# Chapter 3
# Predicting the Removal Performance of Activated Carbon Filters in Water Treatments

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***Abstract:***
*In this paper we investigate a model for the removal of pollutants in surface water via adsorption onto the surface of activated carbon (AC). Both micropollutants and organic matter are present in surface water due to a variety of sources such as industrial waste, agricultural runoff and household pharmaceuticals. The presence of these contaminants makes surface water unsuitable for drinking and so they must be filtered out. One of the final steps in the filtration process involves using AC as an adsorbate. Models used to estimate the removal efficiency of activated carbon for different contaminants have value in that optimal conditions for the process of water filtration can be found, and the removal efficiency of new contaminants can be estimated. We examined multiple approaches to improve the computational efficiency of the model used by KWR Water and conclude by offering recommendations based on our results.*

Keywords: *adsorption filtration*

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## 3.1 Introduction

We consider a problem posed by KWR Water at SWI 2019. KWR Water is a water research institute focused on the entirety of the water cycle, providing the water industry with solutions and advice on their operations. One of the key steps in the water cycle is the treatment of surface water, which comprises around 40% of the drinking water in the Netherlands. In one of the latter stages of the purification process, micropollutants and natural organic matter (NOM) are filtered out of the water via adsorption onto activated carbon (AC).

Carbon filtering is a common type of water purification method, since activated carbon is considered an ideal material for filtration due to its very high porosity. During the process the contaminants that go inside the filter are adsorbed onto each carbon particle's surface. Due to the porous structure of the carbon particles, the contaminants then diffuse inside the pores. The process is illustrated in Figure 3.1. Once all pore space is covered, the carbon gets worn–out and should be changed. Not changing the filter on time will lead to the release of certain contaminants with the outflow from the carbon filter. Therefore simulating the process until the carbon filter becomes saturated is very useful in operation of the process. Frutehrmore, the efficiency of this process is generally unknown for newly detected micropollutants, which leads KWR to developing a model to simulate the filtration process.

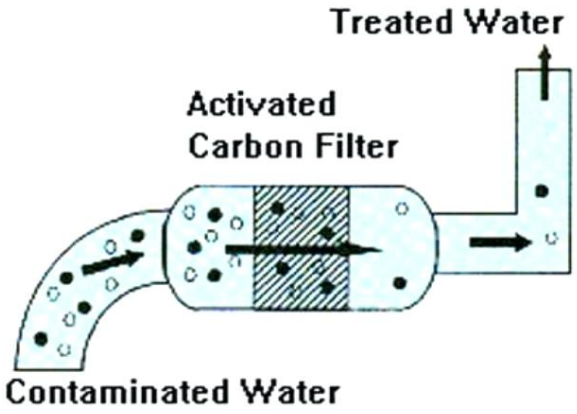


*Figure 3.1: Illustration of water filtration via an activated carbon filter.*

The model used by KWR is based on ideal adsorbed solution theory (IAST) using principles from thermodynamics. A key feature of IAST is that the rate of adsorption of contaminants is dependent on the other contaminants present, if any. For a more

in-depth treatment of IAST and the thermodynamics relevant to it, the interested reader may consult reference [2].
In this report we will reformulate the mathematical model used by KWR water and will further propose numerical methods, which can be used to solve two of the main problems of the company—robustness of the omputational methods (at present, KWR water solver does not always converge to a solution), large run-times for some numerical experiments.

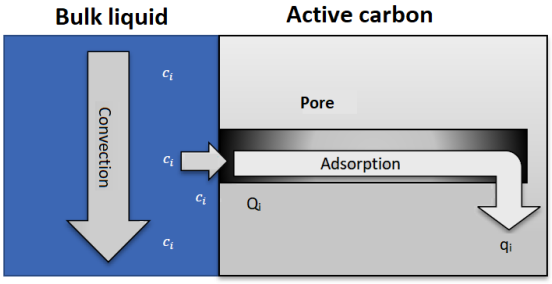


*Figure 3.2: Schematic of the adsorption process in water filtration from [1].*

The organisation of the report is as follows. In section 3.2, the IAST model used by KWR Water is examined and a reformulation in dimensionless quantities is presented. Section 3.3 describes the approach of KWR water for finding the solution of the problem. Section 3.4 presents the approaches we used to address the issues KWR Water had in their approach and Section 3.5 contains results from numerical experiments for troublesome values of the model parameters. We conclude in Section 3.6 by offering recommendations on how to improve the simulations based on our results.

## 3.2 Mathematical model

The process of carbon filtration is modelled in [1] by a system of partial differential equations. For each compound the concentration of micropollutant or natural organic matter is described by a one-dimensional convection-adsorption equation. Diffusion is assumed to be negligible in comparison to convection and the water flow rate is assumed to be constant.

The equation for the concentration is coupled to an equation describing the load on the carbon.

### 3.2.1 Original form of the model

Let $c_i(x,t)$ and $q_i(x,t)$ be the concentration and load of compound $i$ inside the carbon at time $t$ at the point $x$.

Let $t \in [0, T]$ and $x \in [0, X]$, where $x = X$ corresponds to the inlet of the carbon filter.

Then carbon filtration is modelled by the following system of PDEs, following [1]:

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= \frac{\nu}{\epsilon}\frac{\partial c_i}{\partial x} - \rho\frac{1-\epsilon}{\epsilon}\gamma\left(Q_i - q_i\right), \\ \frac{\partial q_i}{\partial t} &= \gamma\left(Q_i - q_i\right). \end{aligned} \tag{3.1}$$

We close the PDE system by imposing the following initial and boundary conditions:

$$c_i(x, 0) = 0,\ q_i(x, 0) = 0, \quad c_i(X, t) = c_{in}.$$

Let us consider the physical meaning of the terms in each equation:

- In the equation for the concentration $c_i$, the term $\frac{\nu}{\epsilon}\frac{\partial c_i}{\partial x}$ is a convection term, where $\nu$ is the constant velocity of the water flow and $\epsilon$ is the filter bed porosity. The term $\rho\frac{1-\epsilon}{\epsilon}\gamma\left(Q_i - q_i\right)$ describes the adsorption, where $Q_i$ is the load of compound $i$ on the surface of the carbon and $\gamma = \frac{6\cdot 10\cdot D_s}{d_p^2}$ is the rate of transfer of a compound into the pore [1]. Here, $D_s$ is the intraparticle diffusion constant and $d_p$ is the particle diameter. The parameter $\rho$ is the density of the carbon, so that $\rho\frac{1-\epsilon}{\epsilon}$ is the mass of carbon per volume unity.

- The equation for the load describes the change of the load due to surface diffusion.

The load on the surface of the carbon, $Q_i$, can be computed, based on empirical laws. If we assume there is only one compound in the water then $Q_i$ can be determined by the Freundlich isotherm

$$Q_i = K_{F,i} c_i^{\frac{1}{n_i}}, \tag{3.2}$$

where $K_{F,i}$ and $n_i$ are the so called Freundlich parameters of compound $i$. If there are multiple compounds in the water, there is competition between the different compounds and adsorption is limited. This competition can be modeled using Ideal Adsorbed Solution Theory (IAST) [1]. In this report, we will not go in further detail about IAST, since for our computations we assumed for simplicity that there is only one compound in the water.

*Table 3.1: Model parameters*

| parameter | description | order of magnitude |
|---|---|---|
| $\gamma[\frac{1}{s}]$ | rate of transfer of a compound into a pore | $\sim 10^{-6}$ |
| $\nu[\frac{m}{s}]$ | velocity of the water flow | $\sim 10^{-1}$ |
| $c_{in}[\frac{mol}{m^3}]$ | initial concentration | $\sim 10^{-2}$ |
| $\epsilon[-]$ | filter bed porosity | $\sim 10^{0}$ |
| $\rho[\frac{g}{m^3}]$ | density of the carbon | $\sim 10^{6}$ |
| $K_F[\frac{mol}{g}\left(\frac{m^3}{mol}\right)^{1/n}]$ | mass based Freundlich constants | $\sim 10^{-2}$ |
| $1/n[-]$ | Freundlich exponent of compound | $\sim 0$ |

## 3.3 KWR's current approach—basic idea and issues

KWR water uses the original form of the model (3.1) to model carbon filtration. To solve the partial differential equations, KWR water discretises space to obtain a system of ODEs. To solve the system of ODEs, KWR water uses a build-in Python solver.To take the competition betweem micro-pollutants and natural organic matter into account a Python built-in package for IAST is used. Figure 3.3 shows a sketch of the approach.

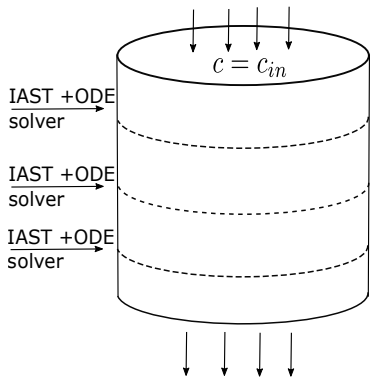


*Figure 3.3: Sketch of the approach of KWR water for simulating carbon filtration.*

As mentioned in Section 3.1, two main problems occur when using the Python solver—for some parameter values the solution does not converge or takes too much time to compute. Our goal was to localise the problem with the current approach and suggest a numerical scheme that is more robust and more efficient. For simplicity we assumed there is only one compound in the water. So we assume there is no competition, therefore we can ignore IAST. The reason for this assumption is that we think the problem of the current approach is due to using the Python built-in ODE solver and that the IAST method does not cause any problems.

In this respect, we note the following. To solve the system of ODEs the built-in Python solver uses adaptive numerical methods with a high order of convergence. However, the spatial discretization introduces a first-order approximation error and it is impractical to use high order methods for integration over time.

Thus, in the following sections we construct several different numerical methods and implement them in Mathematica and MATLAB for numerical experiments.

### 3.3.1 Dimensionless model formulation

Before setting up numerical schemes, we rewrite the system of equations (3.1) in dimensionless quantiities in order to decrease the number of parameters in (3.1). Also, this might reduce the problems in numerical schemes caused by different orders of magnitude of parameters, see Table 3.1.

We perform the change of variables

$$\bar{t} = \gamma t,\ \bar{x} = \frac{\gamma}{\nu} x,\ \bar{c}_i = \frac{c_i}{c_{in}},\ \bar{q}_i = \frac{\rho q_i}{c_{in}}. \tag{3.3}$$

Hence, the system of equations (3.1)-(3.2) now becomes

$$\frac{\partial \bar{c}_i}{\partial \bar{t}} = \frac{1}{\epsilon}\frac{\partial \bar{c}_i}{\partial \bar{x}} - \frac{1-\epsilon}{\epsilon}\left(\overline{Q}_i - \bar{q}_i\right) \tag{3.4}$$

$$\frac{\partial \bar{q}_i}{\partial \bar{t}} = \overline{Q}_i - \bar{q}_i, \tag{3.5}$$

$$\overline{Q}_i = \frac{\rho}{c_{in}} K_{F,i} M W_i^{\frac{1}{n_i - 1}} \left(c_{in}\bar{c}_i\right)^{\frac{1}{n_i}}, \tag{3.6}$$

where $MW$ is the molar weight of the compound and $\overline{Q}_i$ is a function of $\bar{c}_i$ . Very important effect due to rescaling of the variables is the change of the boundary conditions. Namely,

$$\bar{c}(x,0) = 0,\ \bar{c}(X,t) = 1,\ \bar{q}(x,0) = 0. \tag{3.7}$$

Therefore, from now on, we always solve this reformulated model. Also, we omit the bars above the $c$ and $q$.

## 3.4 Numerical methods

The temporal domain is $[0,T]$ and the spatial domain is $[0,X]$, for some parameters $T$ and $X$. We discretize the domain with the mesh $(x_k, t_l)$, where $x_k$ and $t_l$ are defined as follows

$$\begin{aligned} x_k &= k\Delta x, \quad k = 0,\dots n, \quad n = X/(\Delta x), \\ t_l &= l\Delta t, \quad l = 0,\dots m, \quad m = T/(\Delta t). \end{aligned} \tag{3.8}$$

We denote by $c_k^l$ and $q_k^l$ approximations of $c(x_k, t_l)$ and $q(x_k, t_l)$. Taking initial conditions into account, we define $c_k^0 = 0$, $q_k^0 = 0$ for $k = 0, \ldots, n$.

### 3.4.1 Explicit scheme

First we set up an explicit scheme for solving the problem (3.4)-(3.7). The main idea behind any explicit scheme is to calculate the value of an approximation at a later time from the value of an approximation at the current time. Hence, replacing the derivatives by corresponding finite-difference representations, we obtain following system of algebraic equations

$$\frac{c_k^{l+1} - c_k^l}{\Delta t} = \frac{1}{\epsilon}\frac{c_{k+1}^l - c_k^l}{\Delta x} - \frac{1-\epsilon}{\epsilon}\left(Q(c_k^l) - q_k^l\right) \tag{3.9}$$

$$\frac{q_k^{l+1} - q_k^l}{\Delta t} = Q(c_k^l) - q_k^l, \tag{3.10}$$

for $l = 0, \ldots m-1$ and $k = 0, \ldots n-1$. For $k = n$ we have boundary condition $c_n^l = 1$ from which we compute $q_n^{l+1}$ using formula (3.10). This scheme is straightforward to implement due to the fact that we calculate the solution in the time step $l+1$ explicitly using the information we obtained in the step $l$. Hence, we get the following algorithm.

For $l = 0, \ldots, m-1$:

For $k = 0, \ldots, n-1$:

$$c_k^{l+1} = \frac{1}{\epsilon}\frac{\Delta t}{\Delta x}c_{k+1}^l + \left(1 - \frac{1}{\epsilon}\frac{\Delta t}{\Delta x}\right)c_k^l - \frac{1-\epsilon}{\epsilon}\Delta t(Q(c_k^l) - q_k^l),$$
$$q_k^{l+1} = (1-\Delta t)q_k^l + \Delta t Q(c_k^l),$$

For $k = n$:

$$c_n^{l+1} = 1, \quad q_n^{l+1} = (1-\Delta t)q_n^l + \Delta t Q(c_n^l).$$

The function $Q$ is defined as $Q(c) = \frac{\rho}{c_{in}} K_F M W_i^{\frac{1}{n-1}} (c_{in} c)^{\frac{1}{n}}$. Now we describe disadvantages of this method. Recall that we want $c_k^{l+1} \geq 0$, since $c$ represents concentration. In order to achieve this, we rewrite the equation (3.9) as

$$c_k^{l+1} = \frac{1}{\epsilon}\frac{\Delta t}{\Delta x}c_{k+1}^l + c_k^l\left(1 - \frac{1}{\epsilon}\frac{\Delta t}{\Delta x} - \frac{(1-\epsilon)}{\epsilon}\Delta t K_F M W^{\frac{1}{n-1}} {c_k^l}^{\frac{1}{n}-1}\right) + \frac{1-\epsilon}{\epsilon}q_k^l. \tag{3.11}$$

Therefore, in order to ensure that $c_k^{l+1}$ stays non-negative, we derive condition on $\Delta t$:

$$\Delta t \leq \frac{1}{\frac{1}{\Delta x \epsilon} + \frac{1-\epsilon}{\epsilon} K_F M W^{\frac{1}{n-1}} (c_k^l)^{1/n-1}} \tag{3.12}$$

Notice that $c_i^k \ll 1$ and $1/n - 1 < 0$. Therefore, $\Delta t$ must be very small in order to ensure $c_k^{l+1} \geq 0$, which represents a numerical obstacle that is hard to overcome. Therefore, we turn our attention to the implementation of implicit and semi-implicit methods which do not have such a strict requirement on the smallness of $\Delta t$.

### 3.4.2 Implicit scheme

In contrast to the explicit scheme, an implicit method finds a solution by solving an equation involving both the current state of the system and the next one. Replacing the right-hand-sides in the system (3.1) with the corresponding finite-difference approximations, we get the following scheme:

$$\frac{c_k^{l+1} - c_k^l}{\Delta t} = \frac{1}{\epsilon} \frac{c_{k+1}^{l+1} - c_k^{l+1}}{\Delta x} - \frac{1-\epsilon}{\epsilon} \left( Q(c_k^{l+1}) - q_k^{l+1} \right) \tag{3.13}$$

$$\frac{q_k^{l+1} - q_k^l}{\Delta t} = Q(c_k^{l+1}) - q_k^{l+1}, \tag{3.14}$$

for $l = 0, \dots m-1$ and $k = 0, \dots n-1$. If we denote with $\mathbf{c}^l$ and $\mathbf{q}^l$ the vectors $\mathbf{c}^l = (c_1^l, \dots, c_{n-1}^l, 1)$ and $\mathbf{q}^l = (q_1^l, \dots, q_n^l)$, we get the following algorithm.

For $l = 0, \dots m-1$:

$$\mathbf{c}^{l+1} - \frac{\Delta t}{\epsilon} F(\mathbf{c}^{l+1}) + \Delta t \frac{1-\epsilon}{\epsilon} G(\mathbf{c}^{l+1}, \mathbf{q}^{l+1}) = \mathbf{c}^l, \tag{3.15}$$

$$\mathbf{q}^{l+1} - \Delta t G(\mathbf{c}^{l+1}) = \mathbf{q}^l \tag{3.16}$$

$$\tag{3.17}$$

where vector functions $F$ and $G$ are defined as

$$F(\mathbf{c}^{l+1}) = \begin{bmatrix} \frac{c_{k+1}^{l+1} - c_k^{l+1}}{\Delta x} \end{bmatrix} \tag{3.18}$$

$$G(\mathbf{c}^{l+1}, \mathbf{q}^{l+1}) = \begin{bmatrix} Q(c_k^{l+1}) - q_k^{l+1} \end{bmatrix} \tag{3.19}$$

Notice that $\mathbf{c}^{l+1}$ and $\mathbf{q}^{l+1}$ are vectors of dimension $n$. Therefore, in each time step the numerical solver has to find roots of the system of $2n-1$ coupled equations.

After implementing the method in MATLAB, the task of finding roots $(\mathbf{c}^{l+1}, \mathbf{q}^{l+1})$ of nonlinear equations (3.15) and (3.16) seemed to be too difficult, especially for values of $1/n$ close to 0. MATLAB function *fsolve* often resulted with the message that step size became too small and it could make no more progress. Hence, we turned our attention to developing and implementing a semi-implicit scheme.

### 3.4.3 Semi-implicit scheme

Semi-implicit schemes are a compromise between explicit and implicit numerical methods, which both suffer from its standard drawbacks. The explicit method requires very small time step in order to converge while an implicit method brings difficulties in the form of finding roots of highly nonlinear multivariable functions. One possible approach to tackle both problems is to treat some terms explicitly and the others implicitly. Since the requirement in explicit scheme on smallness of $\Delta t$ comes from the nonlinear adsorption term $Q$, we have decided to treat that term implicitly in the calculations of the concentrations $c_k$. Hence, we get the following finite-difference approximation of (3.1).

$$\begin{aligned} \frac{q_k^{l+1} - q_k^l}{\Delta t} &= \frac{Q(c_k^l) - q_k^l}{\Delta x} \\ \frac{c_k^{l+1} - c_k^l}{\Delta t} &= \frac{1}{\epsilon}\frac{c_{k+1}^l - c_k^l}{\Delta x} - \frac{1-\epsilon}{\epsilon}\left(Q(c_k^{l+1}) - q_k^{l+1}\right), \end{aligned} \tag{3.20}$$

for $l = 0, \dots m-1$ and $k = 1, \dots n-1$. Therefore, we propose the following algorithm.

For $l = 0, \dots, m-1$:

For $k = 0, \dots, n-1$:

$$q_k^{l+1} = (1 - \Delta t)q_k^l + \Delta t Q(c_k^l), \tag{3.21}$$

$$c_k^{l+1} + \Delta t \frac{1-\epsilon}{\epsilon} Q(c_k^{l+1}) = \left(1 - \frac{\Delta t}{\epsilon \Delta x}\right) c_k^l + \frac{1-\epsilon}{\epsilon} q_k^{l+1} \tag{3.22}$$

For $k = n$:

$$c_n^{l+1} = 1, \quad q_n^{l+1} = (1 - \Delta t)q_n^l + \Delta t Q(c_n^l).$$

Notice that we have reversed the order of equations. First we calculate $q_k^{l+1}$ using an explicit forward finite-difference formula. Then we find the value $c_k^{l+1}$ as a root of a nonlinear equation (3.22).

## 3.5 Numerical experiments

In this section, we shall present results from numerical simulations, corresponding to parameter values shown in table 3.1, that led to difficulties in the current version of KWR's software. The numerical results are based on an implementation of the semi-implicit scheme (3.20) that we derived in the previous section. The numerical domain in non-dimensional units is defined by $x \in [0, 1]$, $t \in [0, 150000]$. The latter corresponds to a simulation of more than one year in the physical time domain. The space-discretization step is chosen to be $h = 0.1$ and the time-discretization step is $\Delta t = 1$. For all of the simulations we consider the following values of the model parameters, proposed by KWR water: $\gamma = 2.45 \times 10^{-12}$, $\epsilon = 0.4$, $\rho = 440000$ and $\nu = 0.144$.
We shall present results for two different compounds—natural organic matter (NOM) and a micropollutant, namely Furosemide. We believe that the difficulties in the numerical solution, if they exist, should be clearly visible even in the case of a single compound. Thus, we present results for this simple case. It can be further generalized by implementing IAST for multiple compounds.

**Example 1.** We choose parameter values $K_f = 0.018$ and $1/n = 0.9$, corresponding to NOM. Results for $c(t)$ and $q(t)$ are depicted in Fig.3.4 and in Fig.3.5, respectively. The rightmost edge (i.e., $x = 1$) corresponds to the top of the filter, where the inlet boundary condition is imposed, and $x = 0$ corresponds to the bottom.

As can be seen from the pictures, the qualitative behaviour of the numerical solution seems to be physically plausible, given the time the filter gets "exhausted", starting from the top and progressing to the bottom. Following this, the concentration of the contaminant in the water gets also gradually increased, until at the bottom the concentration gets equal to 1, thus, the filter is completely exhausted.

**Example 2.** In this second example, we use parameter values $K_f = 0.34608$ and $1/n = 0.0574$, corresponding to the micropollutant Furosemide. The corresponding results are presented in Fig.3.6 and Fig.3.7.

As can be seen, for the micropollutant it takes more time for the filter to get exhausted, which can also be expected.

Further experiments were conducted with various model parameters, provided by KWR water, corresponding to compounds that KWR water's software was not able to simulate. All the experiments ran successfully and showed similar qualitative behaviour. Thus, we omit them here in order not to make the presentation unnecessarily complicated.

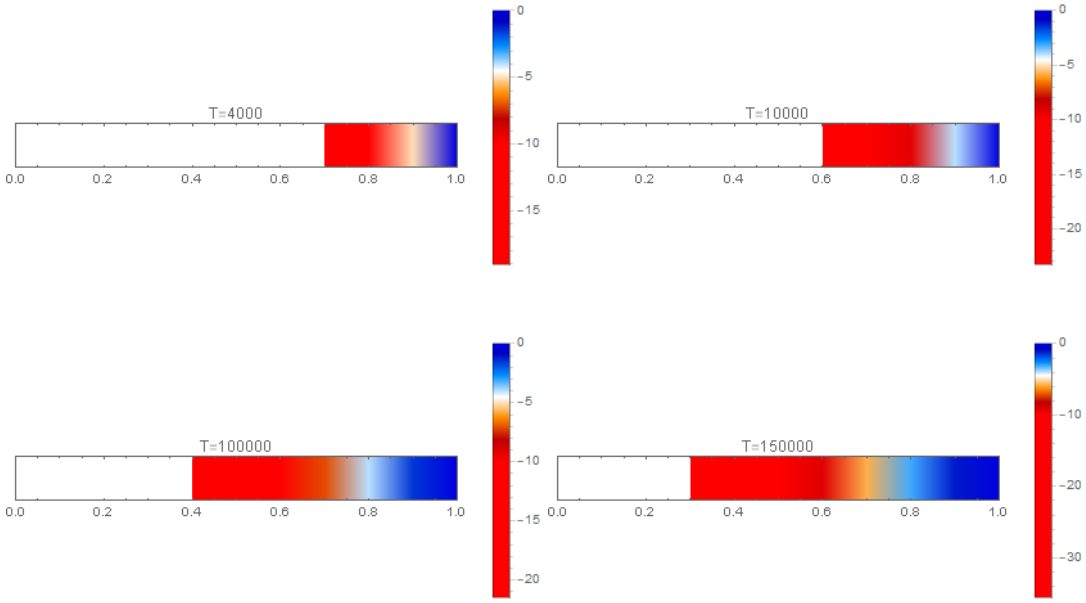


*Figure 3.4: Results for the concentration $c$ in log–scale, natural organic matter, for $T = 4000$, $T = 10000$, $T = 100000$ and $T = 150000$.*

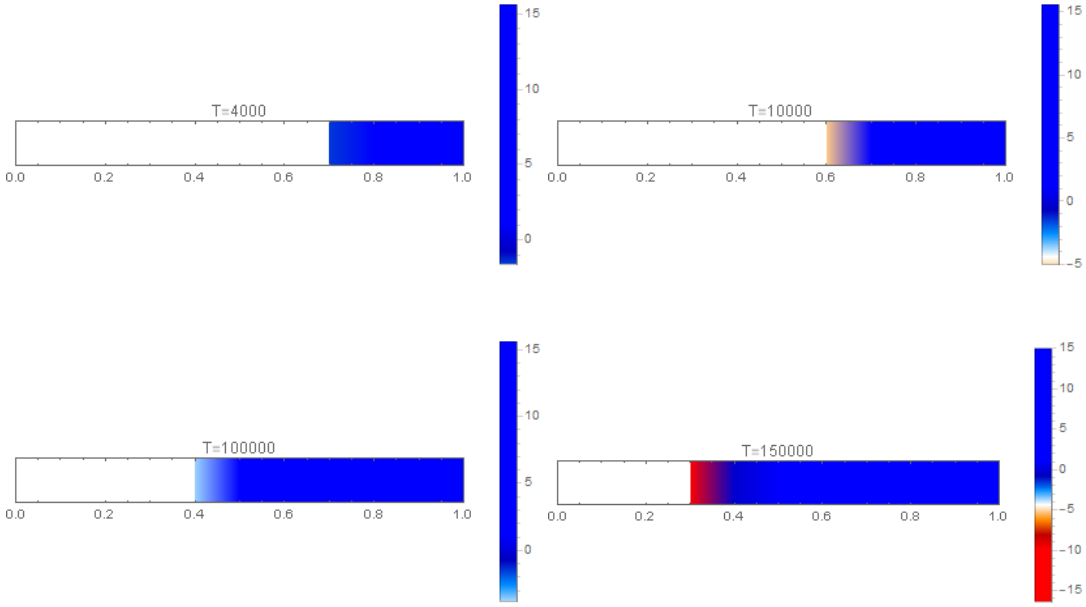


*Figure 3.5: Results for the load $q$ in log–scale, natural organic matter, for $T = 4000$, $T = 10000$, $T = 100000$ and $T = 150000$.*

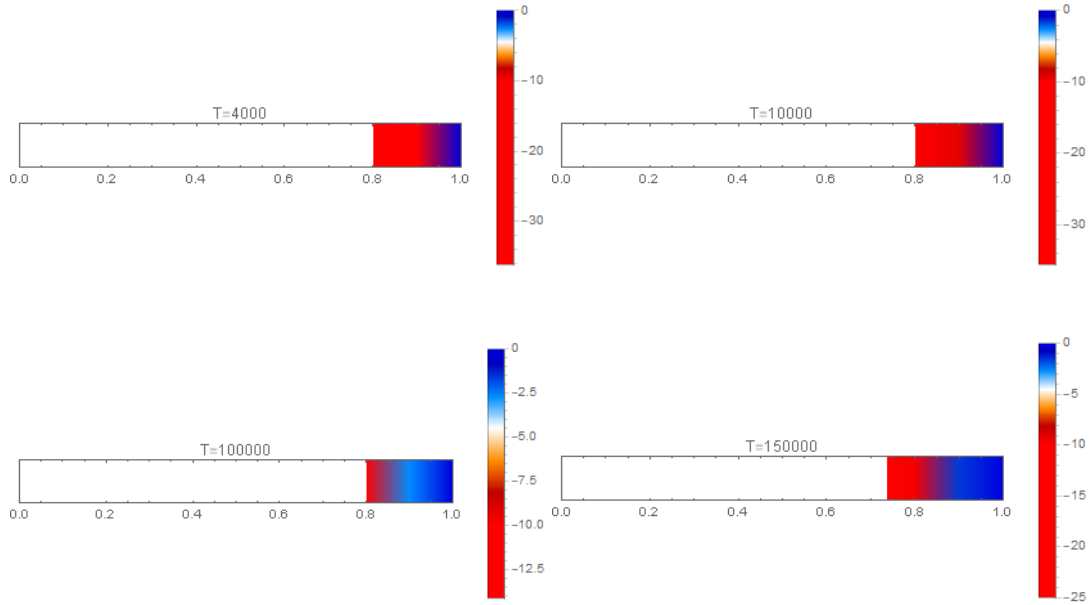


*Figure 3.6: Results for the concentration $c$ in log–scale, micropollutant, for $T = 4000$, $T = 10000$, $T = 100000$ and $T = 150000$.*

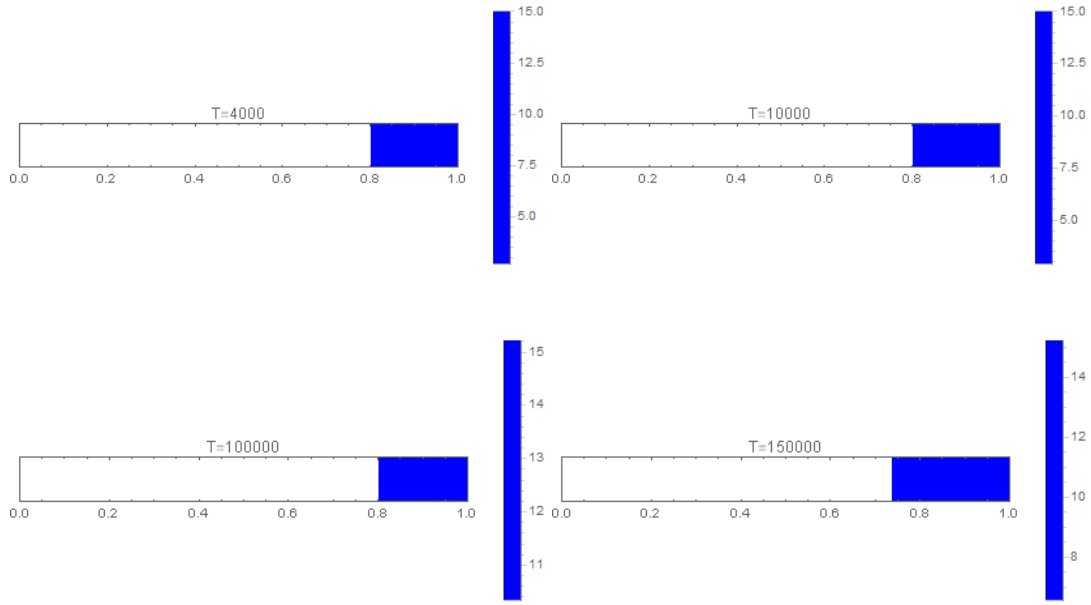


*Figure 3.7: Results for the load $q$ in log–scale, micropollutant, , for $T = 4000$, $T = 10000$, $T = 100000$ and $T = 150000$.*

Concerning computational times, when ran on a PC in Wolfram Mathematica, the

simulations take about 15 min. Of course, the computations are expected to be much quicker, when the algorithm is implemented in a compiled programming language.

## 3.6 Conclusion and recommendations

In the present work, we have considered a well-known mathematical model, describing the process of filtering water by carbon filters. We have pointed out numerical difficulties that the company KWR water was facing, when trying to solve the corresponding system of PDEs. Thus, we have conducted the following steps that seem to give very good results towards solving the problem:

- We have rewritten the mathematical model in dimensionless quantities and hence, reduced the number of parameters;
- We have constructed a semi-implicit finite-difference scheme that seems to be solving the numerical stability problems in the present algorithms. Furthermore, we believe that the correct way to attack this problem is by implementing such an semi-implicit scheme. Many built-in ODE solvers, especially those using adaptive time steps, do not seem to be appropriate for this problem.

Due to the lack of time, we have carried out experiments that include only one compound in water. We suggest that the next step should be to include multiple compounds, using IAST. The generalization should be realtively easy. Further numerical experiments and comparison to empirical observations are needed, in order to validate the applicability of the proposed approach.

# Bibliography

[1] Dirk Vries, Bas Wols, Martin Korevaar, Erwin Vonk, Aquapriori: a priori het verwijderingsrendement bepalen, 2017

[2] Jerry Perrich, Activated Carbon Adsorption for Wastewater Treatment, CRC Press, 1981