31st May 2018

Email: bemar17@student.sdu.dk

Analysis of the filtration of platinum nanoparticles dissolved in hydrochloric acid

Bachelor thesis

Author:
Belén Martínez-Lacuesta Oteiza

Supervisor:
Shuang Ma Andersen

Acknowledgments

Firstly, I would like to thank the SDU Institution for giving me the opportunity to do my Bachelor Final Project in this university.

Thanks to everyone that have helped me during my work in the laboratory, professors and students that spent their time in helping and teaching me with the operation of the equipment.

A huge thanks to my supervisor Shuang Ma Andersen for accepting me in her research group and giving me this valuable opportunity, and to Peter Lund for the orientation provided during the development phase.

Finally, and most importantly, I would like to thank my family and friends for all the support, inspiration and motivation given during the development of this thesis.

Abstract

This thesis work engages in the study of whether nanofiltration would recover platinum catalyst effectively. It first consists on several blank filtrations with water and HCl (0.1 and 1M) for different conditions of feed, pressure and temperature in order to know about the behavior of this kind of experiments. Secondly, the main filtrations of HCl solutions that contain Platinum and, in other cases, cooper, were made varying same conditions. A final filtration of longer duration was made.

To make the comparison between the filtrations and qualify if they were beneficial or not, several aspects were measured, such as, Pt concentration, Cl^- concentration, pH, volume, etc., and compared.

During these experiments it was done a membrane fouling study that consisted in filtering distilled water before and after filtrations maintaining same conditions and comparing results.

Table of contents

1. Introduction

This Project is heavily based on experimental work in O31-511-1 Lab in Tek Building, where so many hours have been spent for both self-learning the equipment and data collection through experiments.
The project is divided into sections; where first a foundation is laid down for the reader to understand the units and materials needed, then tests has been presented and the results and observations are discussed and interpreted in later section followed.

1.1. Project formulation

This project is based in the recover of Platinum as catalyst by Nanofiltration. The aim is to validate whether a filtration would recover catalyst effectively in order to avoid environmental problems related to the use of catalyst.

A study of the filtration behavior of a solution of platinum compounds (simulating residues from catalytic processes) dissolved in HCl was made by using a membrane that theoretically fulfills the characteristics to retain the platinum complexes while varying the conditions on the filtration process (feed, pressure and temperature) and adding other metal compounds that may affect the behavior of the process in order to achieve a clean and concentrated solution.

During these main experiments a fouling study was done in order to get to know about the behavior of the membrane before and after being submitted to the Pt solutions.

1.2. Project background

This Project serves as bachelor Project for the student Belén Martínez-Lacuesta. It has been developed in the University of Southern Denmark. The Project is concerned catalyst recover by Nanofiltration, a research theme which was shortly studied by the group but for technical issues it never succeed.

1.3. Project limitations

During process and development of the thesis project, It will be subjected to the following limitations:

- The project process is constrained to 4-month period from the 1st of February 2018 to the 31st of May 2018.

- This thesis will be developed by a single student being limited in resources and thereby man hours.
- The control of the conditions in some experiments has proved difficult to maintain and that is why it is indicated that they have been carried out in temperature or pressure ranges.
- During the development of the experiments, there was found a problem with the membrane that provoked many data being discarded.
  (more in appendix section 6.1.)

2. Theory

2.1. Porous membranes

Porous membranes consist of a solid matrix with defined holes or pores. These are mainly used to separate colloid particles or large molecular weight solutes from solvent. The degree of selectivity is largely based on the membrane charge and porosity. Membranes with symmetric pores are more uniform, while asymmetric pores have variable pore diameters.

The permeate flux through a porous membrane is often described as the applied transmembrane pressure driving force, TMP, divided by the resistance to mass transfer, R, and the permeate viscosity, μ.

Where the total resistance, R, is described by individual resistances, such as the resistance of the membrane itself, the resistance due to adsorption fouling, and the resistances due to reversible and irreversible fouling.

2.2. Nanofiltration

Nanofiltration is the filtration in which particles until a size of 0,001 μm can be retained by a filter. It can be seen as a coarse of RO (reverse osmosis), but it uses less fine membranes. This makes the feed pressure and fouling rate lower compared to RO systems.
One of the mainly uses of NF is the separation of large mono-valued ions such as heavy metals, as it is the case of platinum being removed from HCl solutions.

The type of filtration carried out in these experiments is cross-flow or tangential filtration. In which feed flows tangentially across a membrane surface. The turbulence created across the membrane surface provides optimal flux performance and prolongs membrane functionally.

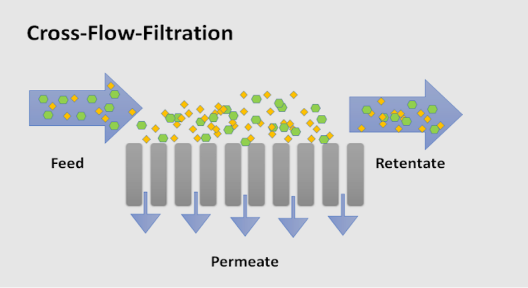


Figure 1. Cross-flow Filtration

In this process there are three main flows. There is the feed solution ready to be separated between the retentate (solution and compounds retained by the membrane that are returned to the feed) and the permeate (solution and compounds that cross the membrane through the pores).

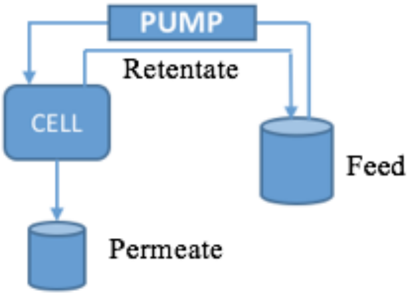


Figure 2. Unit

When returning the retentate to the feed solution it is increasing the concentration of the compounds retained by the membrane and this is how the experiments system works.

3. Experimental procedure

To carry out this project, filtration experiments of several solutions containing the platinum catalyst have been carried out and conditions such as pressure and temperature have been varied, as it is commented in the Project formulation.

To start, tests were made with the same solutions that would contained the catalyst, but without it, in order to know the behavior of the filtration for each type of solution, the membrane, how is going to affect the change of conditions, etc., by measuring permeate, volume and pH.

Then, the main experiments with platinum were made for three solutions; two contained platinum in the same concentration 1 mg/L, one of HCl (0.1M) and other of HCl (1M) respectively; the third contained 0.4 mg/L of platinum and 63.54 mg/L of copper, where pH and concentrations of Pt, Cu, Cl^- have been measured.

3.1. Experimental instruments and material

3.1.1. Membrane

The membrane used in the experiments is a GE Osmosis Duracid NF membrane. Is made of polyamide-TFC (thin film composite). This kind of membrane is used for acid purification, is has a pH range of 0-9, it can work with a flux (GFD) 10-19 and pressure of 225 psi. It has a theoretical pore size of around 150-200 Da, this is the MWCO (Molecular Weight Cut Off), lowest molecular weight solute in which 90% of the solute is retained by the membrane. Higher working temperature for the Duracid NF membranes is around 50°C. It fulfills the requirements specified for the use in the recovery of Platinum complexes (see figure 3).

