CHAPTER 6

DESIGNING AN

ELECTROSORPTION UNIT

6.1. Process description

6.1.1. Overview

An electrosorption unit resembles a classic packed bed adsorption column, but there are differences. The carbon packed bed has two main functions: it must remove the dissolved pollutants from the bulk liquid and it must function as an electrode. These two tasks can be in conflict as can be seen from the bed porosity. In order to minimise the pressure drop, the bed must have a high porosity. In order to have minimal electrical resistance, the porosity should be as low as possible, ensuring good intra-particle contacts. In this chapter an attempt is made to find the optimal design for a commercial electrosorption unit. To obtain all the necessary parameters a mathematical model for the process was developed that was solved numerically using the gPROMS package from Process Systems Enterprise Ltd.

In the electrosorption unit both charge and mass transport takes place. A graphical representation of the packed bed can be found in Figure 6.1. At the left the liquid containing water (A), a polluting substance (B) and inert ions enters the column. Inside the bed axial and radial dispersion can take place in addition to the convective fluid flow. Component B moves from the bulk liquid phase to the solid phase during adsorption and vice versa during desorption.
Electrons are transported to or from the carbon granules by flat graphite current collectors integrated in the bed. In Figure 6.1 a single current collector set-up is shown, but it is possible to use more than one collector to improve charging characteristics. The collectors can be positioned close to the CE (counter electrode) or on the opposite side. If the collector is located at the back, the charging will be counter-current relative to the liquid flow. If the collector is at the front of the bed, the charging will be co-current. No other currents than that for charging the electrode are assumed to flow through the apparatus.

The counter electrode is an essential part of the process. Without it, the packed bed cannot be polarised. However no special attention will be paid to the structure and appearance of the CE as it is not important from a modelling point of view. The CE is in all aspects identical to the WE (working electrode), only its charge is opposite. Completely to the right of Figure 6.1, the depleted liquid leaves the column.

Figure 6.1: Schematic view of an electrosorption unit showing a number of relevant variables. Mass and charge transfer processes occur simultaneously in the bed. The counter electrode can be a second packed bed or a metal electrode.
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The equipment was sized based on a hypothetical wastewater stream of 2 litres per minute \((3.33 \times 10^{-5} \text{ m}^3/\text{s})\) containing 5 mol/m\(^3\) of phenol. The mass transfer resistance is assumed to be external, this means that the carbon particles can be considered a homogeneous phase. During the adsorption stage, the bed is held at a potential favouring adsorption equal to the open circuit potential: \(\phi_{\text{ads}} = 0\). In order to regenerate the bed and desorb the phenol, the potential is changed to a certain value \(\phi_{\text{des}}\). As a result two processes are set in motion: charging of the electrical double layer and replacement of adsorbed organic molecules by water molecules. In chapter 4 it was shown that charging of the double layer is slow due to the resistivity of the system. Surface areas close to the current collector become polarised much faster than areas further away. Both of these processes are characterised by their own characteristic time constants.

6.1.2. Characteristic times

Eisinger and Keller (1990) identified a number of processes taking place in an operational electrosorption unit. Associated with each of these is a characteristic time. For optimal performance some processes need to be completed before others. Using this knowledge, a number of inequalities can be formulated. If all inequalities are satisfied the process design is within the so-called ‘operational window’.

1) The first characteristic time is the average residence time of the liquid in the column \((\tau_R)\). It is defined as the ratio of the volume of the liquid in the packed bed divided by the volume flow:

\[
\tau_R = \frac{\text{volume}}{\text{flow}} = \frac{\varepsilon \cdot V_{\text{bed}}}{\Phi} = \frac{L}{u}  \quad 6.1
\]

where \(u\) is the interstitial speed of the liquid. The residence time depends only on the bed length and the column diameter as the flow rate was used as an external variable.

2) The adsorption time of component B \((\tau_{\text{ads}})\) is the moment that the packed bed has become completely saturated with adsorbed phenol. It is given by:
$$\tau_{ads} = \max \text{ amount adsorbed} \over \text{adsorbate feed rate} = \frac{q P_p (1 - e_{bed}) A_{bed} L}{\Phi_{B,in} \epsilon_{B,in} e_{bed}} \frac{L}{u} \quad 6.2$$

The adsorption time is often close to the breakthrough time because adsorption fronts tend to be very sharp. The breakthrough time itself must be obtained from simulated column performance data.

3) The desorption time ($\tau_{des}$) is related to the adsorption time, but desorption times are much longer than adsorption times due to the non-linearity of the Langmuir-Freundlich isotherm\(^1\). The desorption time is estimated as follows:

$$\tau_{des} = 3 \tau_{ads} \quad 6.3$$

This factor of three is a first assumption. The actual relation between adsorption and desorption time depends on the isotherm used.

4) The dispersion time ($\tau_{ID}$) is the time needed to obtain complete homogeneity in the bed due to dispersion only. It is calculated from the Fourier number set to unity. In this case $\tau = L^2 / ID$, where $ID$ is the axial dispersion coefficient. (The radial dispersion is of no concern as the diameter of the bed is much larger than its length). If only the convective contribution to the dispersion is taken into account the axial dispersion time equals:

$$\tau_{ID} = \frac{2 L^2}{d_p^2 u} \quad 6.4$$

where $d_p$ is the diameter of the particle spheres used.

