry have also demonstrated potential as P-sorbing agents in wastewater treatment [5]. In addition, their alkaline character renders them suitable as agricultural liming materials [9, 10].

Bed filters using reactive materials may provide an effective, low cost and low maintenance approach for on-site wastewater treatment. Application of this technology can limit the amount of P entering surface water systems and groundwater from wastewater effluents, and may provide significant environmental benefits in rural, un-sewered areas. Reactive materials can be classified into two distinct groups. One type promotes chemical reactions that destroy the contaminant or transform it to a more benign species (e.g. reductive dehalogenation, denitrification, biodegradation); the second attempts to transfer the contaminant mass from the aqueous phase to the solid phase (e.g. adsorption, ion exchange, precipitation). The latter reactions provide environmental benefits by concentrating the contaminant mass in a finite and known volume of material, which then allows for easier collection and future disposal, or possibly even acceptable rates of release [2].

The possibility of recycling the spent reactive materials or sorbents to agriculture as a fertiliser and soil conditioner has been investigated in some studies [7, 11, 12]. Their content of P might be low compared with industrial fertilisers but their alkaline properties have positive effects on acid soils [7, 13]. However the benefits of using these materials in agriculture can be outweighed by their content of heavy metals, which can be transferred from soil to crops by plant uptake and become hazardous for man and the environment. Domestic wastewater contains different amounts of metals depending on its source [14]. These metals can accumulate in the filter material during filtration of the wastewater and add to any indigenous content that might be present [15]. Investigations carried out on treatment of landfill leachate and urban stormwater clearly show the ability of reactive materials to remove metals from the liquid to the solid phase, but also leaching from the filter matrix [16, 17].

Several mechanisms, such as sorption, complexation and precipitation, can control metal concentrations in effluent from bed filters employed for wastewater treatment. Divalent metal cations tend to favour sorption on colloidal particles with negatively charged sites, calcite, clay minerals, organics and oxides of Fe, Mn, Al and Si [18]. Complexation is the combination of metal ions with non-metallic ligands by covalent bonds. The humic-like substances formed from wastewater decomposition can serve as ligands for metal complexes [19]. Precipitation occurs when a metal species falls out of solution as a solid. Sulphides and carbonates are capable of forming precipitates with Cd, Ni, Zn, Cu and Pb [20, 21].

A large-scale dynamic column experiment was conducted over a long time period to assess the removal of metals from water by different reactive materials subjected to domestic wastewater loading. In addition, the indigenous heavy metal concentrations in the filter material Polonite (Polonite[®]), which is used for full-scale, on-site wastewater treatment, were analysed. The long-term experiment simultaneously investigated P and N removal, the results of which are presented elsewhere [11, 22].

The aim of the present paper was to (i) study and compare the capacity of six filter materials for metal uptake or release under conditions of intermittent wastewater loading; to (ii) investigate whether equilibrium with solid phases might have controlled metal solubility in the materials; and to (iii) quantify the content of metals

in the filter materials, particularly the Polonite used in small-scale wastewater treatment, and relate that content to statutory limits on metal content in sludge for use in agriculture. In addition, the removal mechanisms were examined with particular reference to the possibilities of preventing metal contamination of the reactive materials.

2. Materials and methods

2.1 Column experiment

Six filter materials were used for the column experiment, which was performed indoors (20 °C) at the Loudden wastewater treatment plant, Stockholm. The design of the research set-up and the physical parameters of the wastewater treatment materials are described in detail elsewhere [11]. The materials, their particle size and total weight in columns were: amorphous blast furnace slag 0.25-4 mm, 46.9 kg (ASC); crystalline blast furnace slag 0.25-4 mm, 44.8 kg (CSC) and 2-7 mm, 38.9 kg (CSVC); limestone from Ignaberga in southern Sweden, 1-2 mm, 45.9 kg; opoka, a bedrock from Poland, rich in CaCO₃ and SiO₂ and formed from marine sediments [23], 2-5.6 mm, 36.4 kg; a calcinated opoka with the brand name Polonite, 2-5.6 mm, 27.2 kg; and washed quartz sand, 0.2-2 mm, 54.1 kg, used as a model for the sand commonly used in infiltration beds in Sweden. Two materials were tested in duplicate columns (CSC, Polonite). The nine 30-cm wide columns were filled to a height of 50 cm.

On average, 0.5 L h⁻¹ of wastewater was pumped to each column intermittently every second hour for 67 weeks. Before being applied to the columns, the wastewater was pretreated in a two-chamber septic tank so that coarse, suspended material and organic particles precipitated out. Equal subsamples of pretreated wastewater were distributed from a distribution tank to all columns. Columns, tanks and tubing were made from polyvinyl chloride (PVC). At the top of each column, a 2.5 cm thick layer of mineral wool was placed as an additional barrier to prevent any larger organic particles remaining in the wastewater from entering the filter materials. The mineral wool also had the function of distributing the wastewater equally over the filter surface. The mineral wool was exchanged in all columns three times during the experiment period to avoid clogging and preferential flow tendencies.

2.2 Full-scale treatment system experiment

A reactive bed filter system for a one-family house, situated 20 km NE of Uppsala city in Sweden, was used for studies of treatment efficiency. The reactive material used was Polonite mixed with 8% peat (w/w), which emerged as the most promising filter among materials tested in previous research [12, 24, 25]. The system consists of a pre-treatment step with septic tank and biofilter followed by a filter well filled with Polonite (volume 800 L, dry weight 560 kg), which receives wastewater intermittently in relation to its production in the household. After 2 years and 3 months of operation, the filter material was removed and exchanged with a new Polonite filter. The total phosphate (PO₄-P) removal was 90% for that period.

2.3 Analyses and calculations

Column influent and effluent samples were collected in 100 mL acid-washed plastic vessels once per week or every second week. The pH was determined and the samples then filtered through a 0.45 µm micropore filter (Sartorius). Biochemical oxygen demand (BOD₇) was determined after 45, 50 and 58 weeks of the column system operation according to Swedish Standards (SS 028143-2 mod. and SS-EN 25814-1).

Samples taken from the influent and each column during periods of approximately every 6 weeks were mixed to one representative sample for analyses of elements. In total, 11 samples were obtained from influent and column effluents, covering the whole experimental period. Column materials were sampled in the 0-5, 5-10, 10-20, 20-30, 30-40, and 40-50 cm layers and dried at room temperature. The Polonite material from the filter well was similarly sampled and, in addition, three samples were taken randomly from the whole filter mass after mixing (in total 14 samples). Metal concentrations in the virgin materials, in the liquids and in the solids from the column and full-scale experiment were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

The removal capacity of the filter materials (R_m , %), i.e. the retention or leaching of dissolved elements during the infiltration of wastewater, was calculated according to the equation:

$$R_m = \left(1 - \frac{C_e}{C_i}\right) 100 \quad (1)$$

where C_e is the effluent concentration and C_i is the influent concentration.

The total metal content (mg kg⁻¹) of filter materials in the columns was calculated as the average of the content in each layer. Analyses were performed in duplicate for the 0-5 cm layers.

To investigate whether equilibrium with solid phases might have controlled metal solubility in the materials, Visual MINTEQ ver. 2.53 [24] was applied for speciation of the column effluents. In these calculations, complexation with dissolved organic matter (DOM) in the effluents, were estimated with the Stockholm Humic Model [25] assuming that 70 % of the DOM consisted of fulvic acid [24]. Because measurements of alkalinity and dissolved organic carbon (DOC) were made only for a few samplings, the results should be considered approximative.

3. Results and discussion

3.1. Characteristics of wastewater

The pH and BOD₇ values for the wastewater used in the experiment and the changes after filtration through the filter materials are presented in Table 1. Wastewater pH was non-typically high, sometimes approaching values of 9.3, which was probably related to loads other than from domestic sources, e.g. industrial effluent, storm water and effluent from the adjacent harbour. Organic compounds measured as BOD indicated normal concentrations for this type of mixed wastewater.