Duracid Series

Industrial Acid Stable Nanofiltration Elements

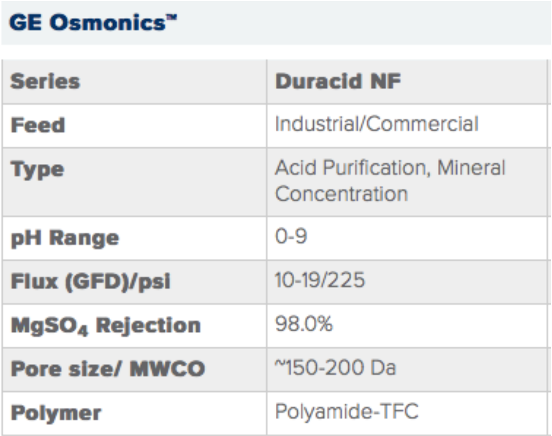
Description and Use

The Duracid NF membrane element is engineered to operate continuously under extreme acid conditions where pH is at or below zero.

Markets

- Metal Surface Treatment / Coating / Galvanic
- Heap Leaching Process in Mining
- Phosphate-based Chemical Production

Figure 3



GE Osmonics™

Series	**Duracid NF**
Feed	Industrial/Commercial
Type	Acid Purification, Mineral Concentration
pH Range	0-9
Flux (GFD)/psi	10-19/225
$MgSO_4$ Rejection	98.0%
Pore size/ MWCO	~150-200 Da
Polymer	Polyamide-TFC

Figure 4. Membrane Characteristics

3.1.2. Pump

For the pumping of the solution from the feed through the membrane and back to the feed a pump is needed.
The typical operating pressure range for the Duracid membrane is until 40-50 bar. A HPLC pump (Knauer Azura, P4.1S) is used (see figure x). The pump is equipped with a ceramic liner in order for the pump to withstand the acidic conditions.

Figure 5. HPLC Pump

Pump features:

- Flow rate range: 0,001-9,999 ml/min
- Pressure of up to 400 bar (but our membrane higher operating pressure is 50 bar)
- Dual piston

3.1.3. Measuring instrument

- AAS (Atomic absorption spectrophotometer): It has been used to measured the platinum and cooper concentrations. During filtrations, 0.5 ml of sample where taken directly from the retentate or permeate. A standard solution of 1,00 mg/L or 0,4 mg/L was used respectively for the Pt, HCl solution and Pt, Cu, HCl solution.
- pH-meter: Used for the pH measurement.
- IC-metrohm: Ion chromatography has been used to know the concentration on chlorides in the retentate and permeate of some of the filtrations.
- Volume measurement: For the measured of volume in the permeate of the blank solutions for water were used just simple pipettes.
- Pressure control: For pressure change a screw that block the pass of liquid is used. It consists in a screw positioned in the tube of the retentate. When it is tight, it blocks

the liquid pass, making the pressure higher. The value of pressure it appears in the pump.

- Feed flow control: Feed is controlled in the pump where it can also be programmed a maximum pressure at which pump turn off in order to not damage the membrane in case pressure goes to high. The flow is maintained constant.
- Temperature control: Temperature of the solution was measured by a simple digital instant read thermometer positioned in the feed.

Some of the conditions appeared already indicated in some of the equipment without needing to be measured with an extra one, as is the pressure or the feed. The pH and the temperature were easily measured without needed to dissolve the samples. However, to know the data of concentrations, platinum, copper or ions, it was necessary to carry out the dissolution of the platinum samples five times, the copper ones a thousand times and the ion ones a hundred times.

3.1.4. Cell

The membrane is positioned in a cell as shown in pictures below. It is held by four screws. There are two canals upside, in one of them, "feed" (Fig. 6), solution is injected inside the cell and it goes through the conducts shown on the right of Fig. 6, that make possible the tangential flow filtration. After crossing the conducts, the not filtrated solution go through the other canal, "retentate" (Fig. 6). What is filtrated goes down to the canal "permeate" (Fig. 6).