5) The mass transfer time ($\tau_{MT}$) is the time needed for a given molecule to reach the solid-liquid interface when coming from the bulk of the liquid. It is equal to $1 / k_L a$, where $a$ is the interfacial area per bed volume (in $m^2/m^3$) which depends on the particle size:

\(^1\) Because the Langmuir-Freundlich isotherm is used to describe the adsorption equilibrium, the bed can never be regenerated completely. This is due to its infinite slope for $c_B = 0$ (at least when $n < 1$).
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\[ a = \frac{6 \varepsilon_{\text{bed}}}{d_p} \]  

6.5

The mass transfer coefficient \( k_L \) can be calculated from the Sherwood number (Wesselingh and Krishna, 2000):

\[ \text{Sh} = \frac{k_L d_p}{ID} = \frac{0.34}{\varepsilon_{\text{bed}}} \frac{\text{Re}^{\frac{2}{3}} \text{Sc}^{\frac{1}{3}}}{d_k} \]  

6.6

with \( \text{Re} \) the Reynolds and \( \text{Sc} \) the Smith number. Using the definitions for these dimensionless numbers, the mass transfer coefficient equals:

\[ k_L = \frac{0.34}{\varepsilon_{\text{bed}}} \frac{ID}{d_p} \left( \frac{ud_p}{v} \right)^{\frac{1}{2}} \left( \frac{v}{ID} \right)^{\frac{1}{2}} \]  

6.7

where \( v \) is the viscosity of the liquid. After rearranging one obtains:

\[ \tau_{MT} = 0.778 \frac{d_p^{\frac{1}{2}} v^{\frac{1}{2}}}{u^{\frac{1}{4}}} \]  

6.8

6) The double layer charging time (\( \tau_{dl} \)) was already encountered in previous chapters. The general expression \( \tau_{dl} = RC \) can be rewritten as:

\[ \tau_{dl} = \frac{S_{\text{BET}} \rho_p C (1 - \varepsilon_{\text{bed}})}{\kappa \varepsilon_{\text{bed}} \varepsilon_{\text{pore}}} L^2 \]  

6.9

In chapter 4 it was found that if \( t = \tau_{dl} \), only 63% of the charging was completed. In order for the bed to become polarised for 95% a time period equal to 3 characteristic times is required. The relevant double layer charging time is therefore \( 3 \tau_{dl} \).
6.1.3. Window of operation

The following rules should be taken into account for an optimal performance of the unit:

- The desorption time should be bigger than the time needed for charging the double layer: $\tau_{\text{des}} > 3\tau_{dl}$ or from our definition of the desorption time it follows that: $\tau_{\text{ads}} > \tau_{dl}$

- The adsorption time should be much larger (about 100x) than the residence time of the liquid: $\tau_{\text{ads}} > \tau_R$.

- The axial dispersion time should be larger (about 10x) than the residence time of the liquid: $\tau_{ID} > \tau_R$.

- Finally, the residence time should be larger (about 10x) than the mass transfer time: $\tau_R > \tau_{MT}$.

In order to calculate the characteristic times the following variable values were used (see Table 6.1).

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
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<td>$q_{\text{max}}$</td>
<td>10</td>
<td>mol/kg</td>
<td>$D_p$</td>
<td>0.5 $10^3$</td>
<td>m</td>
</tr>
<tr>
<td>$C$</td>
<td>0.15</td>
<td>F/m²</td>
<td>$ID$</td>
<td>4.81 $10^8$</td>
<td>m²/s</td>
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<td>$\nu$</td>
<td>$10^3$</td>
<td>m²/s</td>
<td>$L$</td>
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<td>m</td>
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<tr>
<td>$\kappa$</td>
<td>2.352</td>
<td>S/m</td>
<td>$\epsilon_{\text{bed}}$</td>
<td>0.45</td>
<td>-</td>
</tr>
<tr>
<td>$U$</td>
<td>1.92 $10^4$</td>
<td>m/s</td>
<td>$k_L$</td>
<td>9.04 $10^5$</td>
<td>m/s</td>
</tr>
<tr>
<td>$S_{\text{HET}}$</td>
<td>1100</td>
<td>m²/g</td>
<td>$A$</td>
<td>$9 10^1$</td>
<td>m²/m³</td>
</tr>
<tr>
<td>$\epsilon_{\text{BET}}$</td>
<td>5</td>
<td>mol/m³</td>
<td>$\rho_p$</td>
<td>1146</td>
<td>kg/m³</td>
</tr>
</tbody>
</table>

*Table 6.1: Values used to calculate the characteristic times.*

The following results were found:

$\tau_R = 104 \text{ s}$

$\tau_{\text{ads}} = 8.999 \times 10^4 \text{ s}$

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\[ \tau_{des} = 2.70 \times 10^5 \text{ s} \]
\[ \tau_{ID} = 8316 \text{ s} \]
\[ \tau_{MT} = 44.13 \text{ s} \]
\[ \tau_{dl} = 3.93 \times 10^4 \text{ s} \]

Comparing these values to the set of inequalities reveals that almost all of these are satisfied if the bed length is 20 mm and the liquid speed is 0.2 mm/s. The adsorption time is about two times bigger than the double layer charging time. The time needed for adsorption is much larger than the residence time. Also the dispersion time is larger than the residence time. The residence time is larger than the mass transfer time, although not ten times.

Both the bed length \( L \) and the liquid speed \( u \) influence five out of six characteristic times, making them the most important design parameters. Table 6.2 gives the relation between the six characteristic times, the liquid speed and the bed length.

