A. Appendix A – Problems of the Experimental Set-Up

A.1 MMS System Operating Re_{dh} Numbers

The flow rate in the system was determined by calibrating the pump versus the frequency (Hz) in the control box: a single membrane cell was fitted and the flow rate was measured by removing the proportional relief valve (Figure 3.1) by using a stopper and measuring cylinder (protocol suggested by MMS).

The average velocity in the membrane cell was then calculated as the flow rate divided by the cross sectional area of the channel above the membrane surface. This procedure allowed defining the circulating Reynolds numbers for different flow rates as displayed in Table A.1.

The Reynolds number in the membrane cell based on hydraulic diameter (Re_{dh}) was calculated according to equation (A.1),

\[ \text{Re}_{dh} = \frac{\rho v d_h}{\mu} \tag{A.1} \]

where \( d_h \) is the hydraulic diameter (m) defined as \( d_h = \frac{4A}{P} \) (A – cross-section area, P – perimeter), \( \rho \) is the density of the circulating fluid (kg.m\(^{-3}\)), \( v \) is the average velocity (m.s\(^{-1}\)) and \( \mu \) is the fluid viscosity (Pa.s) [1]. Water used as the circulating liquid was assumed to be at 25°C.

The calculations of the flow rate and velocity with three membrane cells fitted, that are presented in Table A.1, assume that the flow rate determined in the calibration process splits perfectly in three equal flow rates. In reality that will not occur since the paths (distance) and local fittings the fluid flows through are different.
(see Figure 3.1). This means that the fluid will experience different hydraulic resistances (translating into different pressure drops) that will cause the fluid to preferentially flow through the easiest path (the one that requires the lowest energy to be spent). However, for the purpose of these calculations, the differences are not relevant.

Table A.1 Reynolds number ($Re_{dh}$) for each frequency for the SPECK pump

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>Flow rate in one membrane cell (L.min$^{-1}$)</th>
<th>Velocity in one membrane cell (m.s$^{-1}$)</th>
<th>$Re_{dh}$ in one membrane cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One cell fitted</td>
<td>Three cells fitted</td>
<td>One cell fitted</td>
</tr>
<tr>
<td>14</td>
<td>4.52</td>
<td>1.51</td>
<td>3.01</td>
</tr>
<tr>
<td>16</td>
<td>5.22</td>
<td>1.74</td>
<td>3.48</td>
</tr>
<tr>
<td>20</td>
<td>6.60</td>
<td>2.2</td>
<td>4.40</td>
</tr>
<tr>
<td>25</td>
<td>8.40</td>
<td>2.8</td>
<td>5.60</td>
</tr>
</tbody>
</table>
A.2 Reynolds Numbers in Spiral-Wound Industrial Applications

In industry, spiral-wound and plate-and-frame modules are frequently used, but due to their channel configuration, characterised by a smaller height compared to the other channel dimensions, flow rates are restricted to typical laminar flows [2]. According to Schock and Miquel [3] the $Re_{dh}$ range used in spiral-wound modules systems in industry for aqueous solutions ranges from 100 to 1000. This Reynolds number is a function of the average velocity in the feed channel and the hydraulic diameter, the characteristic length of the channel. The hydraulic diameter is itself a function of the channel height and feed spacer characteristics.

In the absence of spacers the Reynolds number based on channel height ($Re_h$) of a slit geometry can be defined as:

$$Re_h = \frac{\rho v h}{\mu} \tag{A.2}$$

where $h$ is the channel height, $\rho$ is the density of the circulating fluid, $v$ is the average velocity and $\mu$ is the fluid viscosity [1].

