Phosphorus Transport and Reduction in Compact-bed Filters

Simulations and Experiments

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Preface

The present Licentiate thesis has been carried out at the Division of Fluid Mechanics at Luleå University of Technology, Sweden, from the year 2009 to 2011. This work was funded by the Swedish Research Council Formas.

I would like to express my utmost gratitude to my main supervisor Professor Staffan Lundström, whereby without his advise and support this thesis would never had become a reality. In addition, much appreciation goes to my co-supervisor Dr. Annelie Hedström and my colleague Inga Herrmann, for all their valuable discussions we have had together. More so, I am grateful to my co-supervisor Dr. Vilnis Frishfelds, a great mathematician that has provided solutions to all the complex questions that I presented to him. Furthermore, I would like to express my gratitude to Professor Šimunek and Professor van Genuchten for their valuable contribution and to all my colleagues at the Division of Fluid Mechanics for creating a pleasant working environment. I am also thankful to Gregory F. Simmons for his help in reviewing part of my work for any grammatical errors.

I am grateful to my family in Sweden, Majid, Julia, Zari, Masoud, Maryam, Mohammad, Mahsa, Nima, Adrian and Arvid who have always constantly encouraged me with my studies. I am also thankful to all my friends in Luleå who have supported me during the last 2 years. The numbers are a lot but among them I would like to say thanks to Gabriel, Darya and their family who were always there to help me. A special thank you goes to my best friends Kave and Mohammad Mehdi for all the times that we have shared together.

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Amir Jourak
Luleå, May 2011
Summary

Excessive release of phosphorus from the effluent of on-site sanitation facilities to the environment is one source of aquatic pollution. The primary effect of excess phosphorus in the aquatic environment is eutrophication. In Sweden, there are about one million private on-site wastewater treatment facilities, half of which are considered unacceptable by the Swedish Environmental Protection Agency (SEPA). Recent guidelines issued by SEPA recommended total phosphorus reduction of 70-90% in wastewater in small scale treatment facilities. Using reactive filter materials as compact filter systems following a biological pretreatment can be a convenient option for upgrading the present on-site sewage treatment facilities. Research on reactive filter materials has been undertaken in many different ways as there is no standard method for such investigations. Therefore, there is a need to develop methods and models to evaluate the reduction capacity and predict the longevity of potential reactive filter materials.

In the first part of this thesis a filter material Filtra P (Nordkalk, Finland) is investigated. The phosphorus sorption characteristics of Filtra P were investigated in batch and column experiments. The batch test method was evaluated with respect to the effects of liquid-to-solid ratio and particle size on phosphorus sorption. Column experiments were carried out at different flow rates and phosphate (PO$_4$-P) feed concentrations. The experimental data obtained from batch and column experiments were used to investigate the feasibility of modeling PO$_4$-P breakthrough curves in fixed-bed columns by means of the convection-dispersion equation and a Langmuir isotherm. The model successfully predicted the PO$_4$-P breakthrough curves for the columns with low influent concentration (11 mg dm$^{-3}$), which is within the range normally found in wastewater (5-15 mg dm$^{-3}$). Experimental observations however yield that the possibility to combine the convection-dispersion equation with a model accounting for precipitation of calcium-phosphate compounds in the bulk should be examined.

The second part of the thesis focuses on dispersion in laminar flow through a randomly packed porous-medium model. The study of dispersion in flow through porous media is an important issue in many branches of science and engineering and has direct applications in several industries. For example, dispersion occurs in the disposal of sewage waste into
aquifers and flow through reactive compact-bed filters that are used for on-site sanitation systems. In order to shed light on this phenomenon, a detailed longitudinal and transverse dispersion numerical experiments were performed in two-dimensional (2D) randomly packed beds of thousands of circular particles in a laminar flow regime. The calculated longitudinal and transverse dispersion coefficients were presented as Peclet numbers based on longitudinal and transverse dispersion coefficients versus Peclet number based on molecular diffusion coefficient, and were compared to three-dimensional (3D) experimental data available in the literature. It was found that at very low superficial liquid velocities both longitudinal and transverse dispersions were governed by molecular diffusion. Based on the comparisons between numerical results obtained from the 2D model to the 3D experimental data, it was found that the present 2D approach to study the longitudinal dispersion in flow through porous media can be considered to be acceptable.

The present numerical data may be used to estimate the longitudinal and transverse dispersion coefficients in a 2D process by which one fluid is displaced from a porous medium by a second fluid which is miscible with the first in a laminar flow regime.
Appended Papers


**Paper C:** A. Jourak, V. Frishfelds, T.S. Lundström, I. Herrmann and A. Hedström. The Calculations of Dispersion Coefficients Inside Two-dimensional Randomly Packed Beds of Circular Particles. *manuscript*
Paper Abstracts

Paper A

Phosphorus Sorption Characteristics of Filtra P in Batch Tests.

Recent guidelines from the Swedish Environmental Protection Agency recommend stricter regulations for phosphorus (P) reduction in small-scale wastewater treatment, which raises the need for additional and novel treatment steps in small-scale facilities. Following a biological pre-treatment, filter systems can be a convenient option. In this study, the P sorption characteristics of the sorbent material Filtra P were investigated in batch tests. The batch test method was evaluated with respect to the effects of liquid-to-solid ratio and particle size on P sorption. For initial concentrations \( (c_i) \) between 3 and 100 mg L\(^{-1}\), the P in the solution was completely and rapidly sorbed, indicating that Filtra P was an efficient substrate for this process. The maximum amount of P sorbed was \( 4.3 \pm 0.64 \) g kg\(^{-1}\) at \( c_i = 300 \) mg L\(^{-1}\). P sorption and turbidity measured in the supernatant correlated positively. Turbidity was probably caused by calcium-P-precipitates suggesting precipitation was the major sorption mechanism. Neither liquid-to-solid ratio, nor particle size, affected P sorption significantly \((\alpha = 0.05)\) at \( c_i = 1000 \) mg L\(^{-1}\), confirming that the conditions used in the batch tests were appropriate. In full-scale applications, the precipitate formed may be at risk of being washed out of the filter, leading to low total P reduction and recovery.

Paper B

Modeling of Phosphate Removal by Filtra P in Fixed-bed Columns.

This study investigated the feasibility of modeling phosphate (PO\(_4\)-P) transport and removal in fixed-bed columns filled with commercial filter material Filtra P (Nordkalk, Finland) by means of the convection-dispersion equation and a Langmuir isotherm. Batch experiments on Filtra P were done in order to find Langmuir isotherm. Axial dispersion coefficient was estimated from recommended correlation in the literature. Four column
experiments were carried out at different flow rates and PO₄-P feed concentrations. HYDRUS-1D was used for simulation of PO₄-P breakthrough curves. Simulated breakthrough curves were compared with experimental breakthrough curves obtained from column experiments. The model successfully predicted the PO₄-P breakthrough curves for the columns with low influent concentration (11 mg dm⁻³), which is within the range normally found in wastewater (5-15 mg dm⁻³).

**Paper C**

The Calculations of Dispersion Coefficients Inside Two-dimensional Randomly Packed Beds of Circular Particles.

This study investigates longitudinal and transverse dispersion in two-dimensional (2D) randomly packed beds of thousands of circular particles in a laminar flow regime over a range of superficial liquid velocities. This 2D discrete system of particles is divided into cells using modified Voronoi diagrams in which each cell contains one particle. The relationship between the average vorticity and the alteration of the stream function is obtained by using data from particular configurations of the three nearest particles. The stream function distribution in the system is then obtained by using the principle of energy dissipation rate minimization. Then a finite packed-bed in which a concentration-type condition is set at the inlet boundary is mimicked by adapting boundary conditions to the rectangular 2D domain. With this system transient longitudinal dispersion numerical experiments were performed, and concentration profiles were fitted simultaneously with analytical solutions to estimate the values of the longitudinal dispersion coefficient ($D_L$). Steady-state transverse simulations were performed in the 2D planar domain by adapting fixed concentrations on the side walls of the 2D porous medium in which the flow is directed upwards, and the values of the transverse dispersion coefficient ($D_T$) were calculated from the approximate analytical solutions to that setup. The $D_L$ was found to be scale-dependent, wherein far from the inlet, it increased in a fairly linear manner to the end of the bed. The advection-dispersion equation with a constant $D_L$ for the 2D packed-bed model was not able to represent the long tailings of the breakthrough curves. The estimated $D_L$ and $D_T$ were compared to some three-dimensional (3D) experimental data. At very low
superficial liquid velocities, both longitudinal and transverse dispersions were observed to be governed by molecular diffusion. The values of $D_L$ that were obtained by the present 2D model agreed with 3D experimental data. At very high superficial liquid velocities, the 2D numerical experiments overpredicted $D_T$ a lot as compared to the 3D experiments. This is most likely a result of the 2D approach.
Paper A

Phosphorus Sorption
Characteristics of Filtra P
in Batch Tests
Phosphorus Sorption Characteristics of Filtra P in Batch Tests

Inga Herrmann · Amir Jourak · Annelie Hedström · T. Staffan Lundström

Abstract Recent guidelines from the Swedish Environmental Protection Agency recommend stricter regulations for phosphorus (P) reduction in small-scale wastewater treatment, which raises the need for additional and novel treatment steps in small-scale facilities. Following a biological pre-treatment, filter systems can be a convenient option. In this study, the P sorption characteristics of the sorbent material Filtra P were investigated in batch tests. The batch test method was evaluated with respect to the effects of liquid-to-solid ratio and particle size on P sorption. For initial concentrations ($c_i$) between 3 and 100 mg L$^{-1}$, the P in the solution was completely and rapidly sorbed, indicating that Filtra P was an efficient substrate for this process. The maximum amount of P sorbed was $4.3 \pm 0.64$ g kg$^{-1}$ at $c_i = 300$ mg L$^{-1}$. P sorption and turbidity measured in the supernatant correlated positively. Turbidity was probably caused by calcium-P-precipitates suggesting precipitation was the major sorption mechanism. Neither liquid-to-solid ratio, nor particle size, affected P sorption significantly ($\alpha = 0.05$) at $c_i = 1000$ mg L$^{-1}$, confirming that the conditions used in the batch tests were appropriate. In full-scale applications, the precipitate formed may be at risk of being washed out of the filter, leading to low total P reduction and recovery.

Keywords Clogging · Filters · Particle size · Phosphorus · Precipitation · Wastewater Management

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1 Introduction

Phosphorus (P) treatment and recovery from household wastewater is a crucial process for recycling this important element, as P is a non-renewable resource which has been estimated to become depleted in 60 to 130 years (Steen 1998). In Sweden, there are about one million private small-scale wastewater treatment facilities that together deliver about the same amount of P to the environment as all Swedish municipal wastewater plants (Johansson 2002) while P is often the limiting nutrient for eutrophication in freshwater ecosystems (Berge et al. 1997). Today, in ca. 24% of Swedish small-scale facilities, wastewater is only treated in septic tanks (sludge removal) (Ejhed et al. 2004), and further treatment aimed at nitrogen and P removal is absent. The Swedish Environmental Protection Agency (Swedish EPA) has recommended stricter regulations for P reduction (70 to 90%) in small-scale wastewater treatment plants (Swedish EPA 2006). This has provided an impetus for the development of further and/or novel treatment steps in small-scale facilities. Filter systems used downstream of biological pre-treatment, can be a convenient option in terms of cost, function and maintenance requirements, for treating P in wastewater. Additionally, P-containing filter materials could possibly be reused for the amendment of soil in agriculture, in effect recycling P into the environment (Hylander et al. 2006; Cucarella et al. 2008).

Currently, there are relatively few such filter systems in use, most of which are in Norway. However, many potentially suitable filter materials have been tested to determine their P sorption capacity, which is an important parameter when comparing and selecting filter materials (Drizo et al. 2002). The P sorption characteristics of a variety of reactive filter materials have been reviewed by Cucarella and Renman (2009), Vohla et al. (2011) and Johansson Westholm (2006). The latter two studies classified the materials as natural materials such as e.g. wollastonite (Hedström 2006) and shellsand (Søvik and Kløve 2005), industrial by-products such as slags from steel production (Hedström and Rastas 2006), or man-made products such as Leca (Drizo et al. 1999), Polonite® (Hylander et al. 2006), Filtralite P® (Ádám et al. 2007), and Filtra P. Filtralite P® is commercially available and has also been studied in a subsurface constructed filter bed in a full-scale facility treating wastewater from a school (Ádám et al. 2006), and from a house with three family flats (Heistad et al. 2006). Although these facilities had a reasonable estimated lifetime of 15 and 5 years respectively, they consumed rather large areas of land, requiring 200 and 5 m², respectively (Ádám et al. 2006; Heistad et al. 2006). The filter material Filtra P (Nordkalk, Finland) has recently been developed for use in small downstream wells. Approximately 500 kg of Filtra P is required for a single family house, and must be replaced on an annual basis. Filtra P was also shown to be suitable for use as a soil amendment (Cucarella et al. 2008). However, Filtra P has only been investigated in a few studies to date. Eveborn et al. (2009) studied the speciation of P in Filtra P after use, while Gustafsson et al. (2008) have shown the P sorption characteristics of the material to be promising. In order to compare Filtra P to other materials, further investigations are needed.

In batch tests, the reactive filter material (sorbent) is brought into contact with P (sorbate) solution until equilibrium between sorbate and sorbent is reached. The P sorption capacity of the material is then determined by the difference between the initial
and final sorbate concentrations. Batch tests are widely used to make a first assessment of a material, as they are comparatively easy and cost effective to perform. Their disadvantage is they are performed under conditions that differ substantively from those pertinent to real-scale filters, e.g. extensive contact between sorbate and sorbent under aerobic conditions, excess P availability, and room temperature. Therefore, they can over-estimate the P sorption capacity of the material (Jenssen et al. 2005). However, in some cases P sorption can also be under-estimated (Arias et al. 2001). Furthermore, batch results are highly sensitive to the test conditions in the laboratory. Researchers have performed batch tests in many different ways (Cucarella and Renman 2009), with conditions differing in scale, sorbate concentration range, solution to material (liquid-to-solid, LS) ratio, and shaking time and manner. Therefore, comparison of findings is problematic, as a number of factors may influence the result. LS ratio, for example, has been shown to influence the maximum retained concentration of P in shellsand (Søvik and Kløve 2005) and soils (Chang and Wang 2002).

The aims of this study were twofold. Firstly, the sorption characteristics of Filtra P at different concentrations and reaction times were investigated by means of batch tests, and compared to previously characterized materials. Secondly, the batch test method was evaluated with respect to the effects of liquid-to-solid ratio and particle size on P sorption at high initial concentration.

2 Materials

The sorbent material Filtra P was supplied by Nordkalk, Finland and originated from the lime pit located in Pargas. It is a calcium-based granular material; its composition and particle size distribution are shown in Table 1.

The sample received (about 100 kg) was first split by fractional shovelling and then by using a riffle splitter. Sub-samples of 28.9 ± 2.3 g were obtained and dried overnight at 105 °C. From these subsamples, 25 g were randomly selected and used for the tests.

3 Methods

3.1 Phosphorus sorption

An amount of 25.0 g of Filtra P was placed into 0.5 L Erlenmeyer flasks and 500 mL of phosphate solution added to obtain an LS ratio of 20, as recommended in soil science (Cucarella and Renman 2009) and used by several other researchers. The samples were equilibrated with P solutions containing KH₂PO₄ as P source (sorbate) at initial concentrations \( c_i = 3, 12, 25, 50, 100, 300, 400, 500, 600, 700 \) and 1000 mg P L⁻¹. The flasks were shaken on a shaking plate at 100 rpm for 48 hours, and in some cases P sorption was measured for various shaking times of 0.5, 1, 2, 4, 8, 24 and 48 hours. A number of experiments were performed in duplicate. The experiments were carried out at room temperature (ca. 20 °C).
Table 1: Elemental composition and particle size distribution of Filtra P (TS = total solids)

<table>
<thead>
<tr>
<th>Element</th>
<th>Content in g kg(^{-1}) TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>355</td>
</tr>
<tr>
<td>Si</td>
<td>11.3</td>
</tr>
<tr>
<td>Al</td>
<td>4.57</td>
</tr>
<tr>
<td>Fe</td>
<td>3.24</td>
</tr>
<tr>
<td>Mg</td>
<td>2.22</td>
</tr>
<tr>
<td>K</td>
<td>1.44</td>
</tr>
<tr>
<td>Na</td>
<td>0.69</td>
</tr>
<tr>
<td>Ti</td>
<td>0.26</td>
</tr>
<tr>
<td>P</td>
<td>0.25</td>
</tr>
<tr>
<td>Mn</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particle diameter [mm]</th>
<th>Percentage of material below indicated size [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>5.6</td>
<td>27</td>
</tr>
<tr>
<td>8</td>
<td>89</td>
</tr>
<tr>
<td>11.3</td>
<td>99</td>
</tr>
<tr>
<td>13</td>
<td>100</td>
</tr>
</tbody>
</table>

3.2 Effect of LS and particle size on phosphorus sorption

To assess the impact of LS and particle size on P sorption in batch tests, a 2\(^2\) factorial experiment was performed in duplicate shaking 8 bottles for 48 hours. Table 2 shows the values of LS and particle sizes used. The experiment was performed using an initial P concentration of approximately 1000 mg L\(^{-1}\) (\(c_i = 1010 \pm 55\) mg L\(^{-1}\)). For the small particle size samples, Filtra P was sieved through a 5.6 mm sieve and the fraction passing through the sieve was used for batch testing (corresponding to about 27 % by weight of the initial sample, Table 1). To generate samples with larger particle size, \(\geq 8\) mm, the sample was sieved to remove smaller particles (< 8 mm, corresponding to 89 % of the initial sample, Table 1).

Table 2: Factors and their investigated levels

<table>
<thead>
<tr>
<th>Factor</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid to solid ratio (LS)</td>
<td>20, 40</td>
</tr>
<tr>
<td>Particle size</td>
<td>&lt; 5.6 mm, (\geq 8) mm</td>
</tr>
</tbody>
</table>

3.3 Analyses

After shaking, ca. 100 mL of the supernatant were immediately filtered through 0.45 \(\mu\)m filters, acidified and stored at 5 °C. P was analysed using an inductively coupled plasma (ICP) technique, without prior digestion, as the sample was assumed to be totally dissolved during the procedure.
In the unfiltered supernatants, measurements of pH were conducted using a WTW pH330 pH-meter with a WTW SenTix41 pH-electrode. Turbidity was measured in nephelometric turbidity units (NTU) using a HACH 2100N turbidimeter.

3.4 Statistical evaluation

The Pearson product moment correlation coefficient was used to assess correlation between variables. The factorial experiment was evaluated using multiple linear regression ($\alpha = 0.05$). Statistical evaluations were performed using Minitab 15 by Minitab Inc., 2007.

4 Results and discussion

4.1 P sorption

The maximum amount of P sorbed to Filtra P was $4.3 \pm 0.64$ g kg$^{-1}$ at $c_i = 300$ mg L$^{-1}$ (Fig. 1A). For $c_i = 3$ to 50 mg L$^{-1}$, the initial P in the solution was completely and rapidly sorbed to the material (Fig. 1B). For $c_i = 3$ to 25 mg L$^{-1}$, sorption was completed after 0.5 hours, and for $c_i = 50$ mg L$^{-1}$ after 1 hour (Fig. 1). For $c_i = 100$ mg L$^{-1}$, P was completely sorbed after 8 hours (Fig. 1).

The high maximum sorption at $c_i = 300$ mg L$^{-1}$, coupled with the complete sorption at $c_i = 3$ to 100 mg L$^{-1}$, show that Filtra P is an effective material for sorbing P from aqueous solution. Therefore interestingly, P was sorbed completely by Filtra P at concentrations typical for wastewater, around 12 mg L$^{-1}$ (Swedish EPA 2006). At $c_i < 300$ mg L$^{-1}$, even with complete sorption, the amounts of sorbed P were relatively small. To determine maximum P sorption in this concentration range, higher LS would have been necessary but were not practical. The decrease in P sorption for $c_i > 300$ mg L$^{-1}$ is probably due to decreased pH levels.

The maximum amount of P was sorbed to the material at $c_i = 300$ mg L$^{-1}$ (Fig. 1 and 2) at which concentration the highest turbidity in the supernatant was also observed (Fig. 3). The Pearson product moment correlation coefficient between the amount of sorbed P and turbidity of the supernatant was calculated to be $r = 0.816$. Taking into account only data from $c_i = 3$ to 300 mg L$^{-1}$, the correlation was as high as $r = 0.968$. As the amount of sorbed P decreased at higher concentrations, $c_i > 300$ mg L$^{-1}$ (Fig. 2), the turbidity also decreased (Fig. 3).

Turbidity in water is caused by suspended matter and its extend is manifested in the optical property that causes light to be scattered and absorbed rather than transmitted directly through the sample (Clesceri et al. 1989). Turbidity in the supernatants in this study was most probably caused by precipitation products containing calcium (Ca) and P, since Filtra P is a Ca-based material (Table 1). Additionally, we show below that particle size of the material does not affect P sorption in the batch tests at high $c_i$. This suggests that P sorption is not related to specific surface area, which may indicate that precipitation in the water phase is the dominant P retention mechanism (Ádám et al. 2007), rather than surface reactions.
As Ca ions can form stable and insoluble products with phosphate (Vohla et al. 2011), Ca-phosphates are likely to be formed. The rapid reaction of P in solution (Fig. 1) suggests that the Ca contained in Filtra P (Table 1) was present as CaO, which reacts more readily with phosphate than CaCO₃ (Vohla et al. 2011). Furthermore, conditions in the supernatants were alkaline at $c_i = 3$ to $300$ mg L$^{-1}$, with pH between 11.4 and 12.1 (Fig. 3), which encourages the precipitation of Ca phosphates (Baker et al. 1998; Cheung and Venkitachalam 2000). It is unclear what type of Ca-P-phases are formed.
with Filtra P. Gustafsson et al. (2008) found neither crystalline hydroxylapatite (HA) nor dicalcium phosphate or octacalcium phosphate (OCP) in Filtra P after use. The phosphate phase formed in their experiment seemed to be poorly crystalline in nature. The formation of Al or Fe phosphates is also possible (Gustafsson et al. 2008). XANES results of Eveborn et al. (2009) indicated the presence of amorphous calcium phosphate (ACP) and crystalline calcium phosphates (OCP or HA) in Filtra P. The decrease of P sorption and turbidity at $c_i > 300 \text{ mg L}^{-1}$ was concomitant with a decrease in pH (Fig. 3) and could be explained by the fact that Ca phosphate solubility decreases sharply with increasing pH (Baker et al. 1998).

By assuming that equilibrium was established when the amount of sorbed P as a function of shaking times (Fig. 1) varied by less than $\pm 0.1 \text{ g P kg}^{-1}$ from the preceding time point, it was shown that P sorption was strongly dependent on $c_i$ (Fig. 2). For the samples with $c_i = 1000 \text{ mg L}^{-1}$, equilibrium according to this criterion was never achieved and the amount of sorbed P after 48 hours of shaking time was plotted (Fig. 2). For concentrations $c_i = 300 \text{ to } 700 \text{ mg L}^{-1}$, only 48 h of shaking was performed. The isotherm shows a linear dependence on initial concentration for $c_i = 3 \text{ to } 100 \text{ mg L}^{-1}$ (Fig. 2A), due to the fact that at this concentration range the entire amount of P contained in the initial solution was sorbed to the material (Fig. 1B).

![Fig. 2: Sorption isotherms showing sorption to sorbent over the initial (A) and the equilibrium (B) concentration range tested. When duplicates were performed, standard deviations are shown as error bars.](image)

The isotherm was also plotted over equilibrium concentrations (Fig. 2B). The shape of the isotherm (Fig. 2B) differs from a typical adsorption isotherm, since for $c_i > 300 \text{ mg L}^{-1}$, the amount of P sorbed decreased with increasing $c_i$. Therefore, it was difficult to obtain a satisfactory fit of the data to Langmuir and Freundlich equations. This suggests that adsorption is not the major P binding mechanism of Filtra P at these concentrations.

### 4.2 Comparison to other materials

The maximum sorption capacity of Filtra P in this study was $4.3 \pm 0.64 \text{ g kg}^{-1}$ and is compared to other materials in Table 3. This data shows that a higher maximum
sorption has only been measured previously for shellsand (Ádám et al. 2007). However, comparison between materials is complicated by the fact that maximum sorption capacities for the different materials have been determined at different initial sorbate concentrations, LS ratios, and shaking times (Table 3). In particular, the initial concentration used is important since higher concentrations are generally associated with increased P sorption (Drizo et al. 2002; Ádám et al. 2007). Maximum sorption capacities of the materials are typically determined using initial sorbate concentrations that greatly exceed the concentrations commonly present in municipal wastewater, leading to conclusions that may not be applicable to full-scale treatment. The maximum sorption capacity is sometimes used to assess a material’s total retention capacity in the field, and thereby the lifetime of the filter. However, this approach is not necessarily useful as conditions in laboratory batch tests differ considerably from field conditions and the transfer of results from the laboratory to the field is problematic. Therefore, it can be more relevant to compare the materials’ sorption characteristics at initial P concentrations typical for wastewater, around 12 mg L\(^{-1}\) (Swedish EPA 2006). In this study, however, at this concentration range the material sorbed the entire amount of P in solution implying that the maximum sorption capacity of the material was not reached (equilibrium concentration in the supernatant after shaking being close to zero, Fig. 2). Furthermore, in many previous studies equilibrium was not demonstrated (Arias et al. 2001; Ádám et al. 2007) and data is often not reported for initial P concentrations comparable to wastewater. Therefore it is not possible to compare fully the sorption capacities of all the different materials tested, at typical wastewater P concentrations.

4.3 Effect of LS and particle size on phosphorus sorption at \(c_i = 1000\) mg L\(^{-1}\)

The pH in the supernatants appeared to be constant and equal to \(6.2 \pm 0.1\). The amount of sorbed P ranged from 1.64 to 10.64 g kg\(^{-1}\), the average being \(4.84 \pm 2.87\) g kg\(^{-1}\).
Table 3: Maximum sorption capacities of different materials determined in batch tests

<table>
<thead>
<tr>
<th>Material</th>
<th>(c_i) [mg L(^{-1})]</th>
<th>Amount of sorbed P [g kg(^{-1})]</th>
<th>LS [L kg(^{-1})]</th>
<th>Shaking time [hours]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtra P</td>
<td>300</td>
<td>4.3</td>
<td>20</td>
<td>48</td>
<td>This study</td>
</tr>
<tr>
<td>Leca</td>
<td>320</td>
<td>2.2</td>
<td>25</td>
<td>24</td>
<td>(Zhu et al. 2003)</td>
</tr>
<tr>
<td>Shellsand</td>
<td>480</td>
<td>9.6</td>
<td>2.5</td>
<td>30</td>
<td>(Ádám et al. 2007)</td>
</tr>
<tr>
<td>Fresh blast furnace slag</td>
<td>20</td>
<td>1.5</td>
<td>75</td>
<td>20</td>
<td>Hedström and Rastas (2006)</td>
</tr>
<tr>
<td>Sands</td>
<td>320</td>
<td>0.3…3.9</td>
<td>20</td>
<td>20</td>
<td>(Arias et al. 2001)</td>
</tr>
<tr>
<td>Fly ash</td>
<td>40</td>
<td>0.65…0.7</td>
<td>24</td>
<td></td>
<td>(Drizo et al. 1999)</td>
</tr>
</tbody>
</table>

For particle size > 8 mm and LS 40, an average sorption capacity as high as \(8.8 \pm 2.6\) g kg\(^{-1}\) was determined. Turbidity ranged between 0 and 850, the average being \(176 \pm 322\) NTU. The histograms of the responses (i.e. amount of sorbed P, pH and turbidity) were approximately normally distributed, only turbidity was log transformed because it showed a heavy tail to the right. Using ANOVA and multiple linear regression, it could be shown that, within the investigated LS and particle size range, neither LS nor particle size significantly (\(\alpha = 0.05\)) affected the amount of sorbed P (Table 4).

Table 4: Estimated effects of LS and particle size on the amount of sorbed P to the sorbent (coded units). T: t-statistic, P: probability. \(R^2 = 0.74\); \(R^{2\text{adj}} = 0.54\)

<table>
<thead>
<tr>
<th>Term</th>
<th>Effect</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td></td>
<td>7.05</td>
<td>0.002</td>
</tr>
<tr>
<td>LS</td>
<td></td>
<td>2.320</td>
<td>1.69</td>
</tr>
<tr>
<td>Particle size</td>
<td>2.540</td>
<td>1.85</td>
<td>0.138</td>
</tr>
<tr>
<td>LS\text{x} Particle size</td>
<td>3.060</td>
<td>2.23</td>
<td>0.090</td>
</tr>
</tbody>
</table>

LS ratios have been shown to influence P sorption in other studies, for values from 0.5 to 15. Søvik and Kløve (2005) investigated the influence of LS on the maximum retained concentration of P in shellsand and found the retention to be 10 times higher at LS = 15 compared to LS = 1. This observation is probably due to the fact that, even at equal sorbate concentration, more P per gram sorbent is available for sorption at LS = 15 (higher sorbate to sorbent ratio). Furthermore, adsorption on soils was observed to be much higher at LS = 10 compared to LS = 0.5 (Chang and Wang 2002). Therefore, LS should be chosen to be high enough to ensure good sorption for the initial concentration range of interest. Many authors have chosen LS = 20 for their batch tests (Arias et al. 2001; Drizo et al. 2002), or even LS < 20 (Baker et al. 1998; Sakadevan and Bavor 1998; Cheung and Venkitachalam 2000; Gustafsson et al. 2008). A value of LS = 20 is recommended in soil science (Cucarella and Renman 2009). Therefore, the choice of LS = 20 for the batch tests in this study seems reasonable, particularly since higher LS ratios were shown to not affect the sorption result for \(c_i = 1000\) mg L\(^{-1}\). However, for \(c_i < 100\) mg L\(^{-1}\) LS ratio is important, since at these concentrations...
the entire P contained in the solution was sorbed by the material, therefore higher LS would lead to higher amount of sorbed P.

In most studies, very small samples of material are used for batch tests. Cucarella and Renman (2009) recommend a sample amount as low as 1 to 3 g. For the batch tests in this study, a sample amount of 25 g Filtra P was used, as smaller amounts would have contained only a few particles. By rigorous sample splitting, the samples tested were made as reproducible as possible, but a deviation in the particle size distribution between samples could not be completely eliminated. However, the fact that P sorption was not affected by particle size at \( c_i = 1000 \text{mg L}^{-1} \) indicates that any difference in the particle size distribution between samples would not significantly affect the results obtained.

Within the data set for \( c_i = 1000 \text{mg L}^{-1} \), the Pearson product moment correlation coefficient between turbidity and amount of sorbed P was determined to be 0.916, indicating that these two dependent variables are strongly positively correlated (high turbidity is associated with a high amount of sorbed P). This agrees with the trends shown in the isotherm data.

4.4 Relevance for full-scale filters

Filtra P efficiently sorbed P within the concentration range common in wastewater (Fig. 1B) suggesting that the material may function well even in full-scale treatment. However, alkaline conditions were observed in the batch systems (Fig. 3) indicating that the outflow pH of full-scale filters may be high (pH > 9), exceeding discharge limits (Vohla et al. 2011). The strong correlation between P sorption and turbidity in the supernatants as well as the fact that P sorption was not affected by the material’s particle size, points to precipitation as the main P sorption mechanism. In the batch test, the precipitate most likely consisted of small Ca-P-compounds which were removed from the supernatant by a 0.45 \( \mu \text{m} \) filter. In a full-scale filter, these particles are at risk of being washed out from the filter which would lead to low total P reduction and recovery. As Filtra P filters are operated up-flow, this risk is reduced but it is crucial to investigate the particles formed and their potential transport through the filter. A possible solution to this problem would be to use a low flow speed in the filter, although this may lead to clogging of the filter. Alternatively, washed-out particles could be retained by a downstream particle trap.

5 Conclusions

We have shown using batch tests, that phosphorus (P) completely and rapidly sorbed to Filtra P within the P concentration range typical of wastewater, suggesting that it is a suitable material for P retention in full-scale filters. The maximum P sorption was found to be 4.3 ± 0.64 g kg\(^{-1}\) which is higher than for filter materials tested previously, e.g. Filtralite P®.

Several results indicate that precipitation was the main binding mechanism: P sorption was strongly positively correlated with turbidity in the supernatants, lower sorption
at initial concentrations ≥ 400 mg L\(^{-1}\) was associated with low pH, and P sorption was shown to be insensitive to changing the particle size of the material. Turbidity measurements confirmed that the precipitate was present as small particles which may be washed out from a full-scale filter. Therefore, the design of the filter with regard to flow regime is important.

Liquid-to-solid (LS) ratio and particle size did not affect P sorption to Filtra P at an initial concentration of 1000 mg L\(^{-1}\). Sorption characteristics did not vary within the particle size range of Filtra P. LS ratios between 20 and 40 did not affect P sorption indicating that the LS ratio of 20 which was used for the batch experiment in this study was sufficient at the initial concentration investigated.

Acknowledgements

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Modeling of Phosphate Removal by Filtra P in Fixed-bed Columns
Modeling of Phosphate Removal by Filtra P in Fixed-bed Columns

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Abstract—this study investigated the feasibility of modeling phosphate (PO₄-P) transport and removal in fixed-bed columns filled with commercial filter material Filtra P (Nordkalk, Finland) by means of the convection-dispersion equation and a Langmuir isotherm. Batch experiments on Filtra P were done in order to find Langmuir isotherm. Axial dispersion coefficient was estimated from recommended correlation in the literature. Four column experiments were carried out at different flow rates and PO₄-P feed concentrations. HYDRUS-1D was used for simulation of PO₄-P breakthrough curves. Simulated breakthrough curves were compared with experimental breakthrough curves obtained from column experiments. The model successfully predicted the PO₄-P breakthrough curves for the columns with low influent concentration (11 mg dm⁻³), which is within the range normally found in wastewater (5-15 mg dm⁻³).

Keywords—Fixed-bed column, Filtra P, Modeling, Phosphorus, wastewater

I. INTRODUCTION

Excessive release of phosphorus from the effluent of on-site sanitation facilities to the environment is one source of aquatic pollution. The primary effect of excess phosphorus in the aquatic environment is eutrophication. In Sweden, there are about one million private on-site wastewater treatment facilities, of which are considered unacceptable by the Swedish Environmental Protection Agency [1]. According to Ejhed et al. [2], the most frequent on-site wastewater treatment systems in Sweden are: infiltration systems (40%), septic tanks (24%), collecting tanks (18%) and sand filter beds (13%). Nevertheless, present on-site sanitation systems have often insufficient phosphorus removal efficiency. Recent guidelines issued by Swedish EPA [3] recommended total phosphorus reduction of 70-90% in wastewater in small scale treatment facilities. Using reactive filter materials as compact filter systems following a biological pretreatment can be a convenient option for upgrading the present on-site treatment facilities. An advantage of using reactive filter materials is that they can possibly be used as a soil amendment in agriculture after being enriched with phosphorus [4, 5, 6].

Phosphorus removal capacity of such filter materials has been the main focus of studies so far. Some studies were done on natural and industrial by-products, e.g. wollastonite [7] and slags from steel production [8], respectively. In addition to natural and industrial by-products, some studies have focused on commercial filter materials such as Polonite® [4], Filtralite P® [9], and Filtra P [10]. Filtra P was shown to be a promising material for the removal of phosphate (PO₄-P) from domestic wastewater with removal efficiency of more than 95% [10]. Nevertheless, Filtra P has been only briefly investigated, i.e., [10, 11]. These studies were focused on the PO₄-P removal mechanism and the filtration efficiency of this material. No studies, however, have attempted to model the PO₄-P transport and retention in saturated Filtra P columns which is likely to be valuable for the estimation of the longevity of this filter material.

Several researchers have modeled the transport and retention of phosphorus in natural and artificial filters. For instance, Notodarmojo et al. [12] presented a model for one-dimensional steady state flow in soil columns. McGechan and Lewis [15] reviewed literature on phosphorus sorption by soils with the intention of selecting equations and parameter values for use in a soil phosphorus dynamics model. Lee et al. [16, 17] launched the first study on the PO₄-P transport in saturated slag columns. In all these studies, the general one-dimensional convection-dispersion equation for saturated flow in porous media [18] was applied to model the transport and retention of phosphorus in columns filled with different materials. The only variation between the studies is the approximated phosphorus removal mechanism and thus the removal term in the equations. Rubin [19] listed six different classes of chemical reactions that can take place in solute transport and subsequently investigated the relation between the mathematical nature of the problem formulation and the chemical nature of reactions. PO₄-P removal mechanism of Filtra P was investigated by [10, 11] who state that calcium-phosphate precipitation is important for removal of PO₄-P from wastewater.

One way of determining how much solute can be removed by the specific sorbent is batch experiments. The procedure is that results from the experiment are plotted on a
graph, called an isotherm that shows the solute concentration in equilibrium versus the amount sorbed onto the solid. The most common nonlinear sorption isotherms are the Langmuir and Freundlich isotherms. The application of these isotherms and their limitations are discussed widely in literature e.g. [20]. In the present study, sorption is referred to a process that ranges from adsorption to precipitation reactions which was defined by McBride [21], a definition convenient to use when dealing with reactive materials such as Filtra P for which the chemical processes governing the interaction are not fully known [20].

The main objective of this work was to investigate the feasibility of modeling PO₄-P transport and retention in fixed-bed columns filled with Filtra P by means of the convection-dispersion equation and a Langmuir isotherm. The experimental data used in this study came from [22] and [23]. The latter was used to obtain the Langmuir isotherm. The breakthrough curves obtained by the model were compared with the results from fixed-bed column experiments.

II. MATERIAL AND METHODS

A. Filtra P
Filtra P is a commercial filter material produced by heating up a mixture of limestone, gypsum, and iron. This product is categorized as an alkaline sorbent due to its high content of calcium hydroxide [10]. Table 1 shows the properties of this filter material. This material is delivered in the size of either 500 kg or 1000 kg per household for phosphorus treatment with the functioning time of minimum 1 year (www.nordkalk.com). Samples of Filtra P were obtained from Nordkalk Oyj Abp (Pargas, Finland).

B. Batch experiment
Batch equilibrium sorption experiments were carried out in 0.5 L Erlenmeyer flasks, containing 500 dm³ of the PO₄-P solution (initial concentrations in the range of 3-1000 mg dm⁻³), into which 25.0 g of Filtra P was added. The samples were equilibrated with PO₄-P solutions using KH₂PO₄ as a PO₄-P source. The flasks were placed on a shaking plate vibrating at 100 rpm for 0.5, 1, 2, 4, 8, 24, 48 hours for concentrations between 3-100 mg dm⁻³ and for 48 hours for concentrations between 300-1000 mg dm⁻³. The experiments were carried out at room temperature (ca. 20°C). After shaking, the supernatant was directly filtrated through 0.45 µm filters, acidified and stored at 5°C. The PO₄-P was analysed with the ICP technique without prior digestion since the sample was assumed to be totally dissolved during the procedure. In the supernatants, the pH was measured using a WTW pH330 pH-meter and a WTW SenTix41 pH-electrode.

<table>
<thead>
<tr>
<th>Element</th>
<th>g kg⁻¹ TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>355.21</td>
</tr>
<tr>
<td>Si</td>
<td>11.27</td>
</tr>
<tr>
<td>Al</td>
<td>4.57</td>
</tr>
<tr>
<td>Fe</td>
<td>3.24</td>
</tr>
<tr>
<td>Mg</td>
<td>2.22</td>
</tr>
<tr>
<td>K</td>
<td>1.44</td>
</tr>
<tr>
<td>Na</td>
<td>0.69</td>
</tr>
<tr>
<td>Ti</td>
<td>0.26</td>
</tr>
<tr>
<td>P</td>
<td>0.25</td>
</tr>
<tr>
<td>Mn</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The equilibrium concentration of PO₄-P in the solid phase \( q_e \) (g kg⁻¹), was calculated from the initial concentration \( C_0 \) (mg dm⁻³), and the equilibrium concentration \( C_e \) (mg dm⁻³), in each flask, using the following equation:

\[
q_e = \frac{V(C_0 - C_e)}{m} \tag{1}
\]

In (1) \( V \) is the volume of solution and \( m \) is the mass of Filtra P.

The equilibrium data obtained from batch experiments were fitted using Langmuir isotherm model, which may be expressed as:

\[
q_e = \frac{q_{\text{max}}bC_e}{(1 + bC_e)} \tag{2}
\]

where \( b \) is a constant related to energy of adsorption (dm³ mg⁻¹). The results of the batch experiments from [23] are shown in Fig. 1. When fitting the Langmuir isotherm (2) to the experimental equilibrium data for the PO₄-P in the equilibrium concentrations \( C_e = 0.2-22.93 \) mg dm⁻³ the following values on \( q_{\text{max}} \) and \( b \) were obtained, 4.30 g kg⁻¹ and 0.84 dm³ mg⁻¹, respectively, see Fig. 1b. The Langmuir
isotherm derived in this way will be used as a model input for the modeling of the column experiment later on in the present study while detailed discussion on the results of the batch experiments with Filtra P is dealt within [23].

C. Column experiment

Four column experiments were carried out at different flow rates and PO_4-P feed concentrations, see Table 2. Columns with an inner diameter of about 7.4 cm were made of fibre glass and placed with their axis in the vertical direction. The columns were filled with the Filtra P forming a fixed bed and a synthetic solution of PO_4-P influent (KH_2PO_4 dissolved in distilled water) was driven from the bottom of the columns upward facilitating measurement at water-saturated conditions. The experiments were carried out at room temperature (ca. 20°C). Details of the experimental setup are shown in Fig. 2. Effluent samples were taken twice weekly from each container and analysed with respect to dissolved phosphorus (about 100mL filtrated through 0.45 μm filters), total phosphorus (about 100mL nonfiltrated samples were taken) pH (directly after collection), redox potential, EC, turbidity, and total suspended solids (TSS).

PO_4-P breakthrough curves obtained from column experiments were used in this study. Detailed evaluation of these results can be found in [22]. It should, however, be noted that the experiments indicated that precipitation of calcium-phosphate compounds can be a main PO_4-P removal mechanism within the column.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface load (dm³ m⁻² day⁻¹)</td>
<td>406</td>
<td>1105</td>
<td>423</td>
<td>1083</td>
</tr>
<tr>
<td>PO_4-P concentration (mg dm⁻³)</td>
<td>11</td>
<td>11</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

The area above the breakthrough curve is proportional to the total solute removed from the feed stream upon the complete saturation of the bed [24]. Therefore, if the entire bed comes to equilibrium with the feed, the amount of PO_4-P removed from the solution, \( q_e \), may be calculated as (e.g. Izquierdo et al., [25]):

\[
q_e = \frac{C_\text{e}}{m} \int_0^N \left(1 - \frac{C}{C_\text{e}}\right) dN
\]

where \( q_e \) is the amount of PO_4-P removed (g of PO_4-P per kg of Filtra P), \( C_\text{e} \) and \( C \) are PO_4-P concentration at the column influent and effluent (mg dm⁻³) respectively, \( V_p \) is the bed pore volume (dm³), \( m \) is the mass of Filtra P in the column (g), and \( N \) is the number of pore volumes.

The integral represented by (3) was solved numerically in Matlab.

D. Mass transport model

In order to simulate the PO_4-P breakthrough curves, the convection-dispersion equation which assumes PO_4-P removal under equilibrium condition was used. The following assumptions were applied:

- Isothermal process
- Constant physical properties
- Negligible radial dispersion
- Saturated condition
Figure 2. Experimental setup of the Filtra P fixed-bed column experiments

The convection-dispersion equation for one-dimensional steady state flow in the axial direction is as follows (e.g. Miller and Weber [18]):

\[ \frac{\partial C}{\partial t} + \frac{\rho}{\varepsilon} \frac{\partial q}{\partial Z} = \frac{\partial}{\partial Z} \left( \frac{D_i}{\varepsilon} \frac{\partial C}{\partial Z} \right) - \frac{\partial}{\partial Z} \left( \frac{L D}{\varepsilon} \frac{\partial C}{\partial Z} \right) \]  

(4)

where \( C \) is the solute concentration (mg dm\(^{-3}\)), \( \rho \) is the bulk density of the Filtra P in the column (kg m\(^{-3}\)), \( \varepsilon \) is the porosity, \( q \) is the solid phase concentration (g kg\(^{-1}\)), \( D_i \) is the axial dispersion coefficient (m\(^2\) s\(^{-1}\)), \( u = Q/A \) is the average pore water velocity (m s\(^{-1}\)) in which \( Q \) is the average flow rate (m\(^3\) s\(^{-1}\)), and \( A \) is the cross sectional area of the column (m\(^2\)), \( Z \) is axial coordinate in the column (cm) and \( t \) is time (day).

The following initial and boundary conditions were used:

\[ C(Z,0) = 0, \]  

(5)

\[ -D_i \frac{\partial C}{\partial Z} + \nu C = n C_0 \] for \( Z = 0 \) and

\[ \frac{\partial C}{\partial Z} = 0 \] for \( Z = L \).

(6)

(7)

In this study the axial dispersion coefficient (\( D_i \)) was estimated from the recommended correlation in the literature. One such an empirical correlation which relates the axial Peclet number to the Schmidt number (effect of temperature) and particle Peclet number is as follows (Delgado [26]):

\[ \frac{1}{P_{e_P}} = \frac{P_{e_L}}{5} (1 - p^3) + \frac{P_{e_m}^2}{25} p(1 - p)^3 \exp \left[ - \frac{5}{p(1 - p)P_{e_m}} \right] - 1 + \frac{1}{p P_{e_m}} \]  

(8)

with

\[ p = \frac{0.48}{S_c^{0.175}} \left( \frac{1}{2} - \frac{0.48}{S_c^{0.175}} \right) \exp \left( - \frac{75S_c}{P_{e_m}} \right). \]  

(9)

In (8) and (9), \( P_{e_P} \) is the axial Peclet number, \( P_{e_L} \) is the particle Peclet number, \( S_c \) is the Schmidt number and \( \tau = \sqrt{2} \) (tortuosity), assuming filter pellets to be spherical [26]. The molecular diffusion coefficient (\( D_m \)) used in the calculation of \( P_{e_m} \) and \( S_c \) was estimated using the Wilke and Chang equation [27]. The estimated molecular diffusion of PO\(_4\)-P for the actual experimental condition is 1.295×10\(^{-9}\) m\(^2\) s\(^{-1}\). The effective grain size of \( d_{50} \) was used as an average pellets diameter in calculation of \( P_{e_L} \) and \( P_{e_m} \).

HYDRUS-1D [28] was used to simulate PO\(_4\)-P breakthrough curves. HYDRUS-1D allows simulation of convective-dispersive solute transport coupled with a nonlinear isotherm. The system of equations formed by (2) & (4), together with estimated axial dispersion coefficient by (8) & (9), and with initial and boundary conditions given by (5) - (7), were solved using HYDRUS-1D.

### III. RESULTS

#### Simulation of column dynamics

Table 3 shows from (3) calculated amounts of PO\(_4\)-P removed and number of pore volumes treated at \( C/C_0 = 0.02 \) (breakthrough point for columns C and D), at \( C/C_0 = 0.09 \) (breakthrough point for columns A and B) and \( C/C_0 = 1 \) (saturation point) for columns A, B, C, and D. According to Swedish EPA [3], the maximum allowable phosphorus concentration in the domestic wastewater effluent in areas with environmentally vulnerable recipients is 1 mg dm\(^{-3}\). Therefore, nondimensional breakthrough points for this study (i.e. \( C/C_0 = 0.02 \) and \( C/C_0 = 0.09 \)) were chosen in a way that represent the time that \( C = 1 \) mg dm\(^{-3}\) in the effluent of the columns.

Comparison between the predicted PO\(_4\)-P uptake in the batch experiment by the Langmuir isotherm (3.89 g kg\(^{-1}\) calculated by the Langmuir isotherm at \( C = 11 \) mg dm\(^{-3}\)) and the amounts of PO\(_4\)-P removed in the fixed-bed column experiments at saturation point, \( C/C_0 = 1 \), showed that the batch experiment predicted the amounts of PO\(_4\)-P uptake in column A (4.35 g kg\(^{-1}\)) with approximately 10% deviation. In the case of column B (7.85 g kg\(^{-1}\)), the deviation was almost 50%. Such comparisons were not feasible for columns C and D, due to the fact that the fitted Langmuir isotherm with the batch experiment (Fig. 1b) were in the equilibrium concentration ranges between 0-22.93 mg dm\(^{-3}\).
<table>
<thead>
<tr>
<th>Experiment</th>
<th>C/C&lt;sub&gt;0&lt;/sub&gt; = 0.02</th>
<th>C/C&lt;sub&gt;0&lt;/sub&gt; = 0.09</th>
<th>C/C&lt;sub&gt;0&lt;/sub&gt; = 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PO&lt;sub&gt;4&lt;/sub&gt;-P removed (g kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>Pore Volumes</td>
<td>PO&lt;sub&gt;4&lt;/sub&gt;-P removed (g kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>A</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>2.30</td>
<td>102.9</td>
<td>6.54</td>
</tr>
<tr>
<td>C</td>
<td>3.64</td>
<td>166.3</td>
<td>3.27</td>
</tr>
</tbody>
</table>

TABLE III: PO<sub>4</sub>-P REMOVED AT BREAKTHROUGH AND SATURATION POINT FOR COLUMNS A, B, C, AND D

and moreover no isotherm could be fitted in the concentrations above this range.

Initially, the Langmuir isotherm obtained by the batch experiment was incorporated into the model used to simulate PO<sub>4</sub>-P breakthrough curves. The model obtained this way was successfully simulated the PO<sub>4</sub>-P breakthrough curve for column A only. The incapacity of the model in representing the breakthrough curve for column B can be justified by the 50% deviation between the predicted and experimental PO<sub>4</sub>-P final uptake magnitude.

In order to find the suitable isotherm for simulation of PO<sub>4</sub>-P breakthrough curve for column B, the experimental PO<sub>4</sub>-P uptake values at saturation point for columns B (7.85 g kg<sup>-1</sup>) and D (7.37 g kg<sup>-1</sup>) which had almost the same surface loads, together with experimental data obtained by batch experiment for equilibrium concentrations close to zero (initial concentrations of 0-100 mg dm<sup>-3</sup>) were used to adjust the Langmuir isotherm. Fig. 3 shows the modified Langmuir isotherm.

The Langmuir parameters for this isotherm are: \( q_{\text{max}} = 7.86 \) g kg<sup>-1</sup> and \( b = 1.84 \) dm<sup>3</sup> mg<sup>-1</sup>. The maximum predicted PO<sub>4</sub>-P uptake by this isotherm was almost the same as the PO<sub>4</sub>-P uptake value at saturation point for column B. The adjusted Langmuir isotherm is comparable to the dynamic isotherm found by fixed-bed column experimental data only, which is widely used to simulate the column experiments breakthrough curves (see for instance, Pereira et al. [29], da Silva et al. [30]).

Fig. 4 shows the results of PO<sub>4</sub>-P transport modeling for column experiments. The model accurately predicted the breakthrough points and reasonably reproduced the shape of the experimental breakthrough curves for columns A and B. The model however was unable to represent the PO<sub>4</sub>-P breakthrough curves of columns C and D. Table 4 presents the axial dispersion coefficient (\( D_L \)), Langmuir isotherm parameters, \( q_{\text{max}} \) and \( b \) that were used in the simulation of breakthrough curves. Deviations between the predicted and experimental breakpoint are also presented in table 4 for columns A and B.

IV. DISCUSSIONS

A. Mass transport model

The conventional convection-dispersion equation was used in this study to model PO<sub>4</sub>-P breakthrough curves with rather good results for two of the experiments. The success of column dynamics simulations depends on the selection of equilibrium isotherm [31]. The theory of the Langmuir isotherm is based upon sorption of gases to uniform surfaces, and may in the strict sense only be applied to sorption processes [32]. Sorption processes in this context refer to any surface reactions including adsorption, chemisorption, absorption, and ion exchange. Fetter [33] clarified all these reactions. In the present study however, Langmuir isotherm was used to account for all possible removal mechanisms from surface reactions to classical chemical reactions, e.g. precipitation since no detailed study on the actual mechanisms was carried out. As previously stated the results from the experiment also indicate that precipitation can be a main mechanism.

Søvik and Kløve [34] fitted Langmuir isotherm in the concentrations where precipitation was taking place. In the surface reactions, e.g. adsorption, if the concentration in equilibrium is lowered, the material should release the sorbed solute and thus giving a new higher equilibrium concentration in the system. However, in the precipitation reactions, lowering the equilibrium concentration necessarily will not cause the dissolution of precipitated compounds. Moreover, as it is discussed in [33], as a result of surface reactions, some solutes move much more slowly through the column than the water that is transporting them; this effect is retardation and is considered in the convection-dispersion equation. Although, precipitation decreases the concentration of the solute in the plume, it may not necessarily slow the rate of plume movement [33].
Despite all the limitations discussed in literature for using Langmuir isotherm for a general case, in our study when it was fitted to the concentration ranges where precipitation was likely to happen (Fig. 1b) and incorporated into the model, it could successfully simulate the PO$_4$-P breakthrough curve of column A (Fig. 4a). Considering column B, the Langmuir isotherm had to be adjusted in order to predict the breakthrough curve. An alternative route to the one applied here would be to use several columns with the same surface load and varied concentrations in the range of 0-11 mg dm$^{-3}$ as it is normally done in order to find dynamic isotherm. However, it could be expensive and time consuming to do such experiments just to find a Langmuir isotherm for one column. Moreover, equilibrium concentrations for initial concentrations of 0-100 mg dm$^{-3}$ from the batch experiment were close to zero (initial data values in Fig. 3), which shows
FILTRA P effectively remove PO4-P from the solution in these concentrations. Therefore the adjusted Langmuir isotherm (Fig. 3) is actually fitted to experimental data from column experiments B and D which had almost the same surface load and equilibrium concentrations close to zero which can be considered to be zero.

Langmuir isotherm simply could not be fitted for columns C and D in the batch experiment. This can be seen in Fig. 1a, increasing the concentrations caused decreasing the pH of the system and PO4-P uptake amount decreased abruptly which further confirms the fact that precipitation of calcium-phosphate compounds are likely to be the removal mechanism of PO4-P [23]. In order to just test the model, the Langmuir isotherms (Fig. 1b) and (Fig. 3) were used for simulation of PO4-P breakthrough curves of columns C and D, respectively.

B. Column dynamics

Fig. 4 shows both modeled and experimental PO4-P breakthrough curves of column experiments. Comparison between experimental breakthrough curves of columns A-B (Fig. 4a-Fig. 4b) and C-D (Fig. 4c-Fig. 4d) shows that, interestingly, the columns with higher surface loads were treating PO4-P for more pore volumes than the columns with the same influent PO4-P concentrations and lower surface loads. This can be partially explained by looking at the pH curves of column experiments [22], the columns which were treating PO4-P for more pore volumes were also had higher pH, the condition that precipitation of calcium-phosphate were likely to occur. The reason of faster decreasing of pH in the columns with lower surface loads led us to a hypothesis which is beyond the scope of the present study and is discussed on the paper dealing with column experiments [22].

C. Simulation of column dynamics

The model successfully simulated the PO4-P breakthrough points of columns A and B. Column A had almost the same surface load and PO4-P feed concentration as of a four-person household real scale Filtra P column and the breakthrough curve of it was well fitted by the model which used the Langmuir equilibrium isotherm obtained from the batch experiment. The model was unable to represent the PO4-P breakthrough curves of columns C and D. PO4-P breakthrough curves of columns A and B had the typical S-shape and they reached the breakthrough point C/C0 = 0.09, corresponding to C = 1 mg dm-3 after several pore volumes.

V. SUMMARY AND CONCLUSIONS

This study investigated the feasibility of modeling PO4-P transport and removal in fixed-bed columns filled with Filtra P by means of the convection-dispersion equation and a Langmuir isotherm. Langmuir model was used to represent the PO4-P uptake in the concentrations where precipitations of calcium-phosphate compounds were likely to occur. In this work, the axial dispersion coefficient was estimated from the correlation given in the literature. Four column experiments were performed at different flow rates and PO4-P feed concentrations. Magnitude of the influent concentrations and surface flow rates were chosen in a way that, the low level almost resemble the condition of a real scale Filtra P column filter, while the high levels represent rather extreme laboratory conditions to accelerate the experiment. The model was further compared by the experimental data obtained from fixed-bed column experiments.

The main results obtained can be summarised as follows:

- The breakthrough curve of column A which had almost the same surface load and PO4-P feed concentration as of a real scale Filtra P column was well fitted by the model which uses the convection-dispersion model and the Langmuir equilibrium isotherm obtained from the batch experiment.
- The same convection-dispersion model incorporated with a modified Langmuir isotherm was also able to fit the breakthrough curve of column B which had low level PO4-P feed concentration and high level influent flow rate.
- Experimental observations however yield that the possibility to combine the convection-dispersion equation with a model accounting for precipitation of calcium-phosphate compounds in the bulk should be examined.

NOTATIONS

\( A \) Cross sectional area of the column, m²
\( b \) Langmuir constant, dm³/mg⁻¹
\( C \) PO4-P concentration in the bulk fluid phase, mg dm⁻³
\( C_0 \) Initial PO4-P concentration in the bulk fluid phase, mg dm⁻³
\( C_e \) Equilibrium PO4-P concentration in the fluid phase, mg dm⁻³
\( d_{50} \) Hazen’s effective grain size, mm
\( D_L \) Axial hydrodynamic dispersion coefficient, m² s⁻¹
\( D_m \) Molecular diffusion coefficient, m² s⁻¹
\( L \) Length of the bed, cm
\( m \) Mass of Filtra P in the column, g
\( N \) Number of pore volumes
\( q \) Amount of PO4-P uptake, g of PO4-P per kg of sorbent
\( q_{max} \) Maximum PO4-P uptake capacity for the Langmuir model, g kg⁻¹
\( Q \) Average volumetric flow rate, m³ s⁻¹
\( t \) Time, day
\( u \) Interstitial velocity, m s⁻¹
\( V \) Volume of solution, dm³
\( V_p \) Bed pore volume, dm³
\( Z \) Axial coordinate in the column, cm
\( \varepsilon \) Column void fraction
\( \rho \) fixed-bed density, kg m⁻³
\( \tau \) Tortuosity
\( \Theta \) Diameter of the column, cm

Dimensionless groups
ACKNOWLEDGMENT

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REFERENCES


\[ P_{\text{Eu}} \]

Peclet number of particle \( = \frac{ud}{D_p} \)

\[ P_{\text{Cl}} \]

Peclet number based on axial dispersion coefficient \( = \frac{ud}{D_a} \)

\[ Sc \]

Schmidt number \( = \frac{\mu}{\rho D_p} \)
The Calculations of Dispersion Coefficients Inside Two-dimensional Randomly Packed Beds of Circular Particles
The Calculations of Dispersion Coefficients Inside Two-dimensional Randomly Packed Beds of Circular Particles

Amir Jourak · Vilnis Frishfelds · T. Staffan Lundström · Inga Herrmann · Annelie Hedström

Abstract This study investigates longitudinal and transverse dispersion in two-dimensional (2D) randomly packed beds of thousands of circular particles in a laminar flow regime over a range of superficial liquid velocities. This 2D discrete system of particles is divided into cells using modified Voronoi diagrams in which each cell contains one particle. The relationship between the average vorticity and the alteration of the stream function is obtained by using data from particular configurations of the three nearest particles. The stream function distribution in the system is then obtained by using the principle of energy dissipation rate minimization. Then a finite packed-bed in which a concentration-type condition is set at the inlet boundary is mimicked by adapting boundary conditions to the rectangular 2D domain. With this system transient longitudinal dispersion numerical experiments were performed, and concentration profiles were fitted simultaneously with analytical solutions to estimate the values of the longitudinal dispersion coefficient \( D_L \). Steady-state transverse simulations were performed in the 2D planar domain by adapting fixed concentrations on the side walls of the 2D porous medium in which the flow is directed upwards, and the values of the transverse dispersion coefficient \( D_T \) were calculated from the approximate analytical solutions to that setup. The \( D_L \) was found to be scale-dependent, wherein far from the inlet, it increased in a fairly linear manner to the end of the bed. The advection-dispersion equation with a constant \( D_L \) for the 2D packed-bed model was not able to represent the long tailings of the breakthrough curves. The estimated \( D_L \) and \( D_T \) were compared to some three-dimensional (3D) experimental data. At very low superficial liquid velocities, both longitudinal and transverse dispersions were observed to be governed by molecular diffusion. The values of \( D_L \) that were obtained by the present 2D model agreed with 3D experimental data. At very high superficial liquid velocities, the 2D numerical experiments overpredicted \( D_T \) a lot as compared to the 3D experiments. This is most likely a result of the 2D approach.

Keywords longitudinal dispersion · transverse dispersion · porous media · packed beds · scale-dependent · mass transfer

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1 Introduction

The study of dispersion in flow through porous media is an important issue in many branches of science and engineering and has direct applications in several industries. For example, dispersion occurs in the miscible displacement of oil and gas, the disposal of sewage waste into aquifers, and flow through reactive compact-bed filters that are used for on-site sanitation systems. In the refining industry, the hydrodynamic dispersion properties inside of packed-bed reactors are of utmost importance to controlling adsorption efficiency during the purification and separation processes of chemical species by an adsorption removal mechanism.

Since the experiments of Slichter (1905) and the early studies of Taylor (1953, 1954) and Aris (1956), this topic has been widely studied in both experimental and numerical contexts, and many books have addressed it (e.g., Bear, 1988; Dullien, 1979; Fried, 1975). A large number of theories based on probabilistic approaches have been used to describe dispersion in porous media, including the theory of Saffman (1959, 1960), who modeled a porous medium as a random network of capillaries, and Koch and Brady (1985). Experimental measurements of longitudinal ($D_L$) and transverse ($D_T$) dispersion coefficients are normally conducted separately. In order to measure $D_L$ in laboratory, packed-bed column experiments are usually performed with an inert tracer. Depending on the adopted boundary conditions, and by neglecting transverse dispersion, the breakthrough curve that is obtained from the effluent is fitted with available analytical solutions (for an overview, see van Genuchten and Alves, 1982) to the following one-dimensional (1D) advection-dispersion equation:

$$\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial x} = D_L \frac{\partial^2 c}{\partial x^2},$$

(1)

where $c$ is the volume-averaged solute concentration, $t$ is time, $u$ is the average interstitial liquid velocity defined as $u = U/\varepsilon$, where $U$ is the superficial liquid velocity, $\varepsilon$ is the porosity of inert particles and $x$ is the distance in the main flow direction. The measurement of transverse dispersion by experimentation is normally more difficult than the measurement of longitudinal dispersion (Scheidegger, 1974). Generally, the methods that are used to estimate $D_T$ are based on either tracer tests or dissolution tests. For instance, the methods that have been used to measure transverse dispersion in laboratory columns include the continuous point source and the instantaneous finite source methods (Robbins, 1989). These methods consist of injecting a non-reactive tracer from an injector that has been embedded into a porous medium followed by concentration variation monitoring at several points that are downstream of the injection point. Another method for $D_T$ determination, which was developed by Coelho and Guedes (1988), is based on the measurement of mass transfer rates between flat or cylindrical surfaces that have been buried in a bed of inert particles and the flow flowing along it. The results from such experiments, with different solutes and temperature conditions, are typically plotted as either $D_T/D_m$ (or $D_T/D_L$) versus $Pe_m (= \frac{ud}{D_m})$, or as $Pe_T (= \frac{ud}{D_T})$ versus $Pe_m$ with the corresponding Schmidt ($Sc = \frac{\mu}{\rho D_m}$) numbers. In these expressions, $D_m$ is the molecular diffusion coefficient, $d$ is the inert particle diameter and $\rho$ is density of the liquid. Such curves can be used to find correlation
Displacement inside Two-dimensional Randomly Packed Beds

functions as outlined in Delgado (2006). When available in the literature, these validated correlations are used to estimate the dispersion coefficients inside of packed-bed columns.

Hydrodynamic dispersion in a porous medium can also be investigated and predicted with numerical experiments. In fact, using validated numerical simulation methods is advantageous because they can provide significant time savings. Moreover, one can access and study transport properties (i.e., hydrodynamic dispersions) in the porous medium at the local scale, which is neither easily measurable nor feasible using experimental methods. This paper examines the detailed simulation of mass transport in two-dimensional (2D) packed-bed models in a laminar flow regime. A porous medium is considered to be a discrete system of thousands of particles that are randomly packed in a 2D domain. Modified Voronoi diagrams are used to divide the system of particles into cells that each contains one particle. The flow pattern inside of the porous medium is obtained by minimization of the energy dissipation rate (Hellström et al., 2010A). A similar discrete model of a bed of particles was used to model the drying of a bed of iron ore pellets (Ljung, 2009) and to study internal erosion processes (Frishfelds et al., 2011A), as well as filtration mechanisms during composites manufacturing (Frishfelds and Lundström, 2011B). In the current study, the boundary conditions of the 2D domain were adapted in order to perform longitudinal dispersion numerical experiments so as to calculate $D_l$. To study $D_l$ for each position and time along the packed-bed model, concentration profiles were then fitted with appropriate analytical solutions in order to enable dynamic numerical simulations. By introducing other boundary conditions to the 2D domain, a method that was similar to that developed by Coelho and Guedes (1988) was used to study $D_T$. The results from these 2D numerical data are further compared to experimental results in packed beds.

An alternative way to numerically determine hydrodynamic dispersion inside packed beds of spherical particles is by means of CFD simulation (Augier et al., 2010; Freund et al., 2005; Magnico, 2003; Zeiser et al., 2001). One main problem of this approach is that simulations of large systems of particles become very time-consuming. In addition, the contact point between the particles cannot be correctly meshed; hence, it is necessary to contract the particle diameters so as to allow CFD calculations (Augier et al., 2010). This particle contraction process increases the porosity of the packed-bed model and directly affects the dispersion parameters. Another issue is related to the meshing around the particles in the packed-bed model, that is, the suitability of the mesh must be analyzed in order to estimate the precision of the calculated mass-transport parameters. Moreover, changing the particle distributions in such systems are usually accompanied by time-consuming re-meshing procedures.

When compared to CFD methods, the method that is used in this study to investigate dispersion in packed beds is advantageous because the particle size distribution inside of the 2D packed-bed model, as well as the overall size of the setup, can be easily adjusted.
2 Discrete model of a bed of particles

The consideration of a porous medium as a discrete system of particles facilitates the study of the statistical variation of the macroscopic mass-transfer coefficient that is caused by microscopic stochasticity. Such variation may originate from the size and shape distributions of the particles and their positions; however, in the present case, the shape is always circular, whereas the sizes and positions are allowed to vary. In addition, the methodology proposed herein makes it possible to include the natural dispersion of an inert solute in a fluid (e.g., water) through the porous medium.

2.1 Discretization

Using Voronoi diagrams, the system of particles is divided into cells that each contains one particle. Because the particles can have different sizes, a modified version of the Voronoi discretization process is used such that the Voronoi lines do not cross the surfaces of the particles (Hellström et al., 2010A). The closest Voronoi lines (with respect to the surfaces of the particles) are placed in the middle of the two nearest surfaces of particles and are perpendicular to the lines that connect the centers of the particles (see Fig. 1).

Fig. 1: Example of a Voronoi mesh of a 2D system with dimensions $1.0 \times 0.7 \text{ m}^2$ that consists of 3564 particles. The color represents the value of the stream function for each particle.
2.2 Flow pattern

Here, the particles are assumed to be impermeable, and liquid is assumed to percolate around the particles as it moves through the bed. Therefore, the stream function is constant along the surface of any given particle. No-slip boundary conditions further limit any potential variation in the stream function. The vorticity distribution results from the distribution of the stream function. For that reason, CFD results are used for nearest three particle configurations (Hellström et al., 2010A). This results in nondimensional coefficients that relate the average vorticity to the difference in the stream function within a local area. Such an approach is justified by the fact that the vorticity is always highest at or at least near to the closest spacing between two neighboring particles, as estimated by the analytical formulas in Lundström and Gebart (1995) and the CFD calculations in Hellström et al. (2010B) for regularly packed systems. For low Reynolds number ($Re$), the energy dissipation rate can be minimized according to the following equation:

$$\int \mu \omega^2 dV = \text{min},$$  \hspace{1cm} (2)

where $\omega$ is the vorticity that was used to obtain the distribution of the stream function (Berlyand and Panchenko, 2007; Hellström et al., 2010A). This is, for instance, true for laminar flow as in reactive compact-bed filters. Because the energy dissipation rate quadratically depends on vorticity, a linear system of equations with respect to the stream function values for the particles can be found, and the velocity distribution can be computed as illustrated in Fig. 1.

2.3 Molecular diffusion

The application of Voronoi diagrams facilitates the calculation of molecular diffusion in the space between the particles. Thus, the complete mass transport, taking into account the detailed flow patterns in the system, can be derived. The liquid flows along the Voronoi lines in the system and the same is true for diffusion. Each Voronoi line segment has two neighboring Voronoi lines at one endpoint and two Voronoi lines at the other end point. The diffusion rate along each Voronoi segment is approximately proportional to the distance between the nearest particles that Voronoi line separates. As the flow rate is slow in spaces between closely packed particles, the mass-transfer rate at these locations is low. The discrete numerical schemes for the advection-diffusion equation may have numerical instability. Therefore, a corrected upwind numerical scheme is used. This may slightly increase the apparent diffusion for very high flow rates. Therefore, the whole approach is valid when the discretization Peclet number ($Pe_{\text{dis}} = \frac{ud_{\text{dis}}}{D_m}$, where $d_{\text{dis}}$ is the size of discrete element) is small (i.e., $Pe_{\text{dis}} < 1$). Since the size of an element is comparable with the particle diameter, then $Pe_m = 100$ is used as the uppermost limit where the numerical scheme is still being accurate for the purposes of the paper i.e., dispersion in flow through a porous medium in a laminar flow regime. Herein, only molecular diffusion is assumed as diffusion mechanism and effect of turbulence is neglected. This is valid if $Re$ with respect to the particle diameter
remains small \( i.e., Re < 100 \), Hellström et al., (2010B) or the Schmidt number \( (Sc) \) at any given \( Pem \) remains large \( i.e., Sc > 1 \).

2.4 Longitudinal dispersion

In order to calculate \( D_L \), a rectangular 2D planar system that features a random distribution of particles and an upwardly directed flow is used. The lower side is set to a constant concentration \( c_0 \), whereas, on the upper side, there is no diffusional flux. The side walls have periodic boundary conditions. Because of the random distribution of particles, there is a slight variation in concentration in the direction that is perpendicular to the main flow direction. Therefore, the concentration is averaged in the perpendicular direction in order to obtain the 1D profile of the flow front. This is then compared to the analytical results for the 1D advection-diffusion equation.

The corresponding 1D advection-diffusion problem is set by Eq. (1) and the following boundary conditions:

\[
\begin{align*}
  c &= 0, \quad 0 < x \leq L, \quad t = 0, \\
  c &= c_0, \quad x = 0, \quad t \geq 0, \\
  \frac{\partial c}{\partial x} &= 0, \quad x = L, \quad t \geq 0.
\end{align*}
\]

This set-up has the following approximate analytical solution (van Genuchten and Alves, 1982):

\[
\frac{c}{c_0} = \frac{1}{2} \text{erfc} \left( \frac{x - ut}{2\sqrt{DLt}} \right) + \frac{1}{2} \exp \left( \frac{ux}{DL} \right) \text{erfc} \left( \frac{x + ut}{2\sqrt{DLt}} \right)
\]

\[
+ \frac{1}{2} \sqrt{\frac{u^2t}{\pi DL}} \exp \left( \frac{uL}{DL} \left( \frac{2L - x}{4DLt} \right)^2 \right).
\]

\[(4)\]

The exact solution of Eq. (1) when using the boundary conditions (3) is in the form of an infinite series. Eq. (4) will provide an accuracy of at least four significant digits when the following conditions (whichever condition is met first) are satisfied (van Genuchten and Alves, 1982):

\[
\frac{uL}{DL} > 5 + 40 \frac{ut}{L},
\]

or

\[
\frac{uL}{DL} > 100,
\]

where \( Pe_c = uL/DL \) is a column Peclet number. In these numerical experiments, neither of the above conditions are satisfied \( e.g., Pe_c \approx 42 \) for \( Pem \geq 0.9 \) and \( L = 1 \text{ m} \); however, a comparison of the approximate solution, Eq. (4), to the CFITM code of van
Genuchten (1980) for breakthrough curves that are obtained from the model are used as an example for one numerical experiment at low \( Pe_m \). The difference between the approaches will, therefore, be scrutinized. The \( D_L \) that is used to calculate \( Pe_m \) is chosen based on this comparison and on the fitted breakthrough curves that are obtained from the outlet of the domain. Moreover, using Eq. (4) facilitates a dynamical study of \( D_L \) during numerical experiments, that is, the fitting of Eq. (4) to concentration profiles can be simultaneously achieved during the numerical experiment as described below.

The \( D_L \) was obtained by comparing the numerical result to the solution of the 1D problem, Eq. (4), for a fixed \( u \). This can be achieved by either fitting the analytical result to the concentration profile as a function of \( x \) at a fixed time \( t \) or by fitting the analytical result to the concentration profile as a function of \( t \) for a fixed coordinate \( x \). The fitting is done using Newton’s optimization technique in combination with the least-squares method. In order to achieve such a fitting, the first and second derivatives of the analytical solution must be known. The initial guess of the \( D_L \) should be in the vicinity of the exact value in order to establish a correct fitting.

In the numerical experiment, a fixed \( U \) and \( \varepsilon \) were imposed on the setup. Therefore, fixed \( u \) for the estimation of \( D_L \) (as described above) was used. Another approach that is often used in packed-bed column experiments is to simultaneously fit both \( u \) and \( D_L \) to the measured breakthrough curve. One reason for this is that the measured \( \varepsilon \) before the experiment might slightly differ from that in the packed bed during the experiment. For instance, consider the case that the large pores in the packed bed are clogged by small particles during the experiment, which can cause variation in the \( \varepsilon \). Moreover, the material that is used in the packed-bed column experiment can be heterogeneous, which can lead to variations in \( u \) as a function of distance (see comparison between effective pore-water velocities in homogenous and heterogenous column experiments in Huang et al., 1995). In this numerical setup, however, there is a homogeneous porous-medium model, and the particles cannot move during the numerical experiment; hence, the \( \varepsilon \) and \( u \) are constant for the numerical experiments.

### 2.5 Transverse dispersion

In order to calculate the transverse dispersion coefficient, \( D_T \), in planar 2D systems, a similar method to that developed by Coelho and Guedes (1988) was used.

The model consists of a 2D planar packed bed with uniform porosity (\( \varepsilon \)) through which the liquid flows at a superficial velocity of \( U \) (see Fig. 2). The inlet concentration is set to zero, whereas the concentration of the side walls is fixed to a certain value \( c^* \). Due to natural transverse dispersion, a mass-transfer boundary layer will develop across which the solute concentration will drop from \( c = c^* \), at \( y = 0 \), to \( c \to 0 \) at the opposite side of the boundary layer. By defining a small control volume inside of this boundary layer, a steady-state concentration balance can be defined (Coelho and Guedes, 1988) as follows:

\[
\frac{\partial c}{\partial x} - D_T \frac{\partial^2 c}{\partial y^2} - D_L \frac{\partial^2 c}{\partial x^2} = 0.
\]  

(6)
There is no simple analytical solution for this planar problem; however, if the $D_L$ is neglected, then the solution is easily obtainable. The condition in which $D_L$ might be neglected is an $L/d > 10$ (Coelho and Guedes, 1988). This criterion is fulfilled in the numerical experiments as an $L/d > 31$.

Thus, the set-up of the problem in the system $0 \leq x \leq L$, $0 \leq y \leq a$ neglecting $D_L$ is:

$$\frac{\partial c}{\partial x} = D_T \frac{\partial^2 c}{\partial y^2},$$

(7)

$$c = 0, \quad 0 \leq x \leq L, \quad 0 < y < a, \quad t = 0,$$

$$c = 0, \quad x = 0, \quad 0 < y < a, \quad t \geq 0,$$

$$c = c^*, \quad 0 \leq x \leq L, \quad y = 0 \cup y = a, \quad t \geq 0,$$

(8)

for which an analytical solution for the constant $u$ and $D_T$ can be calculated as follows:

$$\frac{c}{c^*} = \frac{\text{erfc} \left[ \frac{y}{2\sqrt{Dt/u}} \right] + \text{erfc} \left[ \frac{a-y}{2\sqrt{Dt/u}} \right]}{1 + \text{erfc} \left[ \frac{a}{2\sqrt{Dt/u}} \right]}.$$  

(9)

In Eq. (9), the sum in the numerator approximates the side-wall contribution, whereas the denominator normalizes the sum such that boundary conditions at both side walls are satisfied.

The major difference between the present method and that of Coelho and Guedes (1988) and Delgado and de Carvalho (2001) is that in their three-dimensional (3D)
experimental method, the dissolving cylinder was placed along the axis of the packed bed, and the magnitudes of $D_L$ were estimated based on the mass-transfer rate between the soluble cylinder and the fluid flowing parallel to it.

2.6 System setup

The dimensions of the setups that were used for the numerical experiments are shown in Table 1. The standard porosity of the system ($\varepsilon$) was 0.4 and the flow was laminar [i.e., $Re < 100$, Hellström et al., (2010B)]. When the system was not packed with isometric particles, the diameters of the particles that were used in this experiment ranged from 8 to 16 mm. The average particle diameter in these systems was 12 mm.

Table 1: Characteristics of the setups that were used in the present study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$D_L$ numerical experiment</th>
<th>$D_T$ numerical experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Length [m]</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Width [m]</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Particle diameter [mm]</td>
<td>12</td>
<td>8-16</td>
</tr>
</tbody>
</table>

* Porosity ($\varepsilon$) was set to 0.5.

3 Results and discussion

Transient and steady-state numerical experiments were performed in the 2D porous-medium model in order to calculate $D_L$ and $D_T$, respectively. For very low fluid velocities ($u \rightarrow 0$), dispersion is dominated by molecular diffusion, wherein the following condition is valid (Koplik et al., 1988):

$$\frac{D_L}{D_m} = \frac{D_T}{D_m} = \frac{1}{\tau},$$

(10)

where $\tau$ is a tortuosity factor. This case is exemplified in Fig. 3a and 3c for the longitudinal and transverse dispersion numerical experiments, respectively. Increasing the velocity by one order of magnitude results in very different concentration distributions (see Fig. 3b and 3d).

As depicted in Fig 3b, the concentration profiles are not perfectly flat in the direction that is perpendicular to the primary flow direction, the axial direction in this picture. This is due to the natural dispersion that occurs in a random system of particles as previously described.
3.1 The estimation of longitudinal dispersion coefficient

Concentration profiles can be derived from the transient longitudinal dispersion numerical experiments; see the solid lines in Fig. 4. By fitting Eq. (4) to these concentration distributions, see the dotted lines, the values of $D_L$ were obtained (as shown beside each respective curve). Eq. (4) was simultaneously fitted to the concentration distribution curves during each transient longitudinal dispersion numerical experiments. Using such a procedure, the values of $D_L$ can be plotted as a function of time for each numerical experiment; Fig. 5 depicts the case for the numerical experiment E at $P_{em} = 0.9$. Note that the concentration distributions that are shown in Fig. 4 are representative concentration profiles that were fitted by Eq. (4) during the numerical experiment E to calculate $D_L/D_m$ versus time (for Fig. 5). When the concentration front reached the outlet of the domain (i.e., $x = L$), the values of $D_L$ could also be estimated from the breakthrough curves, see the dotted line in Fig. 5.

After the initial peak, $D_L$ increased along the packed bed (Figs. 4 and 5). This increase of $D_L$ is consistent with that of Huang et al. (1995), who found that the longitudinal dispersivity, $\alpha_L (= D_L/u)$, in their homogeneous column experiment increased as a function of scale along their column.

The initial peak in Fig. 5 is probably difficult to experimentally detect because it occurs only in the first or possibly the second layer of the column, in which the thickness of a single layer corresponds to the average diameter of one particle, $d$. The peak is furthermore not captured with the macroscopic advection-dispersion equation which predicts a very small initial spreading. The spreading distance in this equation (i.e., $\sqrt{DLt}$) is initially close to zero whereas in reality the minimum spreading distance is always greater than $d$. Thus, when applying a very short $t$ in a discrete equation ($d = \sqrt{D_Lt}$), $D_L$, must be very large to full-fill this equality. This is unrealistic. If $t$ is long enough such that $d < \sqrt{D_Lt}$, then the macroscopic equation works well.
Fig. 4: Concentration profiles are shown as solid lines at various times versus distance in the bed for a system of size $1.0 \times 0.7$ m$^2$ (numerical experiment E) and $P_{em} = 0.9$. The dotted lines represent an approximation via the analytic formula of Eq. (4). The values of the estimated $D_L$ are shown beside their respective curves.

Fig. 5: The non-dimensional longitudinal dispersion coefficient is plotted versus non-dimensional time. The size of the system is $1.0 \times 0.7$ m$^2$ (numerical experiment E) and $P_{em} = 0.9$. Some representative concentration profiles are shown in Fig. 4 ($t_0 = L/u$).
When $D_L$ of the mean transport equation, Eq. (1), is estimated from a breakthrough curve at a certain location, $x = L$, it represents the average value that pertains to that travel distance (i.e., between 0 and $L$) and the measured time period (Huang et al., 1995). In the present work, the approximate solution Eq. (4) was used to fit the breakthrough curves that were obtained from the outlet of the bed (i.e., $x = L$). For comparison, the CFITM code of van Genuchten (1980) was used to fit the analytical solution of Eq. (1) to the breakthrough curves for a first-type inlet boundary condition and a finite system i.e., boundary conditions in Eq. (3). When one of the conditions in Eq. (5) is satisfied, the CFITM code uses Eq. (4) in order to fit the breakthrough curves. In this study, neither of the conditions in Eq. (5) are satisfied. For example, for $P_{em} = 0.009$, $P_e \approx 2$, whereas for higher values of $P_{em}$ (i.e., $P_{em} \geq 0.9$), $42 \leq P_e \leq 56$ for all of the longitudinal dispersion numerical experiments. Therefore, the CFITM code used the infinite series solution to Eq. (1) in order to fit the numerical experiment breakthrough curves. The difference between the fitting that was obtained by the CFITM code and Eq. (4) was noticeable only when $P_{em}$ and $P_e$ were very low (i.e., as low as $P_{em} = 0.009$ and $P_e \approx 2$, see Fig. 6). For higher values of $P_{em}$ (i.e., $P_{em} \geq 0.9$), the difference between the estimated $D_L$ by the CFITM code and Eq. (4) was around 2%; however, using the CFITM code for these values of $P_{em}$ (i.e., $P_{em} \geq 0.9$) when $42 \leq P_e \leq 56$ did not yield better fittings to the numerical experiment breakthrough curves. The fitted breakthrough curves that were achieved via the CFITM code and those using the approximate solution via Eq. (5) coincide with one another (the comparison could not be shown in Fig. 6). As mentioned before, the present study uses an approximate analytical solution, Eq. (4), in order to fit the breakthrough curves because, when using this method, the variations in the longitudinal dispersion coefficients during the transient longitudinal numerical experiments were easily observed (Fig. 5).

When higher values of $D_L$ were used to simulate the breakthrough curves, a slight shift in time was observed, see dashed lines in Fig. 6. The incapability of Eq. (4), and the CFITM code to represent the long tailing of the breakthrough curves originates from the fact that $D_L$ spatially varied along the porous-medium bed and that both the CFITM code and Eq. (4) were tested if they could fit to the breakthrough curves by a constant $D_L$. Many studies have been carried out to represent such a scale-dependency of $D_L$ with temporally or spatially varied dispersion coefficient models using the advection-dispersion equation. For instance, Yates (1990) obtained an analytical solution for the 1D advection-dispersion equation by using a linearly increasing $D_L$.

Although the approximated breakthrough curves that were obtained by Eq. (4) were not able to represent the entirety of the breakthrough curves, they were successfully fitted to the breakthrough curves up to the breakthrough point of $C/C_0 \approx 0.05$ for all of the numerical experiments, see the dotted lines in Fig. 6 as an example for numerical experiment E. Therefore, the values of $D_L$ that were obtained by fitting Eq. (4) to the breakthrough curves at $x = L$ up to the breakthrough point of $C/C_0 \approx 0.05$ for each longitudinal numerical experiment and $P_{em}$ were used to calculate $P_eL$ (this point is schematically shown with an arrow in Fig. 5).
Fig. 6: Breakthrough curves at $x = 1$ m for a system of size $1.0 \times 0.7$ m² (numerical experiment E) versus non-dimensional time at $Pe_m = 0.009$ and $Pe_m = 0.9$. The dotted and dashed curves represent approximations via the analytical formula, Eq. (4), and the values of $D_L$ are shown in the figure. The dashed-dotted curve shows the fitted breakthrough curve of the CFITM code (van Genuchten, 1980) for $Pe_m = 0.009$; $t_0 = L/u$.

3.2 The effects of numerical setups on estimated dispersion coefficients

The calculated $D_L$ and $D_T$, which are shown as $Pe_L$ and $Pe_T$ versus $Pe_m$ for the different numerical experiments, are displayed in Figs. 7 and 8.

3.2.1 The effects of length and width

Comparisons of longitudinal dispersion numerical experiments A to C and B to D show that by increasing the length of the setup from $L = 1$ m to $L = 1.5$ m, the magnitude of $Pe_L$ decreased by 10 to 12%. This is to be expected because the $D_L$ increases as a function of the measurement scale. When the width of the system increased from 0.3 m in numerical experiment B to 0.7 m in numerical experiment E, no pronounced change in the magnitude of $Pe_L$ was observed, which demonstrates that the width of the porous-medium model for the $D_L$ calculations was sufficient. When the length and width of the system varied in the transverse dispersion numerical experiments, the subsequent changes in $Pe_T$ were irregular. When the length and width of the system changed from 0.5 m in experiment G to 0.8 m in experiment I, the magnitude of $Pe_T$ markedly decreased. The same trend of a decreasing $Pe_T$ with increasing system size was not observed for numerical experiments H and J; in these cases, $Pe_T$ increased as the size of the porous medium increased.
3.2.2 The effects of particle diameter

In all of the numerical experiments, when the systems were packed with isometric particles (i.e., \( d = 12 \) mm), the subsequently obtained dispersion coefficients values were lower than corresponding systems that had been packed with particles with diameters ranging from 8 to 16 mm (notice that \( d = 12 \) mm was used for calculations of \( Pe_L \) and \( Pe_T \) for all cases). The difference in \( D_L \) was slight for the longitudinal numerical experiments (see the differences between numerical experiments A and B and those between C and D in Fig. 7). This was not the case in the transverse dispersion numerical experiments G and H. More specifically, in these cases, the difference between the obtained values of \( Pe_T \) was significant between the equally sized systems that had been packed with isometric and differently sized particles, see Fig. 8. The difference in \( Pe_T \) was small for numerical experiments I and J. Therefore, it is believed that setups G and H were too small in order to accurately calculate the \( D_T \) therein. When the porous medium is packed with differently sized particles, the medium becomes slightly non-homogeneous in comparison to an identically sized system that has been packed with isometric particles. This increase in system non-homogeneity in terms of particle diameters might explain the slight increases in the calculated \( D_L \) in longitudinal dispersion numerical experiments, and \( D_T \) in the transverse dispersion numerical experiments I and J.

3.2.3 The effects of porosity

Increasing the porosity of the porous medium from 0.4 to 0.5 in experiments F and K did not yield any significant changes in the magnitudes of \( Pe_L \) and \( Pe_T \), respectively, see Figs. 7 and 8 for comparisons between numerical experiments C and F and between I and K; however, based on these observations, it is not possible to judge the effects of porosity on the magnitudes of the \( D_L \) and \( D_T \). This is due to the fact that increasing the porosity will change the interstitial velocity; hence, the dispersion coefficient magnitude in the porous medium may vary.

3.3 Comparisons of calculated \( Pe_L \) and \( Pe_T \) to experimental data

The calculated \( D_L \) and \( D_T \) (shown as \( Pe_L \) and \( Pe_T \) versus \( Pem \)) were compared to some experimental data from the literature for high \( Sc \) and \( Pem \leq 100 \) (which is the case in this study, see Figs. 7 and 8). Unfortunately, there is a paucity of reference experimental data for 2D systems. Therefore, the numerical results are presented together with 3D experimental data for dispersion in packed beds. At very low values of \( Pem \), both longitudinal and transverse dispersions are governed by molecular diffusion, and the values of \( Pe_L \) and \( Pe_T \) are the same (i.e., \( Pe_L = Pe_T = Pem \times \tau \), see Figs. 7 and 8). The molecular diffusion line (shown in Figs. 7 and 8) can be calculated based on assuming a tortuosity factor, \( \tau = \sqrt{2} \), as suggested by Sherwood et al. (1975). As can be seen from Figs. 7 and 8, this line does not exactly coincide with the numerical data in the pure molecular diffusion regime.
Fig. 7: Calculated $Pe_L$ in a porous-medium model for numerical experiments A, B, C, D, E, and F in comparison to experimental data from Raimondi et al. (1959) and Miller and King (1966).

Fig. 8: Calculated $Pe_T$ in a porous-medium model for numerical experiments G, H, I, J, and K in comparison to experimental data from Coelho and Guedes (1988) and Blackwell (1962).
It is interesting to point out that this tortuosity factor (i.e., $\tau = \sqrt{2}$) value has been established for spherical particles. For solid cylinders, the typical tortuosity is higher than this value; hence, by using a higher tortuosity factor, the numerical data would have been more consistent with this line. A case where the tortuosity factor $\tau = 1.93$ for solid cylinders was examined according to the suggestions of Gunn (1969); however, this tortuosity factor value overestimated the numerical data in the molecular diffusion regime. The longitudinal dispersion numerical results agree qualitatively with the experimental data (see Fig. 7). Both the numerical and experimental results show that at $P_{em} > 1$, $P_{eL}$ achieved a fairly constant value. The $P_{eT}$ that were obtained from numerical simulations were found to be lower than the experimental data at $P_{em} > 1$.

Based on a comparison of the simulated dispersion coefficients that were obtained by the present 2D porous-medium model to the 3D experimental data, the present 2D approach to investigating the $D_L$ in flow through porous media may be interpreted as acceptable. The observed larger $D_T$ for a high value of $P_{em}$ that was obtained by the present model may be explained by noting that the lateral fluid motion (which strongly affects transverse dispersion) in a 2D porous medium is stronger than that in a 3D case. Moreover, in a 3D case, there always exist gaps (even for closely packed particles) through which the flow can pass. In a 2D case, flow through closely packed particles is impossible, and flow must pass around the closely packed part of the system, which, in turn, increases the magnitude of the transverse dispersion. Nevertheless, the 2D longitudinal numerical data agreed with the 3D experimental data. A more objective approach would be to compare the present 2D simulated data to 2D experiment-derived $P_{eL}$ and $P_{eT}$, such as the obtained $P_{eL}$ and $P_{eT}$ in a flow through a fibrous bed.

4 Conclusions

Longitudinal and transverse dispersion coefficients were calculated via a detailed simulation of mass transport in 2D packed-bed models in the laminar flow regime. A summary of the major findings is as follows:

- The magnitudes of $D_L$ increased as a function of measurement scale and along the 2D packed bed. Far from the inlet, these increases were fairly linear until the end of the bed.
- For the 2D packed-bed model, the advection-dispersion equation, which assumes a constant $D_L$, was not able to represent the long tailings of the breakthrough curves.
- At a low values of $P_{em}$, both longitudinal and transverse mixings were governed by molecular diffusion. These observations were obtained by comparing the numerical results at a low $P_{em}$ to the molecular diffusion line (i.e., $P_{eL} = P_{eT} = P_{em} \times \tau$); however, the value of the tortuosity factor, $\tau$, for solid cylinders (which was the case for present study) was higher than that for spherical particles.
- The values of $D_L$ that were obtained using the 2D model agreed with the 3D experimental data. Based on this comparison, it is not possible to draw major conclusions for the validity of the present 2D numerical data. Nevertheless, the present 2D approach to study the $D_L$ in flow through porous media can be considered to be acceptable.
– At high values of $P_{ec}$, the values of the $D_T$ that were obtained using the present model were several-fold larger than the experimental values. This was possibly a result of the 2D approach that was used to study transverse dispersion in a packed-bed model.

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Nomenclature

$C$  Solute concentration  
$C_0$  Initial concentration  
$C^*$  Equilibrium concentration of the solute (i.e., solubility)  
$d$  Diameter of inert particles  
$d_{dis}$  The size of discrete element  
$D_L$  Longitudinal dispersion coefficient  
$D_m$  Molecular diffusion coefficient  
$D_T$  Transverse dispersion coefficient  
$L$  Length of the packed bed  
$t$  Time  
$u$  Interstitial velocity  
$U$  Superficial velocity  
$x$  Axial Cartesian co-ordinate  
$y$  Transverse Cartesian co-ordinate  

Greek symbols

$\alpha_L$  Longitudinal dispersivity coefficient ($= D_L/u$)  
$\varepsilon$  Column void fraction  
$\mu$  Dynamic viscosity  
$\rho$  Density  
$\tau$  Tortuosity factor  

Dimensionless groups

$P_{ec}$  Column Peclet number ($= uL/D_L$)
The discretization Peclet number ($= u_{\text{diss}}/D_m$)

Peclet number of inert particles ($= u_d/D_m$)

Peclet number based on the axial dispersion coefficient ($= u_d/D_L$)

Peclet number based on the transverse dispersion coefficient ($= u_d/D_T$)

Reynolds number ($= \rho u_d/\mu$)

Schmidt number ($= \mu/\rho D_m$)

References