<table>
<thead>
<tr>
<th>Characteristic Time</th>
<th>Liquid speed</th>
<th>Bed Length</th>
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<tbody>
<tr>
<td>( \tau_R )</td>
<td>( u^1 )</td>
<td>( L^1 )</td>
</tr>
<tr>
<td>( \tau_{ads} )</td>
<td>( u^1 )</td>
<td>( L^1 )</td>
</tr>
<tr>
<td>( \tau_{des} )</td>
<td>( u^1 )</td>
<td>( L^1 )</td>
</tr>
<tr>
<td>( \tau_{ID} )</td>
<td>( u^0 )</td>
<td>( L^2 )</td>
</tr>
<tr>
<td>( \tau_{MT} )</td>
<td>( u^{4/3} )</td>
<td>( L^0 )</td>
</tr>
<tr>
<td>( \tau_{dl} )</td>
<td>( u^1 )</td>
<td>( L^2 )</td>
</tr>
</tbody>
</table>

Table 6.2: The influence of liquid speed and bed length on the characteristic times. The bed length can be used to change the ratio of the electrical and the physical process times.

In Figure 6.2 the characteristic times are plotted as function of the bed length. For all \( L \) and \( u \), the inequality \( \tau_{ads} > 100 \tau_R \) is satisfied so this constraint can be
removed. The grey area indicates the allowable range of bed lengths if all other variables remain unchanged.

![Diagram of characteristic times as function of bed length]

**Figure 6.2:** Characteristic times as function of bed length. The residence time is always lower than the breakthrough time. Other constraints are satisfied between the upper and lower boundaries.

![Diagram of window of operation (grey areas) as function of bed dimensions]

**Figure 6.3:** Window of operation (grey areas) as function of bed dimensions. Drawn: $\tau_{\text{ads}} = \tau_{\text{dl}}$. Dashed: $\tau_{\text{ID}} = 10 \tau_{\text{R}}$. Dotted lines: $\tau_{\text{R}} = 10 \tau_{\text{MT}}$. For the meaning of a, b, c see the text.
For thick beds (> 45 mm), the double layer charging time becomes too large. For very small beds (< 9 mm) the residence time becomes smaller than the mass transfer time. Optimal designs have bed lengths between these two values. A thicker bed can be used if multiple current collectors are installed.

In Figure 6.3 the satisfied constraints are plotted as function of \( L \) and \( d_p \) for four liquid speeds: (a) \( u = 2 \times 10^{-6} \), (b) \( u = 2 \times 10^{-5} \) and (c) \( u = 2 \times 10^{-4} \) m/s. The optimal design should be below the drawn lines and above the dotted and dashed lines. The mass transfer is almost never limiting, only for unrealistically large particles (> 1 m). Smaller particles allow for much higher velocities, but the bed must then be thinner to reduce the double layer charging time.

6.2. The mathematical model

6.2.1. The gPROMS package

The process was modelled using the software package gPROMS. gPROMS is a general purpose modelling, simulation and optimisation tool. It allows for the direct mathematical description of distributed unit operations by entering the appropriate differential equations together with their boundary conditions. The gPROMS program will take care of the solving of these. A second feature is the possibility to combine elementary unit operations (building blocks) to describe higher level and more complex systems.

In gPROMS, the definition of elementary processes is done within MODEL entities. Each input file should contain at least one of these. A MODEL entity contains the knowledge regarding the physical behaviour of the system. It consists of a number of declaration sections in which different pieces of information regarding the structure and behaviour of the given system are specified. The most important are:

- The PARAMETER section. Here the time independent variables are defined. These variables will not be calculated during the simulation and can be considered as constants.
• The VARIABLE section. Here the time dependent variables are defined that are calculated during the simulation.

• The EQUATION section. All equations that involve the declared variables and parameters. They are used to calculate the value of the variables.

Besides the physics and the chemistry of the process, the operating procedures are of equal importance. gPROMS adopts a dual description for processes in terms of MODELs and PROCESSes. The latter operate on the MODELs and describe the operating procedure that is used to run the process. It is here that values are assigned to constants. It allows for a number of steps to be executed in sequence, parallel or conditionally so a number of adsorption and desorption cycles can be simulated in a single run. The most important declaration sections of the PROCESS section are:

• The UNIT section. Here the connections to the underlying MODEL sections are established.

• The SET section is used to assign values to the constants in the various MODEL sections.

• The ASSIGN section. Usually a number of external variables are needed to reduce the number of degrees of freedom. They represent the influence of the external environment on the system and are given a value in this section.

• The INITIAL section. In this section the initial values for the system are determined.

• The SCHEDULE section. Here the operation policy is simulated, the sequence of actions that affect the behaviour of the system. Changes in external variables, specification of the running times etc.

More info on gPROMS can be found at http://www.psenterprise.com. The listings of the models can be found in appendix B.
6.2.2. Theoretical model: The equations

**Mass transfer: liquid phase**

Liquid flowing through a packed bed of granules can be described mathematically with the axially dispersed plug flow model (Alkire and Eisinger, 1983a; Westerterp *et al*., 1983; Chue *et al*., 1992; Tien, 1994; Crittenden and Thomas 1998). In most cases the deviation from plug flow is small and the flow in the reactor can be considered as piston flow with a superposition of some dispersion. Dispersion is caused by molecular diffusion and turbulent mixing. While the effects of axial dispersion are generally undesirable since they reduce the separation efficiency of the apparatus, ideas on radial dispersion in an adsorption column vary from helpful (Tien, 1994) to undesired (Crittenden and Thomas, 1998). The effects of radial dispersion in this system are very small because the bed diameter (0.7 m) is much larger than the bed length (0.02 m). Therefore radial dispersion is not taken into account in this work. From the mass balance over a cross sectional area of the bed perpendicular to the fluid flow one obtains the desired expression for the liquid phase:

\[
\frac{\partial c_B}{\partial t} = -u \frac{\partial c_B}{\partial x} + ID \frac{\partial^2 c_B}{\partial x^2} - aJ
\]

Here \( u \) is again the interstitial liquid velocity, \( ID \) is the axial dispersion coefficient, \( J \) is the flux of component B from the bulk liquid to the solid-liquid and \( a \) is the interfacial area per unit volume of solution interface area.