The $Re_h$ numbers for slit geometries defined by equation (A.2) used by Schock and Miquel [3] varied from 75 to 1087. These Reynolds number correspond to flow rates of 0.1 to 1.5 L.min$^{-1}$ in the cross-flow system used in the present study when one single membrane cell is fitted. This Reynolds number range based on channel height has also been used by other authors, including membrane manufacturers such as Koch [4-6].
A.3 Problems occurred in the system after the by-pass insertion

To overcome the considerable excess flow rate circulating tangentially to the membrane that the pump delivers, a bypass to the cells was inserted connecting the pump exit to the feed tank.

However, a few problems occurred with this new set-up:

1. The proportional relief valve inserted after the membrane cell used to pressurise the system was not suitable for the application. It adjusted the pressure in the system by changing the circulating flow rate making it impossible to control the pressure and flow rate simultaneously and independently, since the change in one automatically changed the other. The control of both pressure and flow rate are crucial for this study since they influence the mass transfer of compounds through the membrane.

2. The needle valve inserted in the membrane cell entrance (see Figure 3.8) replaced the proportional relief valve due to the incapacity of the later in controlling and adjusting the operating pressure as mentioned above, and also due to vibrational problems in the system and shattered noises caused by it. This allowed to pressurise the system without generating the noise and vibrational problems experienced before with the relief valve and, simultaneously, to control the flow rate circulating tangentially to the membrane, which was done by the needle valve in the bypass.

3. The piston pump was not able to perform well with the current set-up and was unable to maintain a constant flow rate and pressure during the experiments. As an example, an experiment starting with 10 bar and 0.52 L.min\(^{-1}\) finished with a flow rate of 0.29 L.min\(^{-1}\) and a pressure of 11.2 bar. This corresponded to a gradual change of 44% and 12% in the flow rate and pressure, respectively, which is not admissible. In fact, changing the feed flow rate in the membrane cell yields a change in the average velocity on the membrane surface, that is, a change in the hydrodynamics of the system during an experiment: summing up, the experiment was performed under
unsteady-state conditions. This affects the mass transfer at the membrane surface while the experiment is running. Comparison between different runs are therefore impossible to perform and inconclusive.

4. Furthermore, after tests with MilliQ water with the bypass inserted the pressure and flow rates were difficult to control for one membrane cell inserted. It was very difficult to achieve the low flow rates and high pressures necessary for the experiments (e.g. 1 L.min$^{-1}$ of flow rate and 15 bar pressure respectively). The pump persisted with its ill performance and the flow rates and pressures decreased with time during most of the performed experiments. This means that the bypass system was not an effective change to the setup due to the very low pump performance.
A.4 Procedures to Track the Membrane Deposit Origin

Several steps were followed to understand the origin of the deposit found in the membrane when performing experiments with the Speck pump:

1. The system was washed several times with NaOH at pH 11, with acetic acid at pH 3 as advised in the MMS manual and flushed with MilliQ water, but the contamination and deposits on the membrane persisted indicating that the problem had its origins from within the system.

2. MilliQ water was recirculated in the system, instead of the hormone solution used to understand the transport of hormones through NF membranes. The same deposits occurred as can be seen in Figure A.1. The result was elucidative since the same brown contaminating deposits persisted: the problem was therefore not related to any hormone reaction with the membrane.

3. The membrane deposits persisted after several washes for at least 30 minutes each (RBS detergent solution of 20 mL in 1 L of MilliQ water, 50% methanol solution, tap water, MilliQ water and 0.1 M NaOH). The previous procedure allowed confirming that contamination was not originated by some accumulation in the system from previous experiments. In fact, the amount of deposits increased as time went by, contradicting the theory that the deposits were originated from previous experiments. The time scale where the membranes were used in Figure 3.14 increases from bottom to the top.

4. The Speck pump fitted in the cross-flow system was replaced by an identical one (same model) to check if the first one was faulty. Identical MMS systems that had never been used were also tested with three Speck pumps. Unfortunately the same kind of contamination occurred in all the trials, showing that the problem was within the pump model that had been fitted in the system.