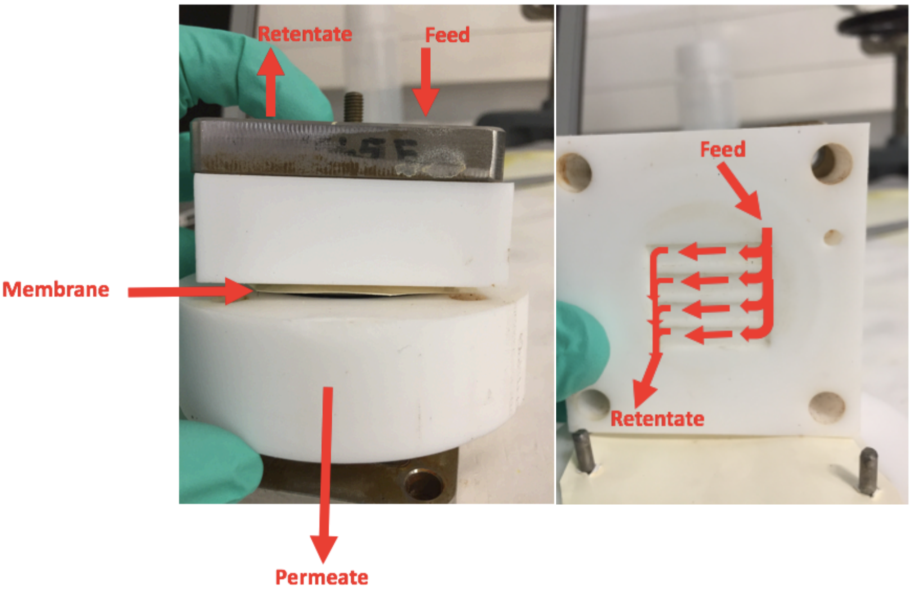


Figure 6. Cell

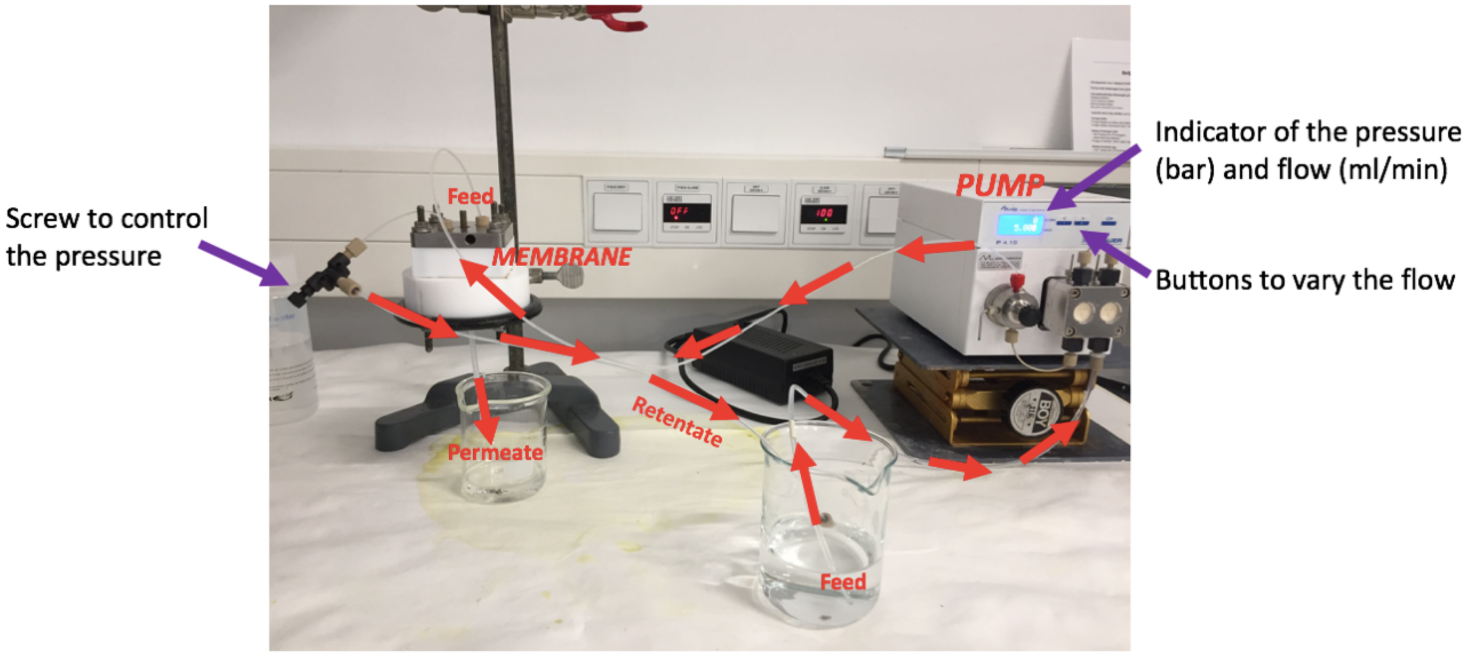


Figure 7. Units

3.2. Blank experiments

During blank filtrations three conditions where modified continuously and some data was recollected. Tests were made for two different temperatures, seven feed flows each temperature and three pressures each flow. The solutions used were distilled water, HCl (0.1M) and HCl (1M).

Based on the theory of porous membranes (explained in section 2.1.) the filtration shouldn't depend on the feed flow but on the pressure and on the the characteristics of the membrane and solution being filtered. Because of the increment of the viscosity it is most likely to be also better higher volume filtered for high temperatures.

Feed flux is in ml/min, pressure in bars and temperature in °C.

In these section almost all of the results are going to be presented in figures and graphics, exact data can be found in appendix.

3.2.1. Filtration of distilled water

First filtrations for water were done for seven different flows from 1 to 7 ml/min and three different ranges of pressure for each flow. The duration of each filtration was 10 minutes. The purpose is to compare the volume filtered in each one, see how affects the variation of pressure, temperature and feed flow.

Results in Fig. 8 show that although the increment of the flow, if the pressure is maintained to be in the same values, the volume filtered is also in same range for every flow.
For example, if we compared the volume filtered for pressure from 22 to 27 bars for 1ml/min and for 7 ml/min the volume filtered is around 3 ml in both cases.

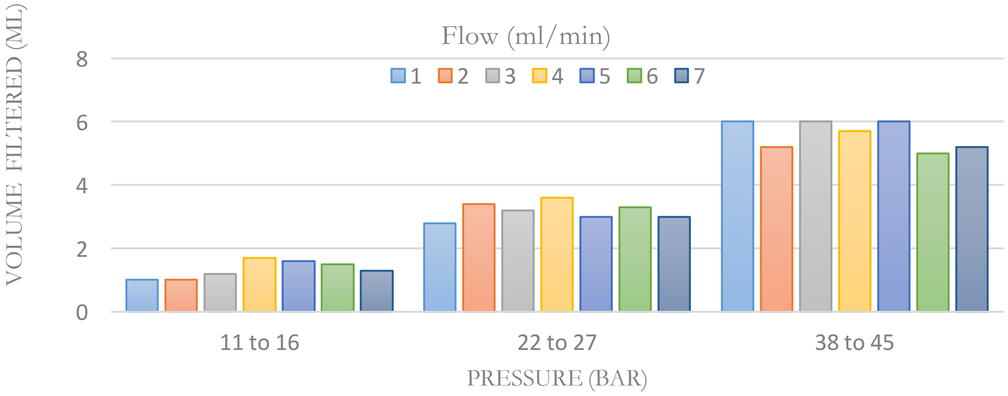


Figure 8. Comparison of volume filtered for water filtrations at different conditions of feed flow, pressure and temperature.

In Fig. 9 it can also be seen that the increment of volume filtered depending on the pressure is very similar for every value of the feed flow.

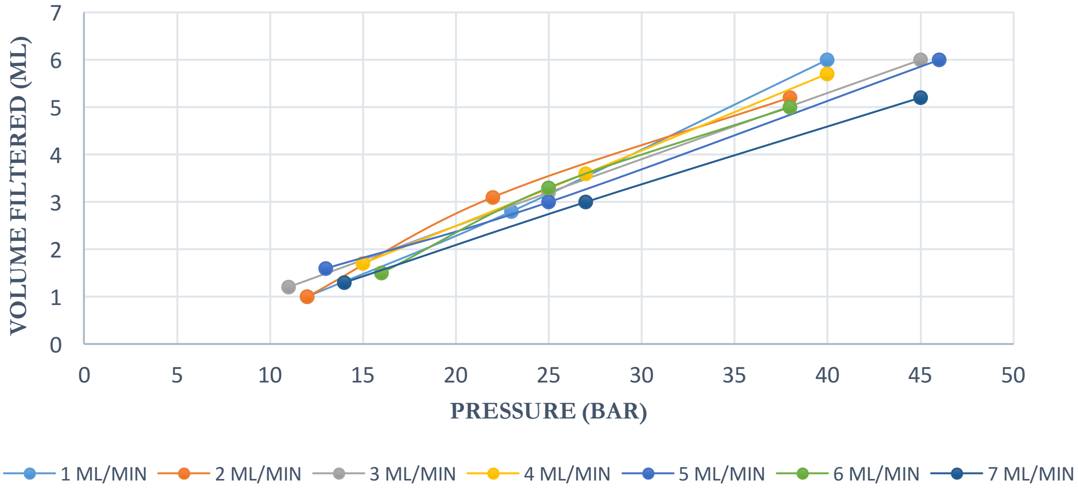


Figure 9. Graphic of Pressure vs. Volume filtered for different feed flows.

Go to table A.1 in section 6.3. to find exact values of Fig. 8 and 9.

After first experiments at room-temperature (25-30ºC) the following ones were made increasing the temperature of the feed using a laboratory hot-plate.