**Mass transfer: solid phase**

The rate expression used in this work contains only a single mass transfer resistance. This resistance lies outside the solid phase in a fluid film surrounding the carbon particles. This greatly simplifies the model, as the bulk of the solid particles can now be considered a homogeneous phase. No intra-particle resistances exist so all solid concentrations are equal. The accumulation of species B in the solid phase again follows from a mass balance. If it is assumed that no B reacts due to unwanted Faraday reactions, one has:
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\[(1 - \varepsilon_{\text{bed}}) \rho_p \frac{\partial q}{\partial t} = \varepsilon_{\text{bed}} a f \quad 6.11\]

where \(\rho_p\) is the particle density.

The flux

The flux can be described using a linear rate expression together with an overall mass transfer coefficient \(k_L\):

\[J = k_L \left( \epsilon_B - \epsilon_{\text{B,int}} \right) \quad 6.12\]

The driving force for the flux is the (small) difference between the solid-liquid interface concentration \(\epsilon_{\text{B,int}}\) and the bulk liquid concentration \(\epsilon_B\).

The isotherm

In chapter 3 isotherm expressions are given that relate the bulk concentration to the surface coverage \(q\). A potential dependent Langmuir-Freundlich isotherm is used in the model because the Langmuir isotherm is unable to properly describe the experimental adsorption data:

\[q = q_{\text{max}} \frac{K(\phi) \epsilon_{\text{B,int}}^{n_f}}{1 + K(\phi) \epsilon_{\text{B,int}}^{n_f}} \quad 6.13\]

The adsorption equilibrium \(K\) is an exponential function of the electrical potential drop (see Eq. 2.52). Alkire and Eisinger (1983a) used an empirical quadratic function to describe the dependence of \(K\) on the potential:

\[K(\phi) = A\phi^2 + B\phi + C \quad 6.14\]

where \(A\), \(B\) and \(C\) are experimentally determined empirical constants. Both Eq. 2.34 and Eq. 6.14 give approximately the same influence of the potential. If no potential is applied, the adsorption equilibrium constant is maximal. If the applied potential increases, the adsorption constant diminishes. In our model \(B\) is set to zero (no preferential adsorption of the organic compound, leading to an additional potential drop). \(C\) is related to the open circuit adsorption
constant and $A$ is related to the exponential of the differences in integral capacity of the system divided by $RT$. The adsorption equilibrium depends upon the local potential difference across the double layer and can therefore differ for various parts of the bed.

**Charge transfer**

In chapter 4 three analytical solutions for the potential distribution function were given. The external losses model gave the best results. In the model the time and position dependent potential is calculated numerically, so:

$$\frac{\partial \phi}{\partial t} = \frac{\kappa_{\text{par}}}{\varepsilon_{\text{bed}}} \frac{\partial^2 \phi}{\varepsilon \partial \varepsilon^2}$$  \hspace{1cm} \text{6.15}

Again the carbon phase is considered homogeneous, no potential distributions inside particles are taken into account. The differential capacity is considered to be constant at first. In reality the differential capacity is a function of potential and surface coverage. The solution of the model for a non-constant capacity is treated in section 6.3.8.

**Additional equations**

In the set of equations Eq. 6.10-6.15 a number of variables appear which must be calculated using additional equations. The dispersion coefficient $ID$ accounts for axial dispersion and for molecular diffusion (Alkire and Eisinger, 1983a; Crittenden and Thomas, 1998):

$$ID = \left( \frac{2\varepsilon_{\text{bed}}}{3 - \varepsilon_{\text{bed}}} \right) D + \frac{\mu d_p}{2}$$  \hspace{1cm} \text{6.16}

The diffusivity coefficient $D$ is corrected for the tortuosity of the packed bed. The mixing part of the dispersion coefficient is expressed by the dimensionless Péclet number. The interstitial liquid velocity is given by:

$$\mu = \frac{\Phi}{A \varepsilon_{\text{bed}}} = \frac{\Phi}{\frac{1}{4} \pi d_{\text{bed}}^2 \varepsilon_{\text{bed}}}$$  \hspace{1cm} \text{6.17}
if the packed bed is a cylinder with diameter $d_{\text{bed}}$ and length $L$. The conductivity in the potential distribution equation is the conductivity of the pores. It can be calculated by correcting the bulk liquid conductivity for the tortuosity of the bed:

$$\kappa_{\text{pore}} = \left( \frac{2\epsilon_{\text{bed}}}{3 - \epsilon_{\text{bed}}} \right) \kappa_{L}. \quad 6.18$$

The liquid electrical resistance inside the bed is therefore larger than outside the bed.

### 6.2.3. Theoretical model: boundary conditions

The condition at the two boundaries of the packed bed ($x = 0$ and $x = L$) must be described with respect to the concentration and the potential. The type of boundary condition is determined by the assumptions made. For the concentration:

1a) $x = 0, \; \forall t: \; \epsilon_B = \epsilon_{B,0}$

1b) $x = 0, \; \forall t: \; \epsilon_B = \epsilon_{B,0} + \frac{ID}{u} \frac{\partial \epsilon_B}{\partial x}$

2) $x = L, \; \forall t: \; \frac{\partial \epsilon_B}{\partial x} = 0 \quad 6.19$

Boundary 1a) corresponds to a so-called closed boundary condition while 1b) is used for an open boundary (Westerterp et al., 1983). At the end of the bed there is a no-flux condition. For the electrical potential:

$$x = 0, \; \phi = \phi_0 - \lambda L \frac{\partial \phi}{\partial x}$$

$$x = L, \left( \frac{\partial \phi}{\partial x} \right) = 0 \quad 6.20$$

These boundary conditions correspond to a co-current set-up of the potential distribution. The current collector is positioned at the front of the bed. If the potential wave and the liquid flow run counter-currently, the two boundary
conditions in Eq. 6.20 are interchanged. The λ appearing in the first boundary condition in Eq. 6.20 determines the amount of potential that is lost (Carslaw and Jaeger, 1959). If the loss factor λ is set to zero, there are no external losses and the mixed boundary conditions turns into the prescribed boundary condition of the no-losses model (see chapter 4).

### 6.2.4. Theoretical model: initial conditions

The following initial conditions are used for all simulations:

\[
\begin{align*}
 t &= 0, \quad \forall x: \quad e_b = 0 \\
 t &= 0, \quad \forall x: \quad q = 0 \\
 t &= 0, \quad \forall x: \quad \phi = 0
\end{align*}
\]

### 6.2.5. Theoretical model: discretisation methods

The differential equations are solved with the use of a spacial discretisation method. The packed bed is divided using a grid and on each of the grid points the variables are calculated. No one method can solve all possible problems so the proper choice of method is very important as an incorrect choice can lead to physically unreal solutions or numerical problems. \textit{gPROMS} allows the setting of three parameters.

<table>
<thead>
<tr>
<th>Numerical method</th>
<th>Abbreviation</th>
<th>Order</th>
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<tbody>
<tr>
<td>Backward finite difference method</td>
<td>BFDM</td>
<td>2, 4, 6</td>
</tr>
<tr>
<td>Forward finite difference method</td>
<td>FFDM</td>
<td>1, 2</td>
</tr>
<tr>
<td>Centered finite difference method</td>
<td>CFDM</td>
<td>1, 2</td>
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<td>Upwind-biased finite difference method</td>
<td>UFDM</td>
<td>2</td>
</tr>
<tr>
<td>Orthogonal collocation on finite elements method</td>
<td>OCFEM</td>
<td>2, 3, 4</td>
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</tbody>
</table>

\textit{Table 6.3: Spacial discretisation methods for calculating distributed systems containing partial derivatives. Taken from the \textit{gPROMS} user’s guide.}
These are the discretisation method, the order of the method and the number of grid lines used. Generally speaking a higher order method and a denser grid leads to more realistic results, but also to much longer calculation times. The methods implemented within gPROMS are listed in Table 6.3.

With respect to the selection of a proper method it is difficult to come up with general rules. From the gPROMS user guide it was abstracted that BFDM and FFDM should be used for convective processes and CFDM or OCFEM for diffusive processes:

- The liquid flowing through the packed bed is strongly convective. The contribution of the second derivative term arising from dispersion phenomena is not very significant. For this reason a one-sided finite difference method, taken opposite to the direction of flow, was used. For the calculation of the liquid flow through the bed, from left \( x = 0 \) to right \( x = L \) a second order backward finite differences method (BFDM) was used.

- On the other hand, the potential distribution inside the bed is a process with a strong dispersive/diffusive effect (no convective contributions at all). gPROMS advises to use either the centred finite differences (CFDM) or the orthogonal collocation on finite elements (OCFEM) for these kind of problems. As the OCFEM led to numerical problems, a second order CFDM method was used to calculate the potential distribution, although the OCFEM is more efficient than CFDM in terms of the number of discretised equations/variables needed for attaining the same accuracy.

### 6.2.6. Theoretical model: the schedule of the simulation

Each simulated run covers two consecutive cycles of the process. First there is an adsorption cycle, followed by a desorption cycle. Initially the packed bed does not contain any B. At \( t > 0 \) a polluted inlet stream is fed into the column. The inlet concentrations were varied between 0.5 and 25 mol/m\(^3\), 5 mol/m\(^3\) being the standard value. No electrical potential is applied during this cycle. The bed becomes saturated with B and the outlet concentration starts to increase. After 160000 s (about 44 hours) the desorption cycle starts which lasts for
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640000 s (about 178 hours). The column is washed with electrolyte solution and a potential difference can be applied during this stage.

6.3. Results

6.3.1. Base case results

A large number of simulations were performed, most of them variations on the base case situation. The gPROMS simulations took about one minute of processor time on a Pentium® 166 MHz computer. The parameter values used for the base case (and most other simulations) are given in Table 6.4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
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</thead>
<tbody>
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<td>mol/kg</td>
<td>dp</td>
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<td>m</td>
<td>C</td>
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<td>A</td>
<td>-0.1</td>
<td>m$^{3/2}$/mol$^{3/2}$/V</td>
<td>dmed</td>
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<td>m</td>
<td>φ</td>
<td>1</td>
<td>V</td>
</tr>
<tr>
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</tr>
<tr>
<td>C</td>
<td>0.2</td>
<td>m$^{3/2}$/mol$^{3/2}$/s</td>
<td>εbed</td>
<td>0.45</td>
<td>-</td>
<td>tads</td>
<td>160000</td>
<td>s</td>
</tr>
<tr>
<td>nLF</td>
<td>0.5</td>
<td>-</td>
<td>Φ</td>
<td>$3.33 \times 10^{-5}$</td>
<td>m$^3$/s</td>
<td>tads</td>
<td>640000</td>
<td>s</td>
</tr>
<tr>
<td>S_BET</td>
<td>1100</td>
<td>m$^2$/g</td>
<td>D</td>
<td>$9 \times 10^{10}$</td>
<td>m$^3$/s</td>
<td>method</td>
<td>BFDM2</td>
<td>-</td>
</tr>
<tr>
<td>εB,in</td>
<td>5</td>
<td>mol/m$^3$</td>
<td>ρ</td>
<td>1146</td>
<td>kg/m$^3$</td>
<td>CFDM2</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4: The set of PARAMETERS used for the base case simulation. Mass transfer related parameters are discretised using the BFDM second order method, charge transfer parameters with the CFDM second order method.

The variables that can be calculated from these input parameters are given in Table 6.5. The bulk concentration is plotted in Figure 6.4 as a function of time for five different positions inside the bed.
Table 6.5: The VARIABLE values obtained from the base case PARAMETERS.

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6600</td>
<td>m²/m³</td>
</tr>
<tr>
<td>u</td>
<td>1.924×10⁴</td>
<td>m/s</td>
</tr>
<tr>
<td>ID</td>
<td>4.844×10⁷</td>
<td>m²/s</td>
</tr>
<tr>
<td>A_{bed}</td>
<td>0.384</td>
<td>m²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>V_{bed}</td>
<td>7.697×10⁻³</td>
<td>m³</td>
</tr>
<tr>
<td>k_L</td>
<td>9.04×10⁻⁵</td>
<td>m/s</td>
</tr>
<tr>
<td>κ_{pore}</td>
<td>2.352</td>
<td>S/m</td>
</tr>
</tbody>
</table>

The left graph shows the adsorption of B and the right graph shows the desorption. As can be seen from the left graph, it takes about 96800 s for the outlet concentration to reach 90% of the inlet concentration of 5 mol/m³ (= τ_{ads}). The loading curve becomes somewhat steeper towards the end of the bed due to the form of the isotherm. In Figure 6.5 the solid phase concentration is plotted for the same simulation. The changes in the solid concentration resemble those of the liquid concentration.

Figure 6.4: Bulk phase concentration as a function of position in the bed. At the left the situation during the first 120000 s (adsorption). At the right the situation between the following 160000 and 480000 s (desorption). No field is applied.

The right graph in Figure 6.5 shows the desorption of B when no field is applied to the packed bed. As can be seen from the long concentration ‘tail’, simply washing the pollutant out of the bed takes a long time. The τ_{des} =
1005400 s. This is the moment that 90% of the adsorbed B is desorbed. For this configuration the desorption cycle will take 10 times more time than the adsorption cycle.

![Figure 6.5: Solid phase concentration as function of position in the bed. At the left adsorption, at the right desorption.](image)

The characteristic adsorption time calculated in section 6.1.2 predicts that after 89990 s the bed will be saturated with phenol. This value lies very close to the value obtained from the simulation (96800 s), the bed performs almost at its optimum efficiency. The difference can be explained from the fact that the earlier calculation does not take into account that part of the phenol entering the bed will leave it before it has become saturated.

Beforehand it was assumed that the desorption time was three times the time needed for adsorption. From the simulation results it follows that for these conditions the desorption time is about 10 times the adsorption time.

### 6.3.2. Influence of the electrical field

In order to improve the desorption of B (reduce τ_{des}), an electrical field of one volt is applied that changes the adsorption equilibrium constant from 0.2 m$^3$/mol to 0.1 m$^3$/mol. In Figure 6.6 the resulting decrease of the isotherm is plotted.
It takes time for the bed to reach the external set potential. In Figure 6.7 the potential is plotted as a function of the bed length. For a loss factor $\lambda = 0.666$ the characteristic time for charging of the double layer to 95% is $143000$ s ($= 3\tau_{dl}$). The external losses model is used to describe the potential distribution. This is the reason that the potential at the front of the bed is not equal to the applied potential of one volt. Comparing the numerical output with the analytical results (shown in figure 4.11) does not reveal any discrepancies.

Again, the simulated characteristic time can be compared to the one calculated in section 6.1.3. The $3\tau_{dl}$ from the simulation is $143000$ s. The analytically obtained $\tau_{dl}$ was $39300$ s, and $3\tau_{dl}$ is $118000$ s. Both are in the same order of magnitude. The first is lower because no potential losses were taken into account. The double layer charging time depends on the loss factor applied. The lower the loss factor, the faster the double layer is charged.
The adsorption constant is a function of the applied potential. If at $t = 160000$ s a potential difference of one volt is applied to the bed (and the inlet concentration is set to zero), the desorptive behaviour is improved as can be seen from Figure 6.8 and Figure 6.9. The grey areas represent the difference with the case when no field was applied.
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The time required for 90% of the adsorbed phenol to desorb is reduced significantly. Without the field $\tau_{\text{des}} = 1005400$ s (11 ½ days), but with a potential of 1 V applied, it is reduced to 408100 s (4 ½ days). The actual influence of the potential on the desorption time depends on the loss factor of the system.

### 6.3.3. Order of the discretisation method

To determine the numerical accuracy of the results, the order and type of discretisation method were varied. In Figure 6.10 concentration loading curves are plotted for a number of situations. As can be seen from the graph the differences are not pronounced. Increasing the order of the BFDM method leads to a steeper concentration curve. Applying an open boundary condition for the concentration at the inlet of the packed bed leads to a more flat curve. It is remarkable that the first order FFDM method yields almost the same result as the second order BFDM method because the FFDM is considered a poorer choice for this system than the BFDM as the change in concentration moves from left to right. In Figure 6.11 the influence of the order on the potential distribution can be found. The situation here is reversed. Second order methods lead to a more flat curve as the potential distribution is a diffusive type of process. This in turn results in larger double layer charging times.
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**Figure 6.10**: Effect of concentration inlet boundary condition, order and discretisation method on the breakthrough curve.

**Figure 6.11**: Effect of the discretisation method order on the potential distribution. The type of method used did not result in significant changes.
6.3.4. The concentration of ions and phenol

The salt concentration has a large effect on the double layer charging time. In Figure 6.12 the effects of different salt concentrations can be seen. Lower charging times give better desorption characteristics, so these processes are related.

\[ \tau_{\text{dl}} \]

\[ \tau_{\text{des}} \]

\[ \tau \] [s]

\[ \epsilon_{\text{ion}} \] [kmol/m\(^3\)]

![Figure 6.12: Effect of the ion concentration on the double layer charging time. A lower charging time results in faster desorption as can be seen from the graph.](image)

The concentration of phenol in the inlet also influences characteristic times. For most simulations a concentration of 5 mol/m\(^3\) was used. In Figure 6.13 it can be seen that for lower concentrations the various \( \tau \) values decrease. If the concentration is reduced by a factor of two, the liquid flow through the column is increased by a factor of two, in order to keep the mole flow of B constant. The double layer charging time remains constant as it is no function of the concentration.
6.3.5. The loss factor

Besides the ionic strength of the electrolyte, the loss factor $\lambda$ mainly determines the charging speed of the bed. A lower value for $\lambda$ means that a smaller part of the applied potential is lost due to ohmic resistances in the liquid phase (see Figure 6.14).

![Figure 6.13: Effect of the phenol concentration on a number of characteristic times. Reducing the inlet concentration (the mole flow remains constant!) leads to reduced characteristic times.](image1)

![Figure 6.14: Effect of the loss parameter on the potential at the opposite end of the bed as a function of time.](image2)
If the bed can be forced to desorbing conditions more quickly, the associated characteristic time will be much faster. The desorption curve as function of the various loss parameters can be found in Figure 6.15.

![Figure 6.15: Bulk liquid concentration profile as a function of loss factor. The 'instantly charged dl' curve represents the case where the bed is fully charged at $t = 0$ and the 'no dl' curve represents the case where no potential is applied to the bed.](image)

If the bed is immediately charged, a large amount of B desorbs instantaneously resulting in a large peak. This peak will gradually decrease with increasing $\lambda$ values. The same is done in Figure 6.15 for the solid concentration.

![Figure 6.16: Solid concentration as a function of the loss factor. Same conditions as Figure 6.15.](image)
Again it can be concluded that the differences between an instantly charged bed and an uncharged bed are quite large. The smaller the loss factor, the more the ideal situation of an instant charged bed is approached.

![Figure 6.17: Two τ's as function of the loss factor. The difference between the two increases if the losses are reduced.](image)

### 6.3.6. Counter current or co current set-up

The actual direction in which the bed is charged might be an important design consideration. In our one-dimensional model, the bed can be charged from left to right (co-current set-up) or from right to left (counter-current set-up) depending on the position of the current collector. In the model, this can be achieved by simply interchanging the potential boundary conditions. For small loss factors, the differences found between the two settings are biggest. In Figure 6.18 the solid and liquid concentration profiles as a function of time are plotted. A semi-log scale was used to obtain a better view on the behaviour at longer periods.
It was found that for all values of $\lambda$ the characteristic desorption time was roughly the same for both configurations, only for the first 50000-100000 s a difference can be observed. This is within the characteristic double layer charging time, so here the bed is not yet completely polarised. For longer periods, the lines start to coincide as the bed is now completely polarised. As no more charging of the double layer takes place, the configuration is no longer of any influence. It can be concluded that only for $t < 3\tau_{dl}$ the configuration of the current collector is of any influence. The counter current set-up will work better as the solid concentration is lower in this case.

### 6.3.7. Multiple current collectors

A way to reduce the double layer charging time is to use more than one current collector. If the packed bed is connected to the external circuit at four points instead of one, it can be considered as four smaller beds in series. The characteristics with respect to mass transfer do not change provided the collectors do not disrupt the liquid flow through the bed. The bed length for calculating the charge distribution is now only $\frac{1}{4}$ of the actual bed length and
because the double layer charging time depends quadratically on the length, the \( \tau_{dl} \) is 16 times smaller.

In the model this is implemented by using a hierarchical structure. The actual bed consists of a number of building blocks, which describe its physical behaviour. A higher level block provides the coupling between these units. A listing for a model consisting of \( n \) packed beds in series can be found in appendix B.

### 6.3.8. A variable electrical capacity

Although the capacity was experimentally found to be relatively constant, it does change with potential and surface coverage. The surface coverage in turn is also a function of the potential. The local potential can be calculated from the distribution function. But the distribution of potential is largely determined by the electrical capacity of the system so both depend on each other. For this reason a constant differential capacity was used as a first approximation. To

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**Figure 6.19: Schematic overview of the multi-layered gPROMS model structure.**
determine what error is made in doing so a variable capacity is implemented in the numerical model and results are compared.

If the total surface is partly covered with water (A) and partly with phenol (B) the parallel condenser model gives the total capacity:

\[ C_{\text{tot}}(\phi, \theta_B) = C_A(\phi)(1 - \theta_B) + C_B(\phi)\theta_B \]  

6.22

The capacities \( C_A \) and \( C_B \) are defined as the reciprocal addition of the capacities of the Helmholtz and Gouy-Chapman layers (compare Eq. 3.9):

\[ C_A(\phi) = \frac{C_{H,A}(\phi)C_{GC}(\phi)}{C_{H,A}(\phi) + C_{GC}(\phi)} \]  

6.23

\[ C_B(\phi) = \frac{C_{H,B}(\phi)C_{GC}(\phi)}{C_{H,B}(\phi) + C_{GC}(\phi)} \]

The Gouy-Chapman capacity \( C_{GC} \) can be calculated with Eq. 2.5. Because the dielectric constant changes with potential (section 2.1), the Helmholtz capacity \( C_H \) is also a function of the potential. All Helmholtz capacities are calculated using the following formula:

\[ C_{H,i}(\phi) = \frac{1}{2r_i} \left( \frac{1}{\varepsilon_0 \varepsilon_{r,i}(\phi)} + \frac{\sqrt{3} + r_{ion}}{\varepsilon_0 \varepsilon_{r,A}(\phi)} \right) \]  

6.24

where \( i \) can be A or B depending on the molecules that are adsorbed (compare with Eq. 2.36). The dielectric constant is calculated from molecular properties using the Kirkwood equation, Eq. 2.34.

When the actual capacities throughout the bed are calculated, the final step is to use them to determine the influence of the potential on the adsorption equilibrium constant \( K \) as derived in chapter 2. No specific orientation of adsorbed compounds was assumed, therefore Eq. 2.51 could be used:
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\[ K(\phi) = K_0 \exp \left\{ -\frac{1}{2}(C_A(\phi) - C_B(\phi))\phi^2 \right\} \frac{1}{RT} \]

In appendix B the relevant gPROMS listing (listing 3) can be found.

The following results where found while running a simulation using a variable capacity. In Figure 6.20 the differential capacity \( C \) and the adsorption constant \( K \) in the middle of the packed bed are plotted as a function of time.

The adsorption of phenol causes the capacity to decrease to a lower value. After the carbon has become saturated with phenol, the capacity becomes constant. Switching on the potential causes an increase in the capacity as water replaces phenol. The final capacity at \( t = \infty \) is somewhat lower than the initial capacity because the field slightly reduces the dielectric constant of the adsorbed water.

The output of the simulations with a potential and concentration dependent capacity were found to be almost identical to that of the constant capacity simulations. In Figure 6.21 the empirical \( K(\phi) \) function is compared to the
more complex equation from chapter 2. Because potential sweeps of 1 V are applied in all simulations, the influence of the actual potential dependency is rather small.

\[
K = K_0 - 0.01\phi^2
\]

\[
K = K_0 \exp \left[ \frac{-(C_{eq} - C_0)\phi^2}{2RT} \right]
\]

Figure 6.21: The difference between the (empirical) quadratic dependence of the adsorption constant on the potential and the dependence predicted by our model (chapter 2) is quite small.

6.4. Looking back

In this chapter, an electrosorption installation was designed and modelled, suitable for cleaning a wastewater stream of 20 litres per minute containing 5 mol/m³ of phenol. A number of assumptions were made. The liquid flowing through the column is described with the axial dispersion plug flow model. No radial dispersion is taken into account. The mass transfer resistance is assumed to be outside the solid phase. No Faraday reactions occur.

To estimate the equipment dimensions a set of characteristic times was used. As some processes in the adsorber need to be completed before others some characteristic times need to be larger than others. If all inequalities are satisfied the process design is within its operational window. The characteristic times used are: (1) the average residence time of the liquid in the column (\(\tau_R\)). (2) The adsorption time of component B (\(\tau_{ads}\)). (3) The desorption time of component
B, estimated to be: \( \tau_{\text{des}} = 3 \tau_{\text{ads}} \). (4) The dispersion time \( \tau_{\text{ID}} \) needed to get complete homogeneity in the bed due to dispersion only. (5) The mass transfer coefficient \( \tau_{\text{MT}} \) is the time needed for a molecule to reach the interface from the bulk. (6) The double layer charging time \( \tau_{\text{dl}} \) or better \( 3 \tau_{\text{dl}} \).

The following inequalities were applied: The desorption time should be bigger than the time needed for charging the double layer. The adsorption time should be much larger (about 100x) than the residence time of the liquid. The axial dispersion time should be larger (about 10x) than the residence time of the liquid and the residence time should be larger (about 10x) than the mass transfer time.

Both the bed length \( L \) as the liquid speed \( u \) influence five out of six characteristic times, so these two are the most important design parameters. It follows that beds length should be in the order of 10 mm and the liquid speed in the order \( 10^{-4} \) m/s.

Numerical modelling of the system was done with the use of gPROMS, a general purpose modelling, simulation and optimisation tool. The mathematical model equations and boundary conditions can be written directly into the program. Two different discretisation methods had to be applied in order to calculate the concentration as a function of place and time (convective behaviour) and the potential as function of place and time (diffusive behaviour).

A large number of simulations was conducted. About the same values for a number of characteristic times were found in comparison to the ones calculated from Eq. 6.1-6.9.

The reduction in \( \tau_{\text{des}} \) due an applied potential of 1 V was almost a factor of three. The resulting field was assumed to reduce the adsorption equilibrium from 0.2 to 0.1. Charging of the bed was completed for 95% at 143000 s.

Comparing the gPROMS solving methods it was found that the first order FFDM method yielded almost the same result as the second order BFDM method. Theoretically the former is considered a poorer choice for this type of
system than the latter. Second order methods give steeper concentration profiles, but flatter loading curves, compared to first order methods. The use of second order methods therefore leads to larger double layer charging times.

The salt concentration has a large effect on the double layer charging time. The $\tau_{dl}$ starts to increase rapidly for reduced concentrations. Higher concentrations give somewhat reduced $\tau_{dl}$ values. The phenol concentration has an opposite effect. Lower concentration gives a decrease of characteristic times.

Higher loss factors give slower charging and therefore poor desorption of the adsorbed phenol.

The effect of system configuration, counter-current or co-current is only visible if the bed is not yet charged. Counter-current performs slightly better.

Implementing a potential and surface concentration dependent capacity into the model did not result in large differences.