Table 1
Characteristics of column influent and effluent samples of wastewater

Filter material ^a	Influent		Effluent	
	pH	BOD ^b	pH	BOD ^b
-	8.18-9.28	87 ± 13	-	-
Sand			6.05-9.27	1.3 ± 0.6
Opoka			8.29-9.95	3 ± 0.6
Polonite			8.23-12.84	2 ± 0.9
CSC			8.09-9.88	1.7 ± 0.5
ASC			8.93-9.73	2 ± 0.4
CSVC			8.49-9.75	2 ± 1
Limestone			7.63-9.81	2.7 ± 0.6

^a ASC = amorphous slag, coarse; CSC = crystalline slag, coarse; CSVC = crystalline slag, very coarse. ^b mg L⁻¹, n = 3

The screening with ICP-AES encompassed a total number of 25 elements in the influent and effluent of the columns. Dissolved concentrations of As, Cd, Co, Mo, Pb, Ti, V and Y in influent wastewater were very low, below the detection limit of the ICP instrument. Other elements in the wastewater applied to the columns showed low concentrations and followed the order Ba > Zn > Cu > Mn > Mg > Ni > Cr. The influent concentrations and the concentrations found in effluent from each of the column materials are shown in Table 2. It is obvious from these data that wide variations occurred in metal concentrations, probably caused by the above-mentioned sources of pollution [cf.14]. In fact, metal concentrations in influent were lower than typical effluent discharge limits with the exception of Cu [19]. Thus the wastewater used in the column experiment had very low dissolved metal concentrations. The treatment preceding the filtration through the column materials probably removed the majority of metal species. These can be trapped by gravity settling of suspended solids in a primary clarifier, e.g. septic tank [26, 27].

3.2. Removal and release of dissolved metals in columns

Differing removal rates of dissolved metals were observed for the filter materials (Table 3). The apparent propensity for accumulating metals among the materials studied here followed the order Polonite > ASC > opoka > CSC > limestone > CSVC > sand. All materials removed Fe with an efficiency of around 60%. This element was actually the only one removed by the sand. Zinc was removed by all materials, except

Table 2
Percentage removal of dissolved metals by the filter materials

Filter material	Removal (%)						
	Ba	Cu	Cr(III)	Mg	Mn	Ni	Zn
Sand	36.2	0	0	0	0	0	0
Opoka	0	0	11.6	0	61.7	0	68.6
Polonite*	0	15.9	0	98.6	98.7	0	62.2
CSC*	44.3	12.9	0.38	0	0	29.6	82.5
ASC	27.1	27.9	9	0	83.8	32.9	80.1
CSVC	47.6	2.8	0	0	0	24.9	74.6
Limestone	13.6	7.2	0	0	44.9	0	53.7

* Average for duplicate materials

the sand, in the range of 53-83%. Only the three blast furnace slags (ASC, CSC, CSVC) were able to remove Ni. Polonite removed over 98% of dissolved Mg and Mn in the wastewater, while fairly efficient removal of Cu was demonstrated by the ASC. Analyses of metal concentrations in the leachate (effluent) from columns (data not shown) showed significant ($p < 0.05$) release, i.e. an increase in concentration, of some elements from sand, CSC, ASC and CSVC. Sand released Cu and Zn, while CSC and ASC showed increased concentrations of Mg. The very coarse crystalline slag (CSVC) exhibited a large loss of Mn, although only in the beginning of the experiment.

3.3. Speciation modelling

According to speciation calculations with Visual MINTEQ, a very large fraction of dissolved copper in the column leachates were bound to DOM (the median value was 99.99 %). The corresponding figures for Cr(III) (assuming that all dissolved Cr existed as trivalent chromium), Zn and Ni were 93, 59 and 24 % respectively. Other ions such as Mn, Ca and Ba were less strongly bound to DOM.

The wastewater trickles through the filter matrix and colloidal matter can attach to the surface of each mineral particle [28]. Bacteria create a biofilm where microbial adsorption of heavy metals can occur [29] and where adsorption and precipitation processes can also retain the metals. The increasing concentrations of dissolved metals in the effluent can be the result of leaching from the materials. The blast furnace slag material, from which Mg and Mn were obviously released, demonstrates this, as did the results of a previous study [16].

Calcite is a principal component of opoka and limestone. The differences between these materials in terms of metal sorption capacities may be due to their affinity to the surface of calcite [30]. The mechanisms involved in metal retention by blast furnace slag are thought to be ion exchange with calcium on particle surfaces and precipitation on $\text{Al}(\text{OH})_3$ and SiO_2 [31]. Sorption / precipitation to sulphuric compounds in blast furnace slag may also be important. However, sulphur was leached in great amounts from blast furnace slag columns in the beginning of the present experiment (data not shown), as previously observed in a column experiment with landfill leachate [16]. In the case of limestone and opoka, chemisorption of metal ions to their rough calcite surfaces can be one mechanism for removal [32, 33]. Moreover the dissolution of alkaline minerals, particularly in the case of Polonite, can

Table 3

Influent and column effluent concentrations of elements. The unit is $\mu\text{g L}^{-1}$, unless otherwise stated (average, SD)

Element	Influent	Column effluent						
		Sand	Opoka	Polonite**	CSC**	ASC	CSVC	Limestone
Ba	62.2±21.3	68.4±12.6	39.7±12.3	90.4±24.7	34.7±8.9	45.3±9.9	32.6±7.6	53.7±26.9
Cr	1.71±0.52	2.71±3.52	1.51±0.34	26.8±32.6	1.68±0.53	1.55±0.5	1.75±0.52	1.72±0.59
Cu	16.2±10.8	26.4±9.6	18.1±6.4	13.6±7.4	15.01±14.1	11.6±4.8	15.7±5.5	15.0±8.6
Mg*	6.26±0.66	6.88±1.86	7.68±1.25	0.09±0.06	32.1±5.99	28.4±10.3	7.26±0.86	26.3±7.03
Mn	10.9±3.1	31.2±32.2	4.21±4.0	0.24±0.19	29.3±65.3	1.77±2.15	82.6±203.1	6.04±6.7
Ni	4.64±1.6	10.1±5.7	5.52±1.58	6.37±4.15	3.26±0.77	3.11±0.49	3.48±1.34	5.79±5.01
Zn	37.5±11.8	221.3±164.5	11.8±5.5	14.2±10.2	6.57±1.96	7.47±1.63	9.54±2.86	17.36±23.5

* mg L^{-1} ** Average and SD for duplicate materials

increase the pH of the percolating wastewater above solubility point, which causes metals to precipitate, probably as metal oxides and metal carbonates [34].

The organic ligands present in wastewater can bring about either enhanced, suppressed or unaffected adsorption of metal ions on clay minerals [35]; at low pH an enhanced effect is often seen, whereas at neutral to high pH (as in the present investigation) DOM is likely to suppress metal sorption, especially for Cu. Predicted purification efficiencies calculated from adsorption isotherms are therefore never reached [36].

3.4. Metal content in the filter materials

All filter materials used in the columns generally showed enhanced concentrations of the heavy metals Cu, Cr(III), Mn, Pb and Zn after wastewater filtration (Table 4). The clearest increase in content for all materials was found for Cu. In the sand, all metals were found in increased concentrations. A small release of Cr(III) was apparent from opoka, Polonite and CSVC.

Chemical analyses of filter layers showed that Zn had a clear distribution pattern in all materials, with its highest concentrations in the surface layer and lowest in the bottom layer of the columns. This was also true for Cu in columns filled with the fine-grained materials ASC, CSC and limestone.

In Table 5, the concentrations of heavy metals in the experimental material Polonite are compared against the permissible limits on metal content in sludge for use in agriculture. The field data included from a domestic filter well differed from the data obtained from the column in that much higher Cr(III), Cu and Mn contents were found in the Polonite used for treating the wastewater from one household than the two columns fed with municipal wastewater. However the systems were operated quite differently. The loading was 1.5 times higher to the columns, where unsaturated conditions existed, whereas the filter well used an intermittent cyclic process with complete saturation of the material.

It is interesting to compare the results on removal of dissolved metals from wastewater (R_m , Table 3) with those from analyses of metal concentrations in the materials (Table 4). The sorption of Cu was clear in all materials regardless of different pH conditions and particle size distributions. However a rather moderate

Table 4
Concentration of heavy metals in the filter columns (mg kg^{-1}). Average values \pm SD for the six layers investigated of each material. Values for virgin materials are shown in brackets

Element (mg kg^{-1})	Filter material						
	Sand	Opoka	Polonite	CSC	ASC	CSVC	Limestone
Cu	11.8 \pm 2.7 (*)	9.5 \pm 1.5 (2.02)	6.9 \pm 1.3 (1.2)	3.6 \pm 1.7 (*)	3.6 \pm 1.3 (*)	3.6 \pm 0.8 (*)	4.3 \pm 2.9 (*)
Cr(III)	3.4 \pm 0.8 (*)	5.7 \pm 1.1 (8.8)	13.9 \pm 3.8 (22.5)	9.8 \pm 1.7 (9.5)	15.8 \pm 3.3 (17.9)	6.2 \pm 1.1 (9.5)	0.5 \pm 0.1 (*)
Mn	22.9 \pm 3 (*)	108 \pm 12.9 (51.8)	76.8 \pm 13.1 (57.7)	3689 \pm 279 (3647)	3268 \pm 513 (3355)	2312 \pm 357 (3648)	505.9 \pm 122.5 (296)
Pb	8.6 \pm 4.5 (*)	14.1 \pm 4.3 (13.5)	8.6 \pm 4.9 (10.1)	4.5 \pm 3.1 (0.5)	5.3 \pm 3.3 (**)	5.7 \pm 3.1 (0.5)	10.1 \pm 6.7 (5.1)
Zn	17.5 \pm 14 (*)	50.1 \pm 15.8 (32.6)	57.9 \pm 30.7 (30.8)	32.3 \pm 37.5 (14.6)	31.2 \pm 29.6 (18.3)	23 \pm 11.8 (14.6)	33.4 \pm 24.9 (14.5)

* Below detection limit ** Not analysed

removal was found for the materials with ASC, the highest values recorded being about 28%. Sand did not show any apparent removal of dissolved Cu, but analysis of material from the column showed presence of the metal. All columns removed BOD efficiently, which indicates that organic matter was retained and partly decomposed.

As regards the mechanisms for metal sorption/dissolution, speciation modelling with Visual MINTEQ suggests that Ba was close to equilibrium with barite (BaSO_4) in all column leachates (Fig. 1). This probably explains why Ba was removed in the CSC and CSVC columns, since these columns generate an increase in dissolved SO_4^{2-} , which would cause barite precipitation. Also Ni seemed to be solubility-controlled (by nickel hydroxide, $\text{Ni}(\text{OH})_2$) in all column leachates except the Opoka column. Dissolved chromium was in most cases slightly lower than predicted by equilibrium with Cr(III) hydroxide. For copper, the results suggest that CuO or a similar phase in the Polonite columns (but not in the other columns) might have controlled the dissolved Cu. Dissolved zinc was very much undersaturated with respect to any zinc mineral phase, suggesting that the processes controlling zinc are likely to involve adsorption/desorption and weathering processes. Also lead was far from equilibrium with any mineral phase. Magnesium was close to equilibrium with brucite in the Polonite columns early in the sampling period, suggesting that magnesium removal by Polonite involved the precipitation of this mineral. However in the latter part of the experiment there was undersaturation also in the Polonite leachates despite a continued very strong Mg removal in these columns (> 95 % throughout the experiment). A possible explanation to this phenomenon is that the pH remained high for a longer time in small pores of the material, permitting brucite precipitation, despite the observed undersaturation in the bulk leachate. This suggests that for successful chemical transport modelling, different flow domains need to be considered (for example using the dual-porosity approach) as recently found for waste materials [37].

Thus the mechanisms determining metal sorption or desorption appear to be different for different metals. For Cu and Cr the binding to organic ligands in the dissolved phase is likely to suppress efficient precipitation of these ions in the materials. Barium and nickel are solubility-controlled, with little influence of organic

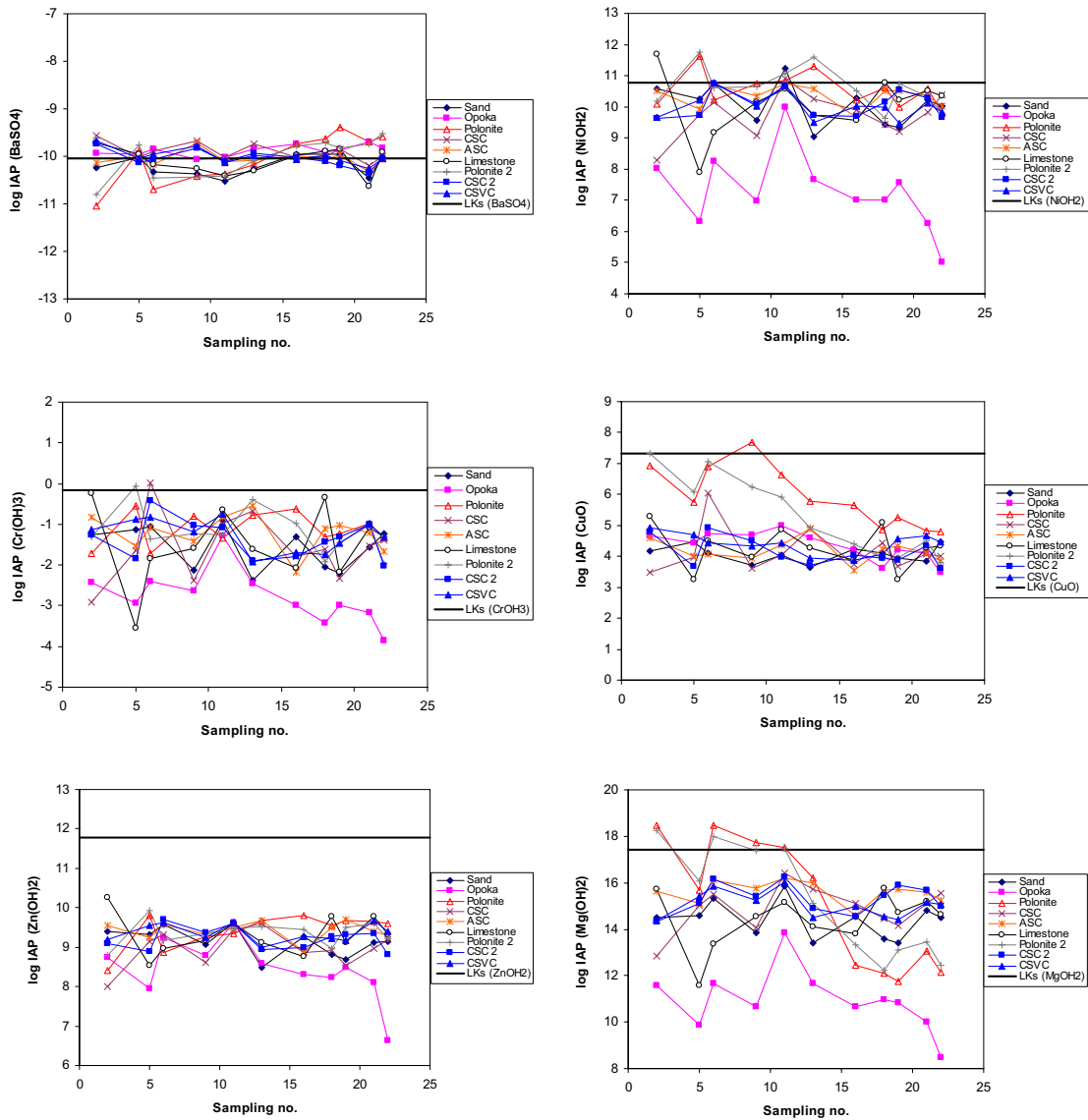


Figure 1. The logarithm of the ion activity products for $\text{BaSO}_4(\text{s})$ (barite), $\text{Ni}(\text{OH})_2(\text{s})$, $\text{Cr}(\text{OH})_3(\text{s})$, $\text{Zn}(\text{OH})_2(\text{s})$ and $\text{Mg}(\text{OH})_2(\text{s})$ (brucite) during the experiment. The black vertical lines correspond to the solubility products of these mineral phases at 20°C according to Visual MINTEQ calculations (Gustafsson, 2007).

complexation. Zinc is neither solubility-controlled nor strongly affected by organic ligands, and so this metal may be controlled by adsorption to inorganic components in the materials.

3.5. Metal flow in wastewater and consequences for filter material recycling

The origin of metals in domestic wastewater is complex, as indicated even by the limited results presented here (Table 5). The reason for elevated concentrations of Cr(III) and Mn in Polonite used in the treatment system for the private house can be related to the specific water supply (drilled well) and tubings. The filter well where Polonite is used is made of stainless steel, which can probably also contaminate. The high levels of Mg in influent wastewater can come from a number of sources, e.g. hard drinking water and seawater intrusion to the sewerage system.

Table 5
European Union and Swedish statutory limits for sludge disposal on arable land compared with the content of heavy metals in the reactive material Polonite exposed to wastewater filtration in long-term column¹ and field-scale experiments² (mg kg⁻¹)

	Pb	Cd	Cr (III)	Cu	Ni	Hg	Zn	Mn
EU directive 86/278/EEC	750-1200	20-40	1000-1500	1000-1750	300-400	16-2.5	2500-4000	n.d.
Sweden	100	2	100	600	50	2.5	800	n.d.
Polonite ^{1***}	8.6 ±4.9	*	13.9 ±3.8	6.9 ±1.3	*	*	57.9 ±30.7	76.8 ±13.1
Polonite ²	n.d.	*	61 ±9.7	13.1 ±5.3	21.7 ±3.1	*	32.0 ±21.6	200± 63.1

n.d. no data, * Not analysed, ** Below detection limit, *** Average for two columns

Polonite is one of the most promising materials for P removal and subsequent recycling as a soil conditioner [11, 13], but the ability to accumulate metals is a disadvantage for this material. However, it must be stressed that one of the metals (Mg) investigated here are considered non-hazardous in the environment and that only Polonite among the materials studied removed Mg from the wastewater.

Another disadvantage is the leaching of dissolved heavy metals from the materials and the indigenous content. However, if the effluent concentrations do not exceed the permissible limits for discharge to receiving water bodies, this is not a problem. The blast furnace slags used in this study had low concentrations of toxic metals compared with other types of slag [38], and the effluent metal concentrations measured were low to intermediate according to Swedish guideline values for natural concentrations of metals in surface water [39].

As can be seen in Table 5, the concentrations of selected heavy metals in the Polonite were far below the European limits for sludge disposal and also much below the stricter Swedish limits. On the basis of the results from the present study it is recommended that for on-site wastewater treatment using reactive filter materials, the preceding treatment steps must be efficient concerning organic matter removal. This

can be achieved by large septic tanks and/or pre-filtration prior to treatment in the reactive filter. In this way metal contamination of the filter material can be avoided and thus there is no risk associated with disposal of the material in agriculture. However, sludge from the septic tank must then be monitored if intended for use as a soil amendment on arable land.

4. Conclusions

This long-term column experiment showed that dissolved metals in wastewater were removed in various amounts by the filter materials studied. The fine-grained, amorphous blast furnace slag showed sorption capacity for all the metals investigated except Mg. Polonite[®] alone among the materials removed this element. According to speciation calculations with Visual MINTEQ, a large fraction of dissolved Cu and Cr(III) in the column leachates were bound to DOM.

Leaching from the materials can contribute to the metal flow, increasing the concentration in the effluent. However the observed metal concentrations in this study were low compared with the Swedish guideline values for natural surface water.

The Polonite material used in both on-site wastewater treatment and the column experiment showed heavy metal concentrations that are much lower than the European limits for sludge disposal. Hence the low content of heavy metals in the filter materials will not interfere with their use as a fertiliser or soil amendment. However for confirmation of the results obtained in this study, more used filter materials from different treatment plants should be collected and analysed.

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VI

Phosphorus removal by Polonite[®] from wastewater - Column experiments and a compact bed filter trial

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ABSTRACT

The reactive bed filter material Polonite[®] was tested for its phosphate (PO₄-P) removal capacity in column and full-scale systems using synthetic and real domestic wastewater. Different flow systems, including upward and downward discharge with periodic filling and emptying of the pore volume and intermittent unsaturated and saturated downward flow, were examined in three long-term experiments (67-92 weeks). The best PO₄-P removal capacity (>96%) was observed in saturated columns for a synthetic solution without organic matter and a loading rate of 400 and 530 L m⁻²d⁻¹. An intermittent unsaturated column system using municipal wastewater and load 76.7 L m⁻²d⁻¹ showed no tendency for PO₄-P breakthrough and effluent PO₄-P concentration was still low (0.2 mg L⁻¹) after 67 weeks. For a compact bed filter containing 560 kg of Polonite and fed with wastewater from a single house, PO₄-P removal was 89% after 92 weeks of operation and clear PO₄-P breakthrough was demonstrated at the end of the experimental period. Monitoring of pH was expected to reveal the point at which PO₄-P removal was insufficient to meet permissible levels, but this pH value could not be established from the existing data. Instead, the P removal longevity of reactive filter materials could be estimated from the volumes of wastewater treated. For Polonite, a minimum of 1-2 kg of material was predicted to be the required amount for treating one cubic metre of wastewater at normal loads in on-site systems.

Key words: effluent standard, filter material, on-site treatment, phosphorus breakthrough, sorption

1. Introduction

The lack of proper wastewater treatment in rural areas contributes greatly to the pollution of surface waters and groundwater. Technical solutions suitable for treating small wastewater flows from single houses or villages are available (Crites and Tchobanoglous, 1998; Jantrania and Gross, 2006). These include e.g. more passive systems such as soil infiltration, or advanced systems such as small package treatment plants. Ecologically based, on-site treatment systems such as constructed wetlands

have also been employed to treat wastewater in a number of studies (cf. Vymazal, 2005). Whereas conventional, large-scale treatment systems are technically constructed in the same way all over the world, small-scale systems are available in a large number of types. The effect of this differentiation is a corresponding variation in treatment results, mainly because of limited management and control of the small systems. In particular, the removal of phosphorus (P) by these systems has been shown to be inadequate when compared against statutory effluent criteria for treated wastewater. In the case of package plants, it is necessary to use reliable dosing equipment and professional personnel for service, maintenance and technical support in order to achieve long-term P removal (Hellström and Jonsson, 2006)

Phosphorus removal from wastewater is of particular concern as it is the limiting nutrient in most fresh, inland surface water systems (Schindler, 1977). However, many types of small-scale systems have demonstrated poor P removal. The sands and gravels used in most constructed wetlands have a negligible long-term capacity for P removal (Vymazal et al., 1998). This has led researchers to look for more efficient materials for use in bed media. A great number of organic and inorganic materials have recently been tested in laboratory and field-scale trials (Baker et al., 1998; Ádám et al., 2007; Drizo et al., 2006; Leader et al., 2008). Mineral-based materials with a reactive character in contact with wastewater have demonstrated good P removal performance (Gustafsson et al., 2008). Among these Polonite[®], a commercial product manufactured from the bedrock opoka, has emerged as a promising material for use in full-scale treatment systems. Powdered and high-thermal treated opoka (Polonite) has a maximum PO₄-P sorption capacity of about 120 g kg⁻¹ in contact with a synthetic P-solution (Brogowski and Renman, 2004). However, powder of any material cannot be included in treatment systems based on filtration as the fine material causes clogging and hydraulic failure. Hence an optimal particle size can be 1-2 mm for achieving a desirable removal and hydraulic capacity simultaneously (cf. Yao et al., 1971).