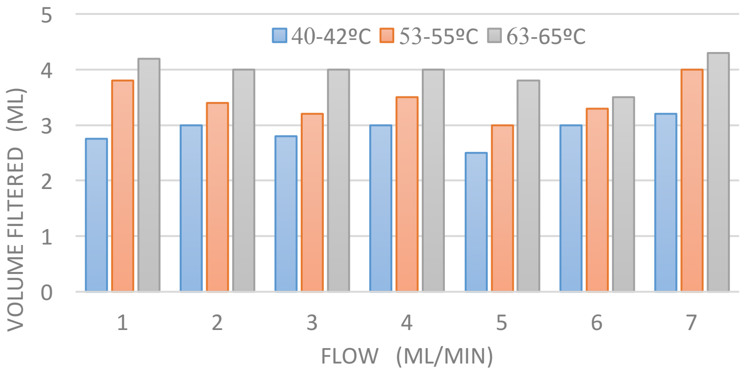


Figure 10. Dependence on volume filtered with temperature.

Go to table A.2 in section 6.3. to find exact values of Fig. 10.

These experiments were made at a pressure of 12-16 bar. It can be seen how the volume filtered increases when increasing the temperature of the solution filtered. Although the membrane should not work with a solution at higher temperatures than 50ºC, when the solution arrives to the cell It is estimated to be 10 ºC less. So even for the last experiment at temperatures over 60 ºC, solution is probably at around 50ºC afterwards.

3.2.2. Filtration of HCl (0.1M)

As a second step, a filtration of Hydrochloric Acid (0.1 M) was done for two different temperatures, seven different flows each temperature and two different pressures each flow. In these graphs It is intended to compare the concentration on HCl in the permeate and the retentate, being higher the concentration of HCl in the samples where the pH is lower.
Low temperature is 28 ºC and high temperature is 41 ºC.

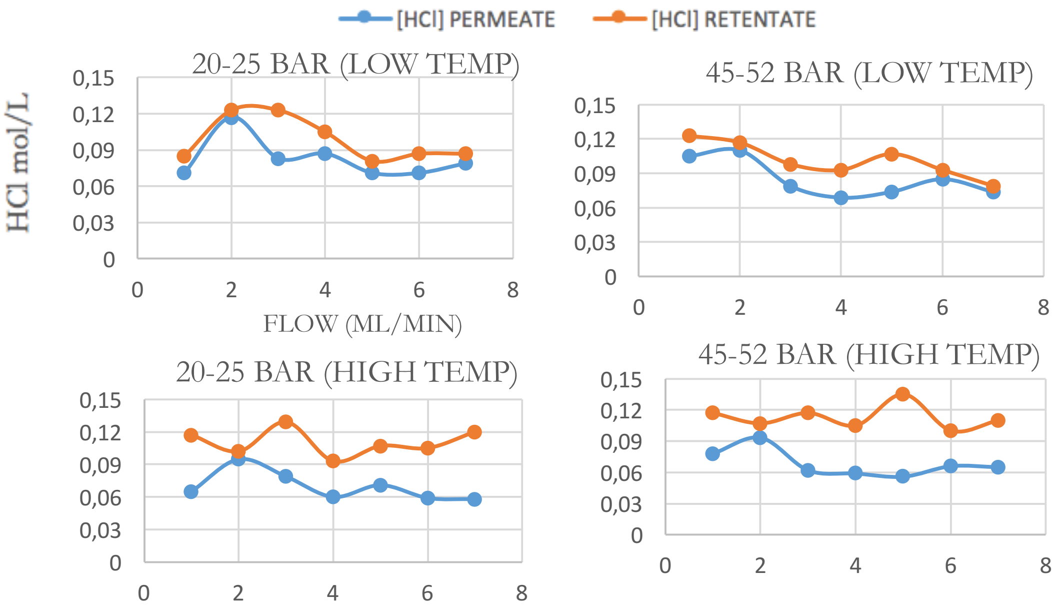


Figure 11. Graphics that represent HCl concentration vs. flow for HCl(0.1M) filtrations.

Go to tables A.3, A.4, A.5 and A.6 in section 6.3. to find exact values of Fig.11.

It can be seen that the concentration of HCl in the retentate is higher, what means that despite the characteristics of the membrane that indicates that HCl should be passing easily, there is some of it being retained.

This is probably because of the type of filtration is being used, tangential one, in which not all the flow is force to go through the membrane to be filtered, so at some point only some HCl in filtered when the solution goes over the membrane.

It cannot be seen any remarkable difference between filtration at higher pressure or at higher temperatures.

3.2.3. Filtration of HCl (1M)

As a third step, a filtration of Hydrochloric Acid (0.1 M) was done for two different temperatures, seven different flows each temperature and two different pressure each flow. Repeating the same process as for HCl (0,1M).
Low temperature is 27 °C and high temperature is 43°C.

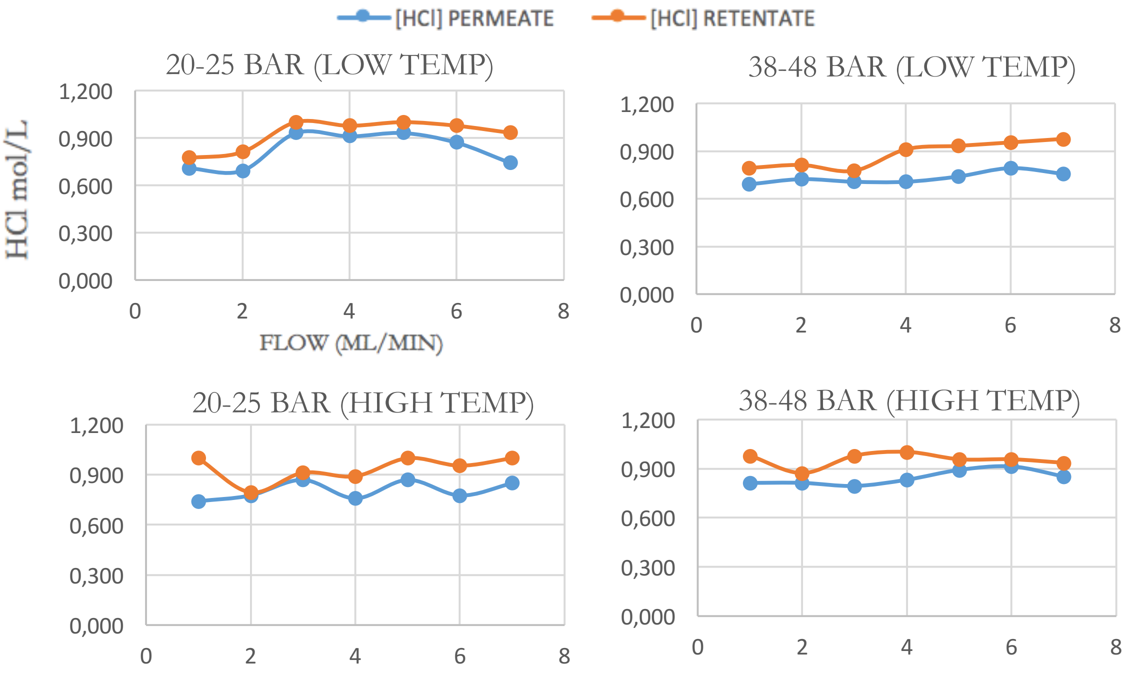


Figure 12. Graphics that represent HCl concentration vs. flow for HCl(1M) filtrations

Go to tables A.7, A.8, A.9 and A.10 in section 6.3. to find exact values of Fig.12.