5. A strong sulphur smell emanated from the feed tank after a few hours in recirculation mode with MilliQ water. To remove the hypothesis of such
smell originating from the membrane itself, several membranes were used in the cross-flow system (NF 270 and TFC-SR). The deposits on the membrane persisted and were independent of the membrane type or manufacturer.

6. Furthermore, bits of membrane were cut and placed in 100 mL of MilliQ water and shaken overnight. The membranes shaken were with and without coating to make sure that if some coating was still left on the membrane it did not give any smell. The results were negative; there was no smell or colouring of the water.

After performing the previous procedures and analysing the results, the hypothesis of an oil leak from the pump started to shape, due to the gold shade of the deposit (see Figure A.1), due to the strong sulphur smell that emanated from the feed tank after a few hours running in recirculation mode and due to a TOC increase from the initial pure MilliQ water in the feed tank compared to the final MilliQ water solution that recirculated for hours in the system.

Figure A.1 Gold shade of deposit on the membrane surface (deposit circled)

To confirm it was an oil leak that originated from the system the following steps were followed:
1. If the solution was contaminated by the pump oil, the reverse could also have happened. A sample of 1 mL of several oils were taken and run in the scintillation counter to see if there had been cross-contamination from the radiolabeled hormone solution to the oil itself. A sample of the pump lubricating oil was taken, as was a sample of the oil of a Speck pump that had never been used and also a sample from a different type of oil for comparison. The results showed no cross-contamination of the oil since all the oil samples showed the same level of radioactivity (an average of 300 DPM was obtained compared to 50 DPM for pure water). This showed that the contamination occurred from the oil crankcase to the fluid solution, and not the reverse. The contamination might have originated from diffusion of the oil to the circulating fluid during operation and rest of the pump.

2. The mentioned strong smell of sulphuric compounds in the feed tank substantiated the oil contamination hypothesis. A MilliQ water solution was recirculated for at least 2 hours with a pressure between 20 and 25 bar. A difference of 6.7 mg.L\(^{-1}\) of TOC was measured between the initial feed (with 0.03 mg.L\(^{-1}\) of TOC, close to a blank of 0.05 mg.L\(^{-1}\) of TOC) and the final feed (6.7 mg.L\(^{-1}\) of TOC) and after the system had been thoroughly washed as previously described (step 3). This proved that the contamination was released during the experiment (Figure A.2).

After the previous tests, analyses and conclusions - oil was definitely contaminating the solution under study during the experiments - it was absolutely necessary to locate the contamination source, the highest probability pointing out the pump itself. For that, every piece of equipment in the system was checked and ruled out as a possible contamination source. For some of the equipments (pressure transducers, pressure relief valves, ball valves) it was checked with the manufacturer and confirmed in their manual that no contamination source was possible from that piece of equipment. The remaining equipments (pressure dampener, needle valves, flow meter, flow cell on the permeate line) were removed from the system and a contamination on the membrane was checked after running for at least 2 hours at 15...
bar in recirculation mode with MilliQ water and a new NF 270 membrane. The results obtained are summarized in Table A.2.

The pressure transducers were not removed since they were necessary to monitor the pressure in the system. According to the manufacturer there is no source of contamination possible from these instruments, since they consist only of a diaphragm and electrical connections.

The 3 way valve, the needle valve and the relief valve could not be removed for safety reasons and to ensure the pressurisation of the system. These were confirmed with the manufacturer not to be a source of contamination since they are made of stainless steel. Furthermore, they were removed from the system and washed thoroughly to make sure they had no contaminant accumulated on them.
Table A.2 Procedure adopted to find contamination source

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Substantial Deposit</th>
<th>Some Deposit</th>
<th>Almost No deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>All the instruments fitted</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Dampener</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Bypass with needle valve</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Flow meter</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Flow cell and Conductivity meter in permeate</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>With Flow cell and Conductivity meter in permeate after washed physically</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>With Flow cell and Conductivity meter in permeate</td>
<td></td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

From all the previous tests and results analyses it was concluded that the contamination was an oil leak from the pump due to the following evidence:

- A golden deposit on the membrane surface;
- An increase of TOC during an experiment of at least 7 mg.L$^{-1}$;
- An intense sulphuric smell (oil);
- Every instrument was ruled out as a contaminant source.

In addition, there was also confirmation from Speck pumps that these piston pumps can leak oil. They are usually used for car wash systems and, therefore, certainly not appropriate for clean applications where a constant and controllable pressure and flow rate are necessary.

The oil leak was originated from the oil case used to lubricate the pistons. As can be seen in Figure A.3 the oil crankcase (No. 1) is filled with oil to lubricate the pistons and the only physical barrier between the oil and the fluid circulating in the system are two o-rings (No. 18 and 21 in Figure A.3).

Besides diffusion of oil as previously referred, when the pump operates two phases occur in the piston chamber: suction of the fluid to the piston chamber where the pressure is lower than in the oil case, followed by expelling of the fluid under pressure from the piston chamber to the exit of the pump. In this second phase the
piston chamber is at higher pressure than the oil chamber, which makes oil leakage not likely to occur. It is possible that during the suction phase, when the pressure on the fluid side is lower, oil transfer occurs to the fluid side; whereas for the phase when the fluid was under pressure the piston chamber was sealed from the oil case, by the o-ring previously mentioned, avoiding this way cross-contamination.

In fact, an oil leakage has been reported in the literature in a study on the removal of iron by reverse osmosis membranes in 1973 [7]. In this study the authors state “The first few fouling experiments performed at different flow velocities showed a wide scattering of results. Each of these experiments had been performed with a new membrane and with new feed brine. Since equipment corrosion […] had been largely avoided, it was felt that the observed irreproducibility might have been caused by oil leakage from a booster pump used during precompaction or from the high pressure pump due to deterioration of the piston packings.” In their study, the effect of oil on iron hydroxide deposits was checked, and deposits on the membrane were two to almost four times higher in the presence of oil.

From the above description it can be inferred that these pumps had clearly not been designed for a membrane cross-flow application for mimicking a spiral-wound membrane in terms of hydrodynamic conditions. Even worse, they had not been designed either for clean applications at trace contaminant levels since the pumps leaked oil.
A.5 The Hydra-Cell Pump Manufacturer Tests and Results

After obtaining contamination on the membrane surface, the new pump (Hydra-Cell) was sent back to the manufacturer together with a membrane cell and membrane samples to be run in their workshops. This allowed finding out if the problem was related to the pump or with the system itself, once the pump had been thoroughly washed.

A system with the pump and a membrane manifold was set up and run for 9 hours in 2 days at 25 bar, according to the manufacturer. The manufacturer experiment was run without a dampener and at high flow rates of 3.7 L.min\(^{-1}\). These two conditions do not favour membrane deposition due to oscillations in the pressure. However, as can be seen in Figure A.4 that the pump manufacturer sent us, the manufacturer obtained the same type of yellow deposit on the membrane surface, showing that the contamination did not originate from the system, but from the pump. Although very faint, explained by the absence of a pressure dampener and the high flow rates used, the appearance of a yellow deposit shows that the contamination problem is originated from the pump and not the MMS system itself.

![Yellow Deposits](image)

Figure A.4 Membrane result of trial by Wanner Engineering with yellow deposits
(Report sent by Wanner Engineering)
The pump oil was substituted by Wanner Eng. by a green oil and the system was run more than 5 hours to check if the membrane deposit colour changed from yellow to green. The membrane obtained was yellow once again, and when a cotton bud was used, it came out as dark green. This was said by Wanner to have come from the oil change with an inevitable passage of oil around the diaphragm and the lack of proper cleaning of the membrane diaphragms after. When the experiment was repeated, and the system run for more than 10 hours, the membrane deposits were dark yellow. However, the colour and nature of the deposits changed, as can be seen in Figure A.5. Although the deposit was not green, it was darker than previously and there was more quantity.

Figure A.5 Membrane deposit after the pump was washed with methanol and the oil was changed to a green oil

When the pump head was opened it was noticed and observed that the metal surfaces where the diaphragms are inserted in were full of oil coming from the oil case and passing around the diaphragms. This was noticed by using a cotton bud on the metal surface around the diaphragms, both above and below as shown in Figure
A.6. The diaphragms themselves also had oil around them, although not visibly on the area where the diaphragm is in contact with the recirculating fluid (centre of the diaphragm in Figure A.6).

Figure A.6 P200 pump head opened and different diaphragms
As can be seen in Figure A.7, the back of the diaphragm is filled with oil in the piston chamber, the green substance shown in Figure A.7. This oil is at the same pressure as the system working pressure when the piston strokes to the oil, which, in turn, pushes the diaphragm and, consequently, rises the circulating fluid pressure to the desired value and imposes the desired flow rate.

![Figure A.7 Removed diaphragm from pump head](image)

Although the diaphragm is tighten against the two metal plates shown in Figure A.6, there is not much resistance to oil transfer from the piston chamber, then around the diaphragm and, finally, to the fluid side.

Different diaphragm materials and shapes were tested to check if the contamination disappeared: Buna and Viton, both of the same shape but of different materials and of different shape compared to the PTFE diaphragm (Figure A.6). The results with Buna were very encouraging since contamination on the membrane surface decreased substantially. However, besides the oil contamination, the diaphragm themselves released a TOC content higher than 10 mg.L\(^{-1}\) in the solution. The diaphragms are covered in carbon black which was probably released during the experiment and contaminated the sample with organic carbon. This was confirmed by immersing the diaphragms in a beaker with MilliQ water and leaving them for a

A-18
Appendix A

few hours. High values of TOC were obtained when analysing this water (100 mgC.L\(^{-1}\)). The Buna material on the other hand is known to be less permeable than PTFE and Viton, which explains the lower contamination obtained when these were inserted in the pump. The Viton diaphragms had the same result as the PTFE ones: high contamination on the membrane surface and TOC content in the solution of about 4 mgC.L\(^{-1}\).

Two contamination hypotheses started emerging: around the diaphragm and also through the diaphragm which is under a lot of stress and stretch during operation. To avoid the contamination around the diaphragm, the pump design was modified as described in Chapter 3.
B. Membrane Thickness Variability

The membrane thickness variabilities were determined from the TEM pictures of the active layer thicknesses (Figure B.1). The Image J software (version 1.40) was used to determine the distance between two points corresponding to the thickness of the active layer.
Figure B.1 TEM image of the TFC-SR2 [8], the NF 270 and the NF 90 (courtesy of Prof. Polizzi and Dr. Davide Cristofori (University of Ca’ Foscari Venezia, Italy) and the BW 30 [9]

The several measurements for the distances obtained for the different membranes are presented next, including the average value and the variability obtained.
B.1 TFC-SR 2 membrane

For the TFC-SR 2 membrane, the following results for the active layer thickness were obtained (Table B.1):

| 371.43 | 302.86 | 325.71 | 332.02 | 360.971 | 350.646 |
| 400    | 342.86 | 337.14 | 352.37 | 371.429 | 328.578 |
| 388.57 | 325.71 | 354.29 | 303.362| 306.89  | 356.635 |

The average active layer thickness obtained was: 345 nm
The variability in the active layer thickness obtained was: 28 nm (8%)

B.2 NF 270 membrane

For the NF 270 membrane, the following results for the active layer thickness were obtained (Table B.2):

| 19.1   | 23.2  | 20.7  | 22.4  | 17.7  | 18.1  |
| 21.6   | 19.7  | 18.6  | 19.6  | 17.4  | 22.1  |
| 26.2   | 23.4  | 17.4  | 19.0  | 23.0  | 23.4  |
| 20.0   | 24.4  | 21.2  | 17.4  | 19.8  | 20.1  |
| 20.1   | 19.5  |       |       |       |       |

The average active layer thickness obtained was: 21 nm
The variability in the active layer thickness obtained was: 2.4 nm (11.5%)
B.3 NF 90 membrane

For the NF 90 membrane, the following results for the active layer thickness were obtained (Table B.3):

Table B.3 NF 90 active layer thickness

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>268.5</td>
<td>197.5</td>
<td>206.5</td>
<td>228.1</td>
<td>218.7</td>
<td>268.5</td>
</tr>
<tr>
<td>200.9</td>
<td>169.8</td>
<td>191.2</td>
<td>242.6</td>
<td>228.1</td>
<td>197.5</td>
</tr>
<tr>
<td>262.9</td>
<td>179.0</td>
<td>200.5</td>
<td>232.6</td>
<td>206.5</td>
<td>318.5</td>
</tr>
<tr>
<td>172.7</td>
<td>182.0</td>
<td>239.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The average active layer thickness obtained was: 218 nm
The variability in the active layer thickness obtained was: 40 nm (18 %)

B.4 BW 30 membrane

For the BW 30 membrane, the following results for the active layer thickness were obtained (Table B.3):

Table B.4 BW 30 active layer thickness

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>334.5</td>
<td>216.5</td>
<td>290.2</td>
<td>254.8</td>
<td>226.3</td>
<td>224.0</td>
</tr>
<tr>
<td>306.8</td>
<td>133.2</td>
<td>160.2</td>
<td>442.0</td>
<td>146.9</td>
<td>285.2</td>
</tr>
<tr>
<td>109.5</td>
<td>173.1</td>
<td>196.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The average active layer thickness obtained was: 233 nm
The variability in the active layer thickness obtained was: 88 nm (40 %)
C. Instrument Calibration

C.1 Scintillation Counter

A Beckman LS6500 liquid scintillation counter (Fullerton, USA) was used to measure the concentration of radiolabelled hormone concentration in the feed and permeate samples. All hormones were labelled with tritium ($^3$H) which is a beta emitter. The hormone sample was dissolved in a liquid scintillation cocktail which converted the radioactive energy into light which can be detected by the counter. The units of activity are disintegrations per minute (DPM). To improve accuracy of detection a liquid scintillation cocktail suitable for low level tritium counting in aqueous samples, Ultima Gold LLT, was selected.

The hormones estrone and estradiol detection limit, shown in Figure C.1 and Figure C.2 were of 1 ng.L$^{-1}$.

![Figure C.1 Estrone (E1) detection limit](image1)

![Figure C.2 Estradiol (E2) detection limit](image2)
C.2 Total Organic Carbon Analyser

A Total Organic Carbon Analyser (TOC-V<sub>CPH</sub>) (Shimadzu, Milton Keanes, UK) was used to measure the feed and permeate concentration of the organics used for the membrane pore radius characterization.

The Non-Purgeable (NPOC) mode was used with the high sensitivity catalyst, allowing for very low organic concentration measurements.

![Figure C.3 TOC potassium hydrogen phthalate (PHP) calibration curve](image)

The sample is firstly mixed pre-acidified to pH 2-3 with 1.5% HCl (2 M) and purged for 1:30 minutes with N<sub>2</sub> to remove any vestige of CO<sub>2</sub> that might be in the sample. Once this process is carried out, the sample is sent to the catalyst, where the organic carbon is combusted to CO<sub>2</sub> at 680°C. The CO<sub>2</sub> is then sent to a nondispersive infrared detector (NDIR), where a peak is obtained.

This peak is then converted into a concentration by using the relationship obtained in a calibration curve with potassium hydrogen phthalate (Figure C.3).
D. Reproducibility of Results of Hormone Filtration

Triplicates of a few selected experiments are presented Figure D.1, Figure D.2 and Figure D.3 to show reproducibility and define the variation in retention, normalized permeate flux and total mass adsorbed. The full symbols represent the transient feed concentration and the hollow symbols represent the transient permeate concentration. Each symbol represents one repeat.

Figure D.1 Repeats for estrone (E1) and the NF 270 1 membrane (Reₜ=998, Cₚₑₑₜ=100 ng/L, 11 bar, pH 7)

Figure D.2 Repeats for estrone (E1) and the NF 270 1 membrane (Reₜ=427, Cₚₑₑₜ=100 ng/L, 11 bar, pH 7)
Figure D.3 Repeats for estrone (E1) and the NF 270 1 membrane \( (R_{ch}=427, C_{feed}=50 \text{ ng/L}, 11 \text{ bar, pH 7}) \)

The results for steady-state mass adsorbed, retention and normalized flux are shown in Table D.1, Table D.2 and Table D.3 where the average and variation of the presented parameters is shown in the average row of each table.

Table D.1 Repeat results for the experiment with estrone (E1), \( C_{feed}=100 \text{ ng/L}, P=11 \text{ bar, } R_{ch}=427 \)

<table>
<thead>
<tr>
<th>Repeated Experiment</th>
<th>( M_{ads} ) (ng)</th>
<th>Retention (%)</th>
<th>( J/J_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.4</td>
<td>67.0</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>67.4</td>
<td>75.5</td>
<td>0.97</td>
</tr>
<tr>
<td>3</td>
<td>71.0</td>
<td>66.6</td>
<td>0.98</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>68.4 ± 2 ng</td>
<td>69.7 ± 5 %</td>
<td>0.98 ± 0.01</td>
</tr>
</tbody>
</table>
Table D.2 Repeat results for the experiment with estrone (E1), $C_{\text{feed}}=100 \, \text{ng/L}$, $P=11 \, \text{bar}$, $Re_h=998$

<table>
<thead>
<tr>
<th>Repeated Experiment</th>
<th>$M_{\text{ads}}$ (ng)</th>
<th>Retention (%)</th>
<th>$J/J_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>62.4</td>
<td>87.5</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>60.4</td>
<td>77.2</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>56</td>
<td>81.6</td>
<td>0.95</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>59.6 ± 3 ng</td>
<td>82.1 ± 5 %</td>
<td>0.97 ± 0.02</td>
</tr>
</tbody>
</table>

Table D.3 Repeat results for the experiment with estrone (E1), $C_{\text{feed}}=50 \, \text{ng/L}$, $P=11 \, \text{bar}$, $Re_h=998$

<table>
<thead>
<tr>
<th>Repeated Experiment</th>
<th>$M_{\text{ads}}$ (ng)</th>
<th>Retention (%)</th>
<th>$J/J_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36.0</td>
<td>66.7</td>
<td>1.03</td>
</tr>
<tr>
<td>2</td>
<td>32.6</td>
<td>77.0</td>
<td>1.02</td>
</tr>
<tr>
<td>3</td>
<td>29.0</td>
<td>70.6</td>
<td>1.00</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>32.5 ± 3.5 ng</td>
<td>71.5 ± 5 %</td>
<td>1.02 ± 0.02</td>
</tr>
</tbody>
</table>

The above repeats (Table D.1, Table D.2 and Table D.3) show that results presented in Chapter 3, 4, 5, 6 and 7 are statistically different.
E. Membrane Internal Surface Area

Variability

The uncertainty of the total internal surface area of the membrane active layer thickness, $A_{\text{total}}$, caused by variability of its parameters such as porosity $\varepsilon$, active layer thickness $\delta$, and pore radius $r_p$ was determined from equation (E.1).

$$A_{\text{total}} = A_{\text{sm}} + A_p = WL(1 - \varepsilon) + \frac{2WL\varepsilon}{r_p}$$  \hspace{1cm} (E.1)

The error propagation method was applied to equation (E.1), as expressed in equation (E.2).

$$\Delta A_{\text{total}}^2 = \left(\frac{\partial A_{\text{total}}}{\partial \varepsilon}\right)^2 \Delta \varepsilon^2 + \left(\frac{\partial A_{\text{total}}}{\partial \delta}\right)^2 \Delta \delta^2 + \left(\frac{\partial A_{\text{total}}}{\partial r_p}\right)^2 \Delta r_p^2$$  \hspace{1cm} (E.2)

The uncertainty of $A_{\text{total}}$ is hence given by equation (E.3):

$$\Delta A_{\text{total}}^2 = \left(-WL + \frac{2W\varepsilon}{r_p}\delta\right)^2 \Delta \varepsilon^2 + \left(\frac{2WL}{r_p}\right)^2 \Delta \delta^2 + \left(-2WL\varepsilon\delta\right)^2 \Delta r_p^2$$  \hspace{1cm} (E.3)

The variability of $\Delta \varepsilon$ was calculated from error propagation from equation (E.4):

$$\varepsilon = \frac{\delta}{(\delta/\varepsilon)} = \frac{\delta}{A}$$  \hspace{1cm} (E.4)
where $\delta$ is the membrane thickness and $(\delta/\varepsilon)$, or $A$, is the parameter thickness to porosity ratio.

Propagation of equation (E.4) gives equation (E.5) and (E.6):

$$\Delta \varepsilon^2 = \left| \frac{\partial \varepsilon}{\partial A} \right|^2 \Delta A^2 + \left| \frac{\partial \varepsilon}{\partial \delta} \right|^2 \Delta \delta^2$$  \hspace{1cm} (E.5)

$$\Delta \varepsilon^2 = -\frac{\delta}{A^2} \Delta A^2 + \left| \frac{1}{A} \right|^2 \Delta \delta^2$$  \hspace{1cm} (E.6)
F. Appendix F

The numerical model developed in Chapter 7 is dependent on several solute and membrane characteristics, such as solute diffusivity, membrane pore radius, amongst others.

These characteristics have been estimated either experimentally, or by using theoretical or empirical equations and their average values and variability obtained are represented in Table F.1.

Table F.1 Numerical model parameter variability

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active layer thickness $\delta$</td>
<td>21</td>
<td>2.4</td>
</tr>
<tr>
<td>Average pore radius $r_p$</td>
<td>0.42</td>
<td>0.02</td>
</tr>
<tr>
<td>Thickness to porosity ratio $\delta/e$</td>
<td>1.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Adsorption Constant $\chi$</td>
<td>0.21</td>
<td>0.02</td>
</tr>
<tr>
<td>Hormone Diffusivity $D_e$</td>
<td>$5.87\times10^{-10}$</td>
<td>$5.87\times10^{-11}$</td>
</tr>
<tr>
<td>Affinity constant $B$</td>
<td>35.01</td>
<td>3.50</td>
</tr>
</tbody>
</table>

The variation in the estimated adsorption given by the numerical model by varying each of these parameters as shown in Table F.1 is represented in Figure F.1.

As can be seen in Figure F.1, variations in all the parameters give very small differences compared to the experimental results. The only exception is for the membrane average pore radius $r_p$. Decreasing the pore radius from 0.42 to 0.40 nm yields a 28% reduction in the predicted mass adsorbed of E2 whereas an increase of pore radius from 0.42 to 0.44 nm yields a 43% increase. When the pore radius increases a higher concentration of hormone partitions inside the membrane pore, increasing substantially the mass adsorbed, as was extensively discussed in Chapter 6.
Figure F.1 Comparison of the estrone (E1) mass adsorbed experimental results with the numerical model results by varying the model parameters ($C_{\text{feed}}=100\,\text{ng.L}^{-1}$, $Re_h=427$, $P=11\,\text{bar}$, $\text{pH}=7$, $T=25^\circ\text{C}$, NF 270)