A compact filter system using the filter media Filtralite-P[™] with a particle size of 0-4 mm has been developed in Norway (Heistad et al., 2006). This system has proved to be robust when applied on-site in rural areas, with stable P removal over many years. However, the filter material used showed an overall P sorption capacity of 52 mg P kg⁻¹ applied in a full-scale system, which was 85 x 10³ times lower than the findings from a laboratory small-scale system using a synthetic P-solution (Ádám et al., 2006). This large discrepancy raises many questions, particularly concerning the estimation of P-retention lifetime of filter materials. The present paper describes a similar compact filter system developed in Sweden, which uses Polonite as the reactive filter material for P removal, and its design allows for easy replacement of material and reuse of the spent material in agriculture. In contrast to the chemical products used for precipitation of P in wastewater, Polonite is more valuable as a multi-component fertiliser or amendment in soils (Hylander and Simán, 2001; Hylander et al., 2006; Cucarella et al., 2008).

The overall aim of the present study was to examine the potential purification capacity of Polonite in pilot-scale columns using artificial and real wastewater and a compact bed filter treating domestic wastewater. Specific objectives were to: (1) estimate the long-term PO₄-P removal capacity under various flow conditions and intermittent P-loading; and (2) assess whether the pH of the treated wastewater could be used as an indicator for P breakthrough and P saturation.

Reactive bed filter systems (RBF) are designed for simple operation and minimal management, which renders them useful for treatment of wastewater from single houses or small populations. The compact filter well construction Biop[®], which is based on Polonite, is a type of RBF recently launched in Sweden.

2. Experimental methods

Three different experiments were used to determine the effect of different scales and flow regimes on P removal by Polonite (particle size of 2-5.6 mm). Experiments I and II were performed in indoor columns at room temperature (20 °C), while experiment III was a full-scale operating filter well. The filter well was an underground construction with an insulated lid visible on the surface and hence the filter was exposed to varying temperature (4-20 °C).

2.1. Polonite[®] – the reactive material used

Polonite is produced from the sedimentary rock Opoka after thermal treatment to 900 °C, crushing and sieving into appropriate fractions. Opoka is a Polish-Russian term with no English equivalent. The rock, of Cretaceous age, is calcareous, but hardened as a result of the presence of organic silica (Brogowski and Renman, 2004). After heating, CaCO₃ is transformed to the more reactive CaO, a procedure aimed at enhancing the P removal capacity of the material. Polonite is usually produced in the 2-5.6 mm fraction, and thus has very good hydraulic properties (800 m d⁻¹). This fraction was used here in all three experiments. However a tail of fine particles less than 1 mm can sometimes be found in the manufactured material, thereby decreasing the hydraulic conductivity. The elemental composition of Polonite varies (Brogowski and Renman, 2004). The composition of the material used in experiment I is shown in Table 1.

Table 1. Elemental composition* (g kg⁻¹ dry matter) of the Polonite used in experiment I

Si	Al	Ca	Fe	K	Mg	Mn	Na	P
241	27	245	16.5	9.15	4.4	0.12	1.46	0.34

* Determined using ICP-OES

2.2. Columns fed with synthetic solution (I)

Two columns filled with Polonite were used in a long-term laboratory experiment carried out at room temperature (20 °C). The columns were constructed of PVC tubes of 60 cm length and 10 cm inner diameter. The filter bed was 50 cm and the Polonite used was sieved to remove particles less than 2 mm. To minimise any effects of chemical clogging, the composition of the Polonite was modified by the addition of 10% (w/w) *Sphagnum* peat. The starting pH of the mixture was 11.8. Other potential filter materials for P and N removal were also involved in this experiment and are dealt with in other publications (Poll, 2005; Gustafsson et al., 2008).

A synthetic solution containing 5 mg L⁻¹ PO₄-P and 30 mg L⁻¹ NH₄-N was prepared by adding KH₂PO₄ and NH₄Cl to tap water. The solution was stored in two containers (200 L each) and pumped automatically to the top of each column three

times per day (times 08.00, 13.00, 17.00) throughout the experimental period of 68 weeks. Data on loading rates and number of pore volumes treated in all experiments are shown in Table 2. In experiment I, each loading of solution was proportional to the pore volume of Polonite in the two columns, i.e. 1.4 L and 1.05 L respectively. However, one of the two columns (Ia) was constantly saturated while the other (Ib) was intermittently saturated for one hour following each pumping. A time-regulated valve in the outlet of the column Ib controlled the cyclic process of filling-up, saturation and draining.

2.3. Columns fed with municipal wastewater (II)

Duplicate columns (height 50 cm, diameter 30 cm) containing Polonite were installed and fed with wastewater at the Loudden wastewater treatment plant (WWTP) in Stockholm as part of a long-term experiment involving six filter materials. Details of the entire column experiment can be found in Renman et al. (2004) and Hylander et al. (2006). The raw wastewater was pre-treated by sedimentation and filtration before discharge to the columns at an average volume of 0.45 L every second hour for a period of 67 weeks. The concentration of P (as PO_4^{3-}) in the influent wastewater was $4.11 \pm 0.93 \text{ mg L}^{-1}$ and the starting pH of the filter material was 12.5.

2.4. Bed filter fed with wastewater from a single household (III)

The operation of a RBF plant installed for treatment of domestic wastewater from a single household in Viksta By, adjacent to the city of Uppsala, Sweden, was studied. The principle of this on-site treatment system is shown in Fig. 1. The treatment system consists of a septic tank (3 m^3) from which the wastewater flows to a pump chamber. A timer, overrun by a float switch, controls the pump that doses portions of wastewater in relation to its production to the Polonite bed filter. This is housed in a circular container with an inner diameter of 1.43 m and depth of 0.75 m, filled to a depth of 0.6 m. The container can be removed from the filter well for exchange and recycling of Polonite. The experiment started with pumping and filling from the base of the container, i.e. upward flow and saturation of the entire pore volume (320 L), followed by complete drainage of the filter via a pump. This method was stopped after 18 weeks because of unacceptable BOD values measured in the effluent. Thereafter, and to the end of the experimental period, the filter material was filled and saturated with wastewater in downward flow. In order to increase BOD removal, a biofilm carrier consisting of a coarse plastic media filter was placed on the Polonite (Fig. 1). This device also served to distribute the wastewater over the entire surface of the Polonite. The duration of the experiment was 92 weeks. The average concentration of P (as PO_4^{3-}) in the influent wastewater was $4.94 \pm 1.87 \text{ mg L}^{-1}$ and the starting pH of Polonite was 11.9.

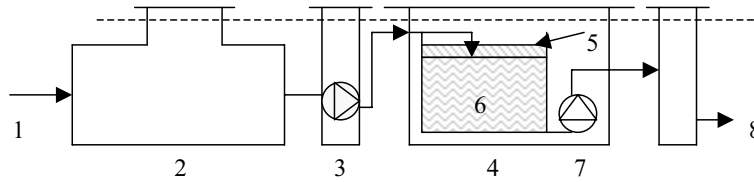


Figure 1. The filter system layout (not in scale): (1) Inlet of household wastewater, (2) septic tank, (3) dosing pump, (4) filter well, (5) biofilter, (6) Polonite bed filter, (7) pump and (8) sampling well and outlet.

Table 2. Hydrological conditions for the three experiments

Parameter	Experiment			
	Ia	Ib	II*	III
Flow system	Saturated	Intermittent saturated	Unsaturated	Intermittent saturated
Average loading rate ($L m^{-2} d^{-1}$)	530	400	76.7	60.2
Hydraulic conductivity ($m d^{-1}$)	226	226	800	n.d.
Pore volumes treated (number)	1410	1330	151	216
Hydraulic residence time (h)	4-15	1-1½	n.d.	1- 72 h

* Average value for the two columns used

2.5. Filter performance measurement and analyses

The performance of each filter set-up was monitored continuously by sampling influent unpurified and effluent purified wastewater weekly or biweekly. However, experiment III had a sampling interval of only once per month during the last 5 months. In experiments I and III, one representative sample was taken from the volume flushed out from the system, i.e. the pore volume treated. The influent sample was taken from the containers in the case of experiment I, and from the wastewater pumped to the filter in experiment III. In experiment II samples were taken from the pre-treated influent and from the column outlets. The samples were collected in plastic bottles of volume not less than 100 mL. The pH was measured and samples were thereafter stored in a freezer at $-18\text{ }^{\circ}C$ until analysis of $PO_4\text{-P}$. The pH and electric conductivity (EC) were measured using a Radiometer Copenhagen PHM 82 Standard pH Meter and Radiometer Copenhagen CD 80 Conductivity Meter, respectively. Before analysis, the samples were filtered through a $0.45\text{ }\mu m$ Micropore filter (Sartorius). Flow injection analysis (Aquatec-Tecator autoanalyser) was applied for colorimetric determination of $PO_4\text{-P}$ according to the acid molybdate method.

The percentage removal of inorganic $PO_4\text{-P}$ was calculated as the difference between influent and effluent concentrations for samples collected at the same time. The sorption of $PO_4\text{-P}$ to the filter matrix (S_p , $mg\text{ kg}^{-1}$) was calculated using the following mass balance equation:

$$S_p = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_e is the effluent concentration and C_i is the influent concentration, V is the volume of wastewater treated during the experiment and m the mass (kg) of the filter material.

Total concentrations of P in the used Polonite were determined by means of ICP-OES. Representative samples ($n = 1-12$) were dried and melted with LiBO_2 and thereafter dissolved in HNO_3 before analysis.

3. Results and discussion

3.1. Phosphorus removal in different systems

The Polonite reduced the inorganic phosphorus ($\text{PO}_4\text{-P}$) in the three different treatment systems to varying degrees (Table 3). These systems all received wastewater with similar $\text{PO}_4\text{-P}$ concentrations. The artificial solution and the highest loading rate used in Experiment I achieved the highest removal efficiency among the systems tested. No significant difference in $\text{PO}_4\text{-P}$ removal efficiency was found between the columns operated with saturated and unsaturated flow (Ia; 97%, Ib; 96%). The unsaturated flow system in experiment II also showed very P high removal efficiency (97%), but the wastewater load was much lower than in experiment I. The full-scale on-site system investigated in experiment III showed an overall removal of 89%. However, it must be borne in mind that two modes of wastewater discharge to the filter bed were used in this experiment (Table 3). At the end of the experiments the concentration of $\text{PO}_4\text{-P}$ was still very low in the effluent from columns used in experiments I and II (Table 3). In contrast, the filter used in experiment III showed increasing concentrations of $\text{PO}_4\text{-P}$ in its effluent. However, this system had the longest run-time.

There was no organic matter present in the P feeding solution in experiment I except for that possibly produced by bacteria, which was observed as a biofilm inside the containers. This lack of organic matter might have been the reason why experiment I showed the best results for $\text{PO}_4\text{-P}$ removal. The loading of organic matter in terms of BOD measurement was highest in experiment III (data not shown) due to low efficiency of the septic tank and pre-filtration unit. However, there were no operational problems such as clogging causing hydraulic failure and overflow. Chemical clogging was expected from previous experience (unpublished data) and problems with clogging have been observed in many experiments due to formation of precipitates in the outflow system (e.g. Drizo et al., 2006), so a small amount of peat was incorporated to prevent this. However, the Polonite used in experiment II performed excellently under the particular hydraulic load despite being peat-free.

Table 3. Influent and effluent concentrations of PO₄-P (mean, SD) and average removal efficiencies of the systems studied in experiments I-III

Experiment	Operation time (weeks)	Influent concentration (mg L ⁻¹)	Effluent (mg L ⁻¹)	Removal (%)
I. Laboratory	68	4.47±0.91	0.13±0.17	Ia: 96.8±4.06
		4.58±0.82	0.17±0.21	Ib: 96.1±4.69
II: WWTP	67	4.11±0.93	0.10±0.09	97.3±2.58
III. On-site treatment	92*	4.68 ±1.88	0.47±0.69	91.3±11.1**
		5.19±1.86	0.76±1.24	87.4±19.4***

*18 weeks up-flow, ** up-flow and *** down-flow period of operation

3.2. Phosphorus removal vs. time and pH development

The long-term changes in PO₄-P removal and pH in experiments I-III are presented in Figs. 2-5. The concentrations of PO₄-P in the influent wastewaters varied widely during the experimental period, especially in the single household wastewater used in experiment III. The variation in the artificial solution used in experiment I was probably mainly due to biological activity in the containers where the solution was stored. The influent pH was lowest in experiment I and highest in experiment II. The EC varied accordingly (Table 4).

Table 4. Range of pH and electric conductivity in untreated and treated wastewater

Experiment	pH		Conductivity mS cm ⁻¹	
	Influent	Effluent	Influent	Effluent
I. Laboratory	5.26-7.55	8.20-12.00	0.36-0.52	0.55-1.30
II. WWTP	8.18-9.40	8.23-12.78	0.32-0.63	0.35-6.64
III. On-site treatment	7.09-8.30	6.94-11.86	0.33-1.20	0.33-3.26

The columns fed with municipal wastewater in experiment II showed surprisingly constant high removal efficiency despite a clear decrease in pH from 12.5 to 8.2 towards the end of the 67-week study period. In contrast, the columns receiving artificial solution and also with a pH near 8 showed increasing concentrations of PO₄-P in the effluent after 68 weeks. This increase was probably the beginning of a breakthrough, but this could not be confirmed as the experiment was terminated due to time constraints. As can be seen in Figs. 2 and 3, the difference in operation of the two columns did not have a significant effect on PO₄-P removal. An obvious decrease in PO₄-P removal efficiency in relation to time was demonstrated by the filter well experiment. This was correlated with a sudden drop in pH from about 10 to below 9.

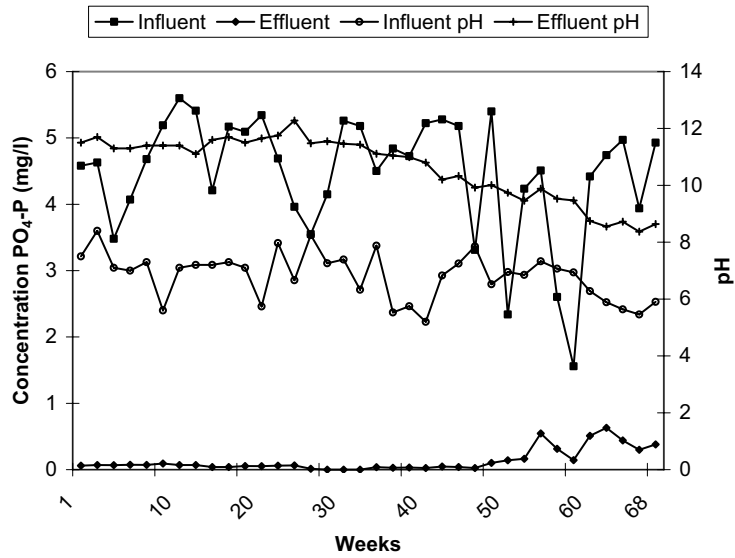


Figure 2. Changes in pH and influent and effluent concentrations of PO₄-P for column run under saturated flow and with artificial solution (Experiment Ia) over a 68-week period.

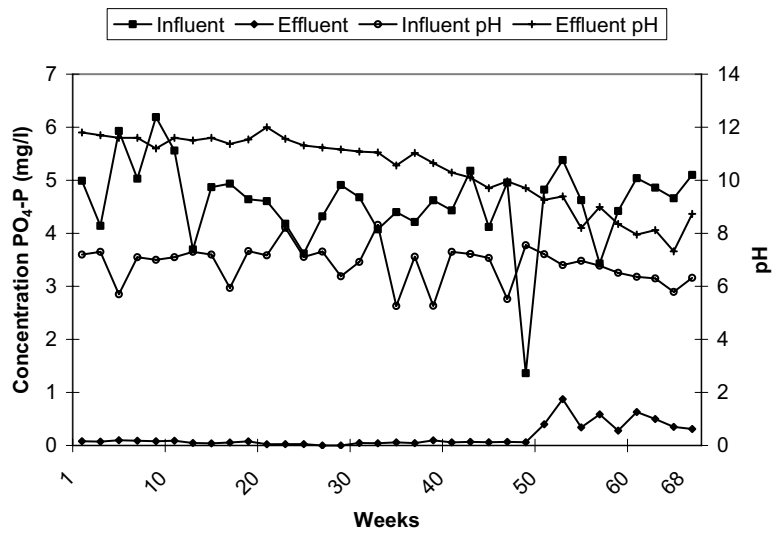


Figure 3. Changes in pH and influent and effluent concentrations of PO₄-P for column run under intermittent saturated flow and with artificial solution (Experiment Ib) over a 68-week period.

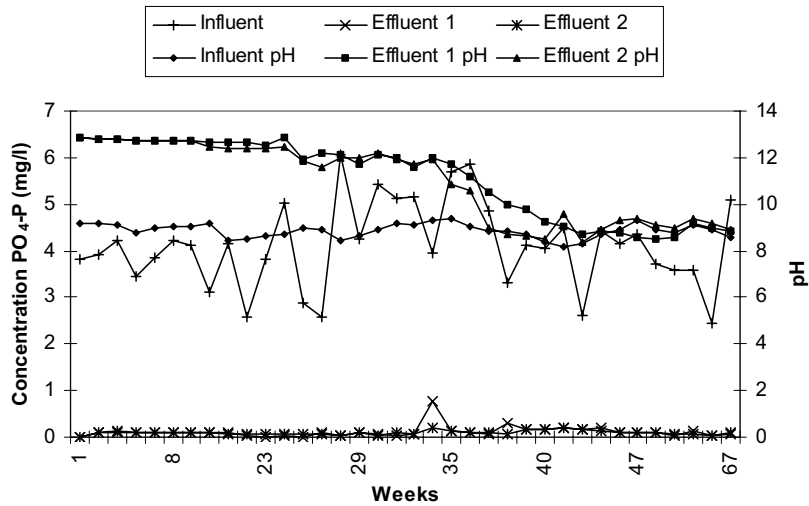


Figure 4. Changes in pH and influent and effluent concentrations of PO₄-P for two columns fed with municipal wastewater (Experiment II) over a 67-week period.

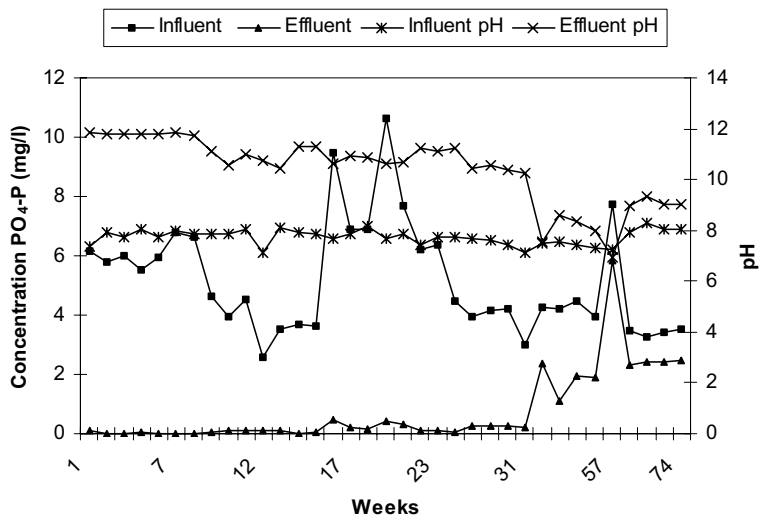


Figure 5. Changes in pH and influent and effluent concentrations of PO₄-P in a filter well used for domestic wastewater treatment (Experiment III). The points represent the last 74 weeks of the sampling period (total 92) when the filter was fed in downward flow.

3.3. Phosphate breakthrough and removal capacity indicated by the pH

The phosphate breakthrough curve for experiment III is presented in Fig. 6 (no breakthrough occurred in the other experiments). After 128 pore volumes had been treated in the bed filter in down-flow mode, the C_e/C_i ratio started to rapidly increase, coinciding with the pH drop seen in Fig. 5. After 75% breakthrough, the rate of increase of the breakthrough curve seemed to even out to the end of the experimental period. The effluent $\text{PO}_4\text{-P}$ concentration was 2.49 mg L^{-1} by then. The filter well was operated for an addition 4 months with the same Polonite material after termination of this experiment and analyses of a few samples of the effluent showed that complete breakthrough was not achieved in this period. This suggests that $\text{PO}_4\text{-P}$ removal continued, possibly by precipitation and/or biological mechanisms.

Plotting the removal capacity against pH for the filter well experiment revealed a good correlation and a strong relationship between $\text{PO}_4\text{-P}$ removal and pH for Polonite (Fig. 7). Other studies of alkaline filter materials have shown the same relationship, although in batch experiments (Ádám et al., 2007). The pH could be an easy parameter to use for decisions on replacing the filter material in the filter well. Hence a certain pH could correspond to a minimum effluent concentration or removal capacity according to local discharge limits. In Norway (Heistad et al., 2006) and Sweden (www.avloppsguiden.se), the effluent criterion is normally a total P concentration of 1 mg L^{-1} . This value corresponds to a total P reduction of 90%. The data presented here for the full-scale treatment system show that effluent pH cannot indicate when a reactive bed filter has to be exchanged. The filter material Polonite had an extraordinary high P removal capacity during two-thirds of the operation time, while a gradual breakthrough developed during the last one-third. Overall, the average $\text{PO}_4\text{-P}$ removal efficiency was 89% over the 92-week period. Total-P was not measured in this study and the environmental authorities ask for this parameter. However, most of the P was in inorganic form after the septic tank storage and pre-treatment step, when the wastewater was infiltrated into the reactive material. We suggest that the exchange interval of filter material be estimated from the total wastewater volume treated. The particular filter well studied here, which received wastewater from a household with only two people, obviously used much less water than would be expected.

The 800 L (560 kg) Polonite used in the filter well was a sufficient amount for treating approximately 70 m^3 of domestic wastewater, i.e. 11 L (8 kg) were required per cubic metre. The corresponding value for the column in experiment Ia was 2 L (1.6 kg m^{-3}). However, this and the other column experiments were far from breakthrough, so this value is not relevant for comparison. These results can be compared with the expected lifetime of the Filtralite P material as calculated by Heistad et al. (2006), where a total filter volume of 6 m^3 was expected to meet the required effluent limit of 1.0 mg P L^{-1} for 5 years. Based on the data given by Heistad et al. (2006), our calculations show that 1 m^3 of wastewater could be treated by filtration through approximately 5 L of Filtralite P. This is half the amount required for treatment to approximately the same effluent limit by Polonite. A comparison of expected maximum P sorption capacity has revealed that Polonite has a much higher capacity than Filtralite P (Brogowski and Renman, 2004; Ádám et al., 2006; Cucarella and Renman, 2008). Hence Polonite could be expected to have shown better removal capacity in the full-scale treatment system tested. There are several possible explanations for the observed lowered capacity.

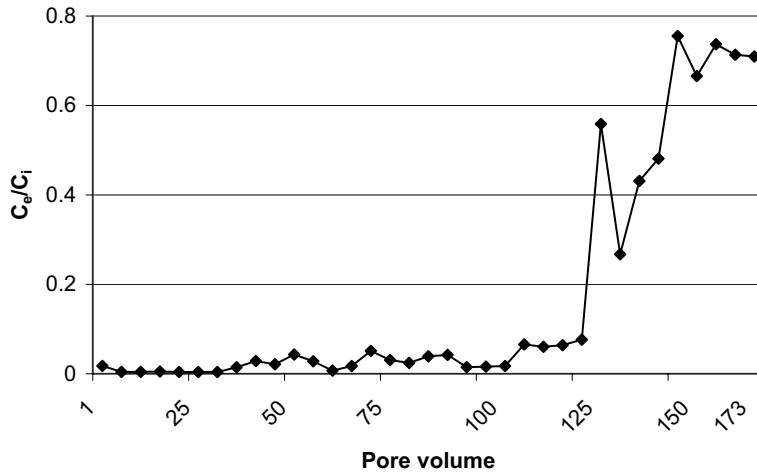


Figure 6. Phosphate breakthrough curve for experiment III (period with down-flow feeding of filter).

The properties of the material can vary depending on the manufacturing process. The Polonite used in experiment III had a starting pH of 11.9, compared with 12.5 for that used in experiment II. Polonite is normally produced in the particle size range 2-5.6 mm but it was observed that the material used in the filter well contained coarser fractions. Finer fractions of Polonite give higher P sorption capacity (unpubl. data). The loading of organic matter to the filter was high during the first 18 weeks of operation because of inadequate pre-treatment in the septic tank. This improved when the wastewater was discharged to the filter through a biofilter but the effect of dissolved organic matter could be present, which is suggested to reduce the P-sorption capacity of many alkaline filter materials. By further improvement of the Polonite material and filter well design, including pre-treatment steps, we believe it is possible to achieve a P removal efficiency such that only 1-2 kg would be required as a design volume for treatment of one cubic metre of wastewater. However, other parameters such as nitrogen and BOD have to be considered too.

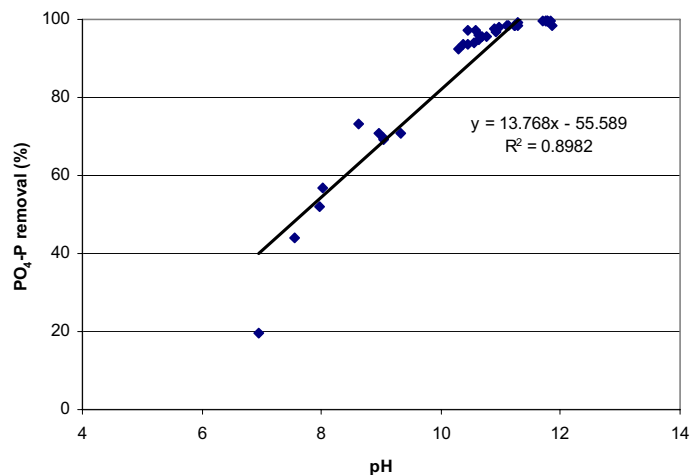


Figure 7. Correlation between phosphate removal and pH for experiment III.

3.4 Phosphorus sorption measured in the material

The amount of sorbed P (as elemental P) in the Polonite used in the three experiments was measured as total concentration using ICP-OES. Mass balance calculations were not undertaken because of the low sampling frequency, since discrepancies often occur between mass balance calculation and total content determination, as discussed in similar studies (Søvik and Kløve, 2005; Ádám et al., 2007). The content of total P in different layers, including background values, is presented in Table 5.

Table 5. Total concentration of P (g kg^{-1} dry matter) in selected layers of Polonite at the end of the experiments (P content of virgin material excluded)

Experiment	Layer (cm, from top of the filter)					
	0-5	5-10	10-20	30-40	40-50	50-60
Ia	7.05	4.97	n.d.	n.d.	1.53	-
Ib	4.7	n.d.	n.d.	n.d.	n.d.	-
II	1.3	1.3	0.8	0.28	0	-
III	1.27±0.06	-	0.36±0.02	0.50±0.02	n.d.	0.34±0.03

The amount of sorbed P in Polonite can be compared with other alkaline materials and experiments where domestic wastewater has been used over a longer period of time. An experiment with steel slag showed a maximum total P removal potential of 1.23 g kg^{-1} (Shilton et al., 2006) and an electric arc furnace slag (EAF) 1.18 g kg^{-1} (Drizo et al., 2002). These values are similar to those obtained in our study, but the calculations were based on material volumes and treatment facilities that were much different to the compact filter well studied here. For instance the steel slag facility used 17,700 tonnes of material. The material Filtralite P[®] tested in a column experiment using secondary wastewater showed a P concentration of $0.276 \pm 0.117 \text{ g kg}^{-1}$ dry matter (Ádám et al., 2007). Our investigation showed that the

Polonite used (particle size 2-5.6 mm) was at least able to remove 1.3 g P kg⁻¹ dry matter from domestic wastewater.

Calcite precipitate was observed in the effluent of columns used in experiments I and II and therefore some P sorbed to calcite could have left the columns. Our previous research has shown that P accumulation decreases with depth of filter and wastewater flow direction (Hylander et al., 2006; Gustafsson et al., 2008). Surprisingly, large differences were found between the surface and bottom layers of the saturated filter used in experiment I. The bed filter in experiment III was fed with wastewater from two directions (upflow, downflow), which obviously resulted in smaller vertical differences in P content. The mode of intermittent, pore volume batch feeding of wastewater interrupted by drying periods of the filter was predicted to prolong the PO₄-P sorption lifetime of the Polonite. However the present results show that this cyclic procedure, used in experiment Ib and III, did not increase the longevity of the filter, at least concerning PO₄-P removal.

4. Conclusions

The results obtained in this study show that Polonite has strong potential as a filter material in wastewater purification, as it can successfully remove phosphate over long periods of time. Although this study dealt only with phosphate, it is most important to remove this water-soluble form of P since it is one of the main causes of eutrophication, which negatively affects many natural water bodies.

The columns filled with Polonite and exposed to high synthetic wastewater loading showed the best long-term removal capacity of the three systems tested. A clear PO₄-P breakthrough was demonstrated in the experiment of the longest duration, which tested a full-scale bed filter system. The Polonite in the column systems examined was still 'active' at the end of the experimental period, showing no clear breakthrough tendency. Cyclic loading of wastewater to the filters interspersed with periods of saturation/drying up did not improve P removal capacity.

The compact filter well studied is designed for regular replacement of the Polonite, with the spent material recycled as a P-rich soil amendment. Wastewater production from the test household using this filter well was rather low, which gave a lifetime of 2 years for the 560 kg of Polonite applied here.

The pH proved not to be a simple parameter for determining when the filter material should be replaced. Instead, the P removal longevity of reactive filter materials can be estimated from the volume of wastewater treated if a water meter is installed in the house.

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