Results are very similar to the ones obtained for HCl (0.1 M), being higher the concentration in the retentate than in the permeate.

3.3. Filtration of Pt solutions

After results from water filtration where experiments does not depend on feed flow, so henceforth, the experiment will be carried at one feed flow 2,5 ml/min. It has been chosen randomly. The duration of each filtration is 40 minutes and the initial volume in the feed is 40 ml.
When changing to new solution, the membrane is change to a new piece.

3.3.1. Filtration of Pt dissolved in HCl (0.1M)

The first test with platinum solution contained initially 1 mg Pt/L in HCl (0.1M). Several experiments at two temperatures and three pressure ranges took place. These filtrations had a duration of 40 minutes each.

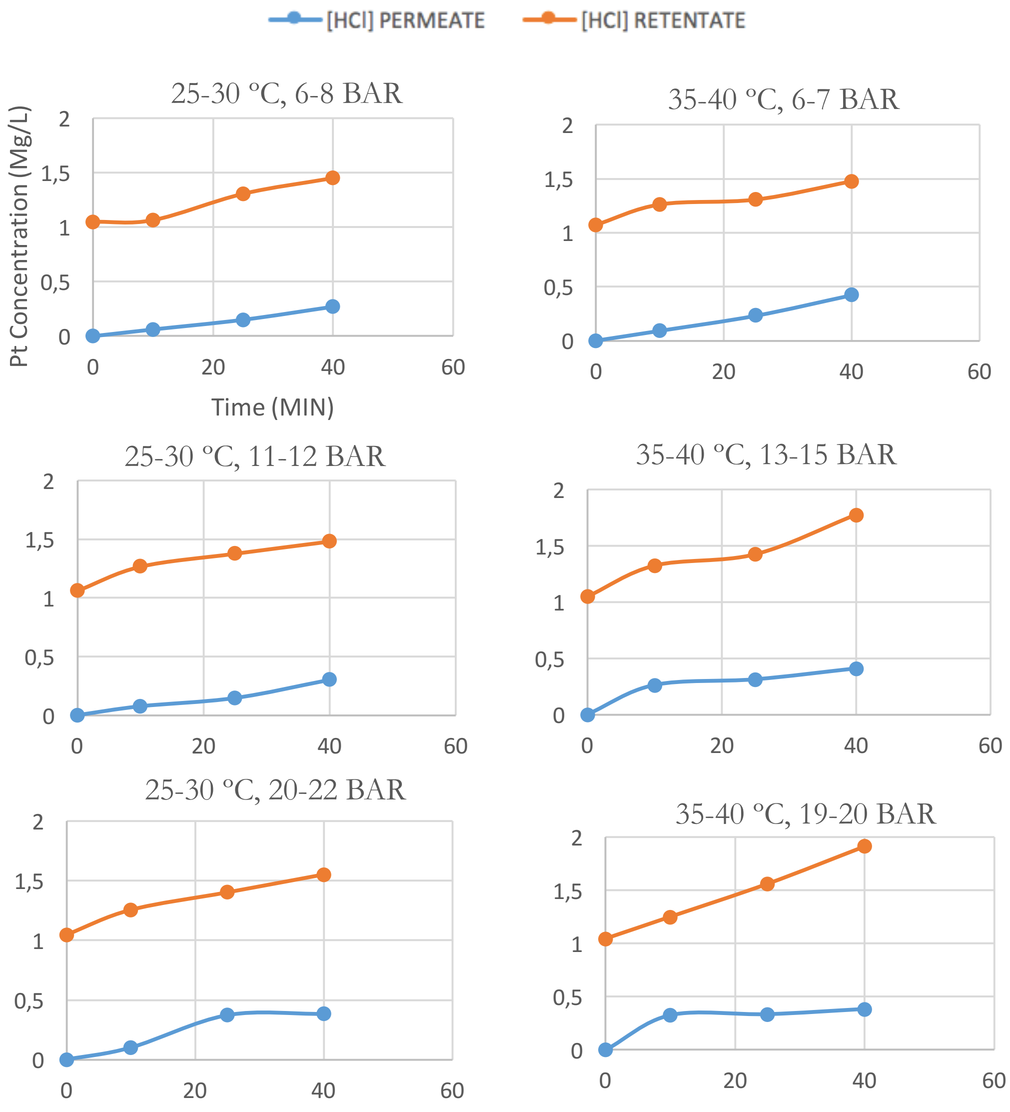


Figure 13. Graphics that represent Pt concentration vs time for HCl(0.1M)+Pt filtrations

Results from Fig. 13 show that although membrane characteristics assure no platinum should go though the membrane, concentration is being over zero in the permeate. Fortunately, concentration is increasing faster in the retentate than in the permeate, specially at higher pressure and temperature. It can reach almost two times the initial concentration in 40 minutes in the feed achieving a concentration of 1.916 mg/L at 35-40ºC and 22 bars. While at same pressure but lower temperature it is only reach 1.552 mg/L.

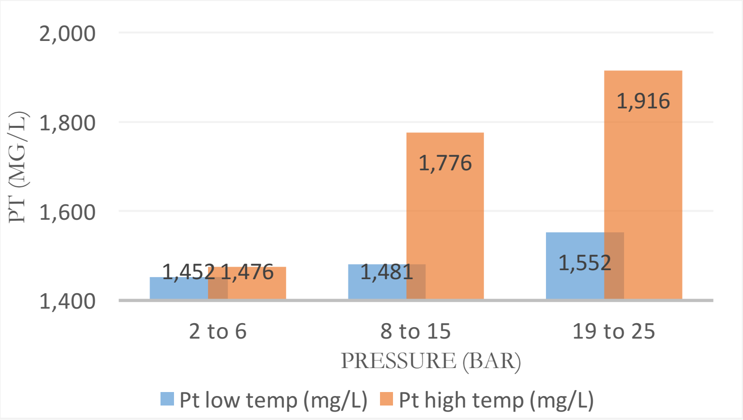
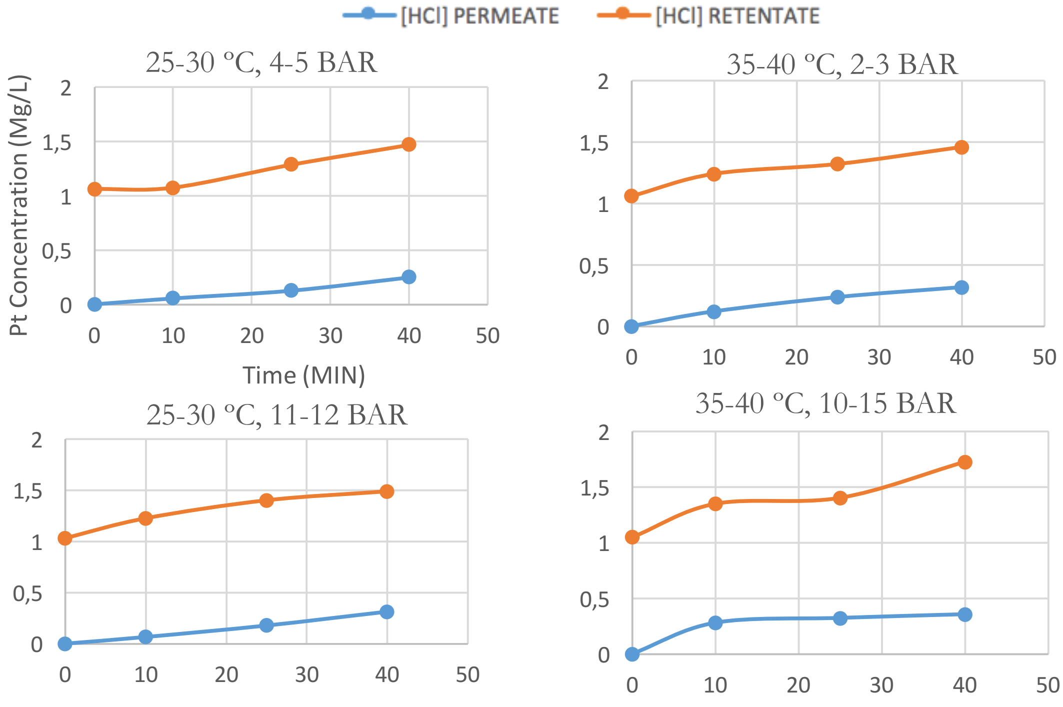


Figure 14. Comparison of final Pt concentration in retentate for HCl(0.1M) +Pt filtrations.

Go to tables A.11, A.12, A.13, A.14, A.15 and A.16 in section 6.3. to find exact values of Fig.13 and 14.

3.3.2. Filtration of Pt dissolved in HCl (1M)

Because of previous problems with the membrane (It can be found in section 6.1.), It was important to know if there was any difference between filtering HCl (0.1M) and HCl (1M) in order to see if there is a change with the membrane working at lowest pH. HCl (1M) tests were made for the same conditions of temperature and pressure as for 0.1 M.



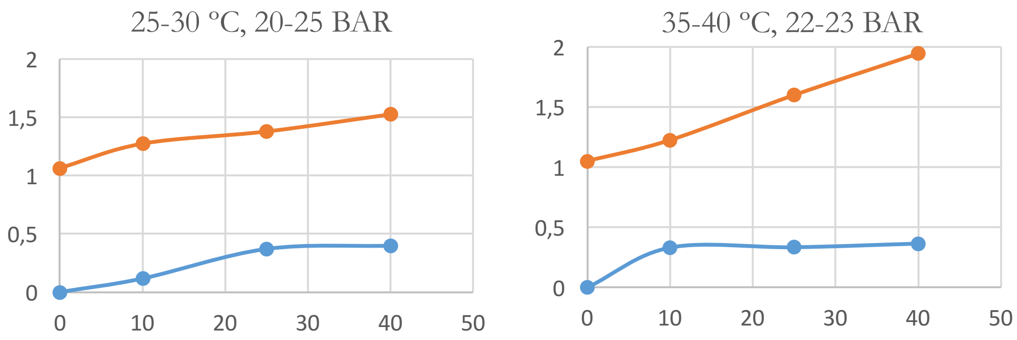


Figure 15. Graphics that represent Pt concentration vs time for HCl(1M) +Pt filtrations.

In this case, concentration of platinum in the retentate achieves also almost double of the initial, 1.945 mg/L; while in the permeate there is again some platinum, but compared to HCl (0,1M) is very similar, what indicates that the membrane is not being affected. Retentate concentration is basically same as the one obtained for HCl (0.1M) solution.

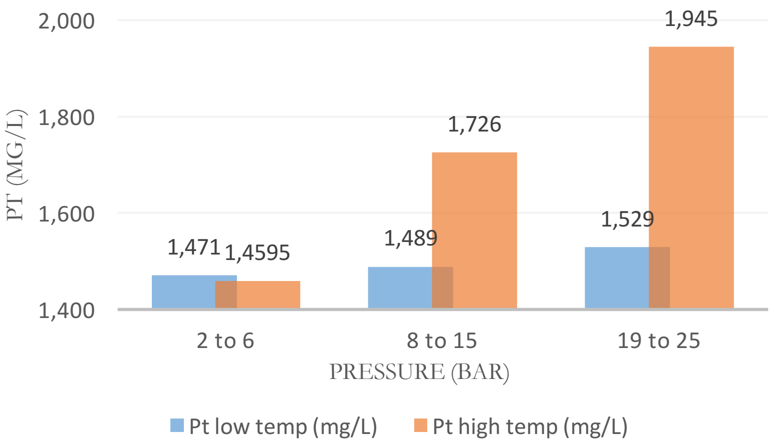


Figure 16. Comparison of final Pt concentration in retentate for HCl(1M) +Pt filtrations.

Go to tables A.17, A.18, A.19, A.20, A.21 and A.22 in section 6.3. to find exact values of Fig.15 and 16.

3.3.3. Filtration of Pt and Cu dissolved in HCl (0.1M)

It is known that when filtering a solution of platinum dissolved in HCl, the concentration of the feed can reach double. Next tests were made to see if this behavior would be repeated if there is another metal compound interfering in the solution.

The solution used is HCl (0.1M), has platinum and cooper dissolved in it. The concentrations are 0,4 mg/L of Pt and 63,54 mg/L of Cu (this solution was available in the group work and not prepared by the student, so cooper was not chosen for any articular reason).

These tests were made for two temperatures and three pressure ranges

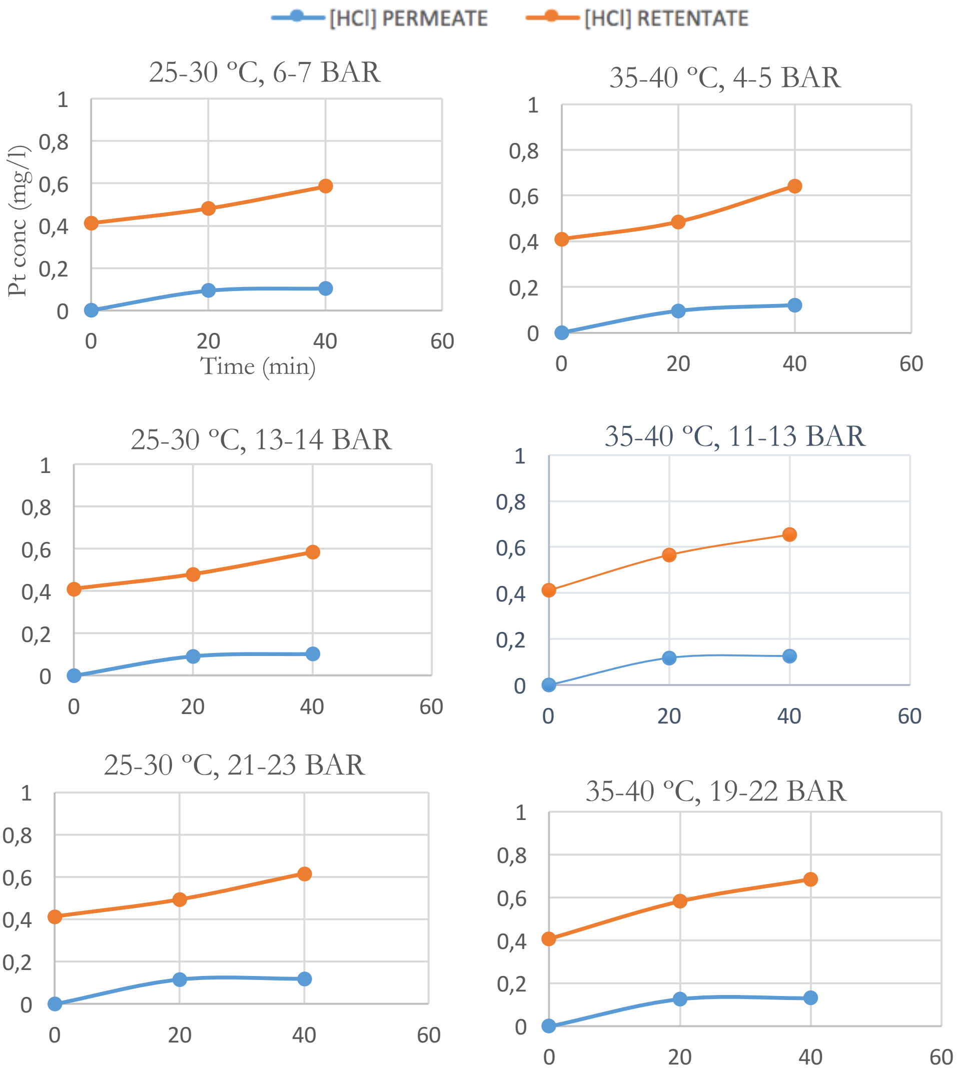


Figure 17. Graphics that represent Pt concentration vs time for HCl(0.1M) +Pt+Cu filtrations.

In presence of cooper it is not achieve double of the initial concentration as it happened without it. The highest concentration reach is 0,68 mg/L, 75% over the initial platinum concentration.

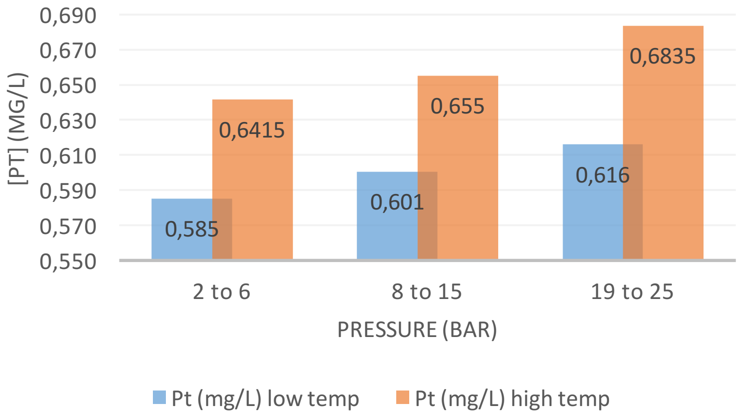


Figure 18. Comparison of final Pt concentration in retentate for HCl(0.1M) +Pt+Cu filtrations.

Go to tables A.23, A.24, A.25, A.26, A.27 A.28 in section 6.3. to find exact values of Fig.17 and 18

If the copper concentration in the permeate and retentate samples is analyzed, it can be seen that the copper is being slightly retained by the membrane as well as the platinum compounds. Most likely, the fact of having more solid particles takes more time to the membrane to filter the solvent.

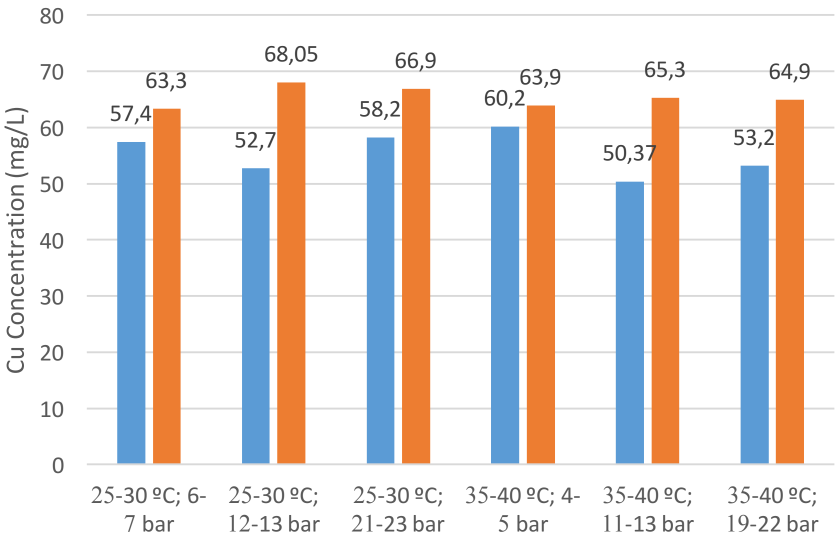


Figure 19. Comparison of final Cu concentration in retentate for HCl(0.1M) +Pt+Cu filtrations.

Go to table A.29 in section 6.3. to find exact values of Fig. 19.

3.3.4. Long filtration

In recent experiments it can be seem like the concentration of platinum in the permeate stabilizes and stops growing as fast as it initially did. To verify this and to know what would happen if the filtration were left for longer, a filtration that has lasted about five times as long as the other tests lasted has been carried out.

The solution used is HCl (0.1M) which contains the catalyst and copper.

The experiment took 190 minutes, and it was done at 25-30 ºC and 6-8 bar.

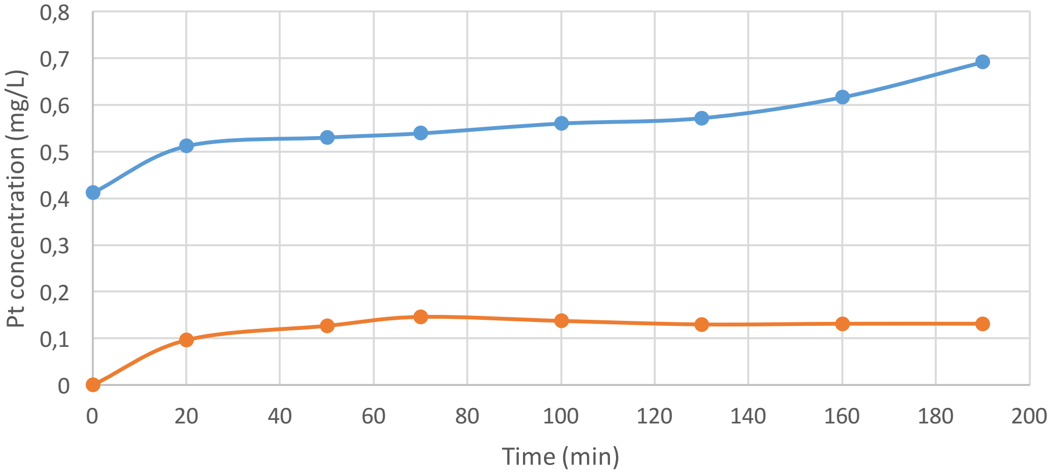


Figure 20. Graphic that represent Pt concentration vs time for HCl(0.1M) +Pt+Cu Long filtrations

Go to table A.30 in section 6.3. to find exact values of Fig. 20.

There is a clear indicator that for some reason the concentration of metals in the permeate stops growing and remains constant, while, when this happens, the retentate begins to grow faster.

3.4. Ions concentration

3.4.1. H^+ concentration

In order to know more about the possible compounds that platinum has formed. PH measurements have been made to know about H^+ concentration in permeate and retentate for all filtrations.

Concentration unit is mol/l.

The pH and concentration of H^+ are presented in the following tables.

Table 1. pH value and H^+ concentration for solution HCl(0.1M) +Pt

Filtration	pH Retentate	[H+] Retentate	pH Permeate	[H+] Permeate
25-30 º C, 6-8 BAR	0,92	0,12	1,03	0,09
25-30 º C, 11-12BAR	0,95	0,11	0,98	0,10
25-30 º C, 20-22 BAR	0,92	0,12	0,96	0,11
35-40 º C, 6-7 BAR	0,95	0,11	1,04	0,09
35-40 º C, 13-15 BAR	0,91	0,12	0,99	0,10
35-40 º C, 19-20 BAR	0,88	0,13	1,06	0,09

Table 2. pH value and H+ concentration for solution HCl(1M) +Pt

Filtration	pH Retentate	[H+] Retentate	pH Permeate	[H+] Permeate
25-30 º C, 4-5 BAR	0,01	0,98	0,02	0,95
25-30 º C, 11-12 BAR	0	1,00	0	1,00
25-30 º C, 20-25 BAR	0,04	0,91	0,03	0,93
35-40 º C, 2-3 BAR	0,02	0,95	0,05	0,89
35-40 º C, 11-13 BAR	0	1,00	0,04	0,91
35-40 º C, 24-26 BAR	0	1,00	0	1,00

Table 3. pH value and H+ concentration for solution HCl(0.1M) +Pt+Cu

Filtration	pH Retentate	[H+] Retentate	pH Permeate	[H+] Permeate
25-30 º C, 6-7 BAR	1,01	0,10	0,91	0,12
25-30 º C, 13-14 BAR	1,07	0,09	0,95	0,11
25-30 º C, 21-23 BAR	0,94	0,11	0,92	0,12
35-40 º C, 4-5 BAR	1	0,10	0,97	0,11
35-40 º C, 11-13 BAR	0,93	0,12	0,89	0,13
35-40 º C, 19-22 BAR	0,94	0,11	0,86	0,14

From these results it can be concluded that concentration of H^+ in the retentate is slightly higher than in the retentate. Compared to the blank filtrations with HCl, results are very similar. So as proton concentration is not changing when adding platinum, the catalyst is probably not forming compounds with H^+.

3.4.2. Ion measurement

IC-methrom gives information about conductivity. The more concentrated a solution is, the higher the conductivity is. In most cases it is a proportional relationship. As the ion concentration increases, the conductivity increases. Some solutions have a limit to how conductive it can be, once that point is reached, increasing the solution concentration will actually lower conductivity. This is observed in sulfuric acid solutions.

Ion measurements have been made to know about chlorides concentration in permeate and retentate. What is sought is to confirm that platinum is forming compounds with Cl^-. It is already known that platinum concentration is higher in retentate, so if it is really forming chloride complexes, there should also be more concentration of Cl^- in the retentate.
For the measurement, samples were diluted 100 times.

The samples measured are from: long filtration solution (190 min); 35-40 ºC, 19-20 bar HCl (0,1M) + Pt; and 35-40 ºC,19-22 bar HCl (0.1M)+Pt+Cu.

Table 4. Conductivity value for different retentates and permeates diluted 10 times

		Conductivity (µS /cm)
3 hours filtration (190 min)	Retentate	67,64
	Permeate	52,7
Solution that contains Pt	Retentate	67,39
	Permeate	47,65
Solution that contains Pt + Cu	Retentate	67,02
	Permeate	62,36

Results from Table 4 show that there is higher concentration of Cl- in the retentate than in permeate, this confirms the theory that platinum is forming chlorine compounds and that these compounds are being retained.

3.5. Fouling

Membrane contamination is usually called fouling. Membrane fouling is characterized by the accumulation of feed stream components onto the surface of or within the pores of a membrane. This contamination causes higher energy use, higher cleaning frequency, shorter life span of the membrane and a decrease in permeate flux.

Membrane fouling is often characterized in the laboratory by flux decline experiments, where an increase in transport resistance due to accumulation of foulants on and/or in a membrane is manifested as a decrease in permeate flux with filtration time at fixed transmembrane pressure.

This decrement of permeate flux is what is used in the experiments to measured fouling in the membrane after different filtrations.

To carry out this experiments filtration of distilled water were made before and after filtration with solutions that contained platinum and cooper particles. These water filtrations where made maintaining same conditions. The idea is to compared the volume of the permeate filtered in the filtration before experiments with Pt and the volume of the permeate filtered in the filtration after experiments with Pt. As both of them are made during 20 minutes of filtrations, flux can be calculated. So the final value that is compared is the flux (ml/min) of the permeate. If the flux is higher for the filtrations of before, then there is fouling that has appeared.

$$\%\ Decrement = 1-(Before\ flow\ (ml/min)/After\ flow\ (ml/min)) \quad \text{[Ec. 2]}$$

The different experiment to measure fouling are not rigorous because they were made between filtration of Pt solution and not all of them were made at exactly same pressure.

Before and after filtrations were made for 20 minutes, a flow of 2,5 ml/min and 15 bars for tables 5 and 6; and 10 bars for tables 7 and 8.

Table 5. Decrement of flux after filtrations of solution HCl (0.1M) + Pt.

	VOLUME FILTERED (ML)	Flow ml/min
Before filtration	7,4	0,37
After 120 minutes of filtration	6,3	0,31
After 240 minutes of filtration	5,8	0,29
Decrement of permeate flux (%)	21,6	

Table 6. Decrement of flux after filtrations of solution HCl (1M) + Pt.

	VOLUME FILTERED (ML)	Flow ml/min
Before filtration	5,8	0,29
After 120 minutes of filtration	5,2	0,26
After 240 minutes of filtration	5	0,25
Decrement of permeate flux (%)	13,8	

Table 7. Decrement of flux after filtrations of solution HCl (0.1M) + Pt + Cu

	VOLUME FILTERED (ML)	Flow (Ml/min)
Before filtration	6	0,3
After 120 minutes of filtration	5,6	0,28
After 240 minutes of filtration	5	0,25
Decrement of permeate flux (%)	16,67	

Table 8. Decrement of flux after long filtration of solution HCl (0.1M) + Pt + Cu

	VOLUME FILTERED (ML)	Flow (Ml/min)
Before filtration	5,7	0,285
After 190 minutes filtration	3,8	0,19
Decrement of permeate flux (%)	33,33	

Average of decrement of permeate flux for six non-continuous filtrations of 40 minutes: 17,02 %.
Decrement of permeate flux for continuous filtration of 190 minutes: 33,33%
So it can be considered to be fouling during non-continuous filtrations of 240 minutes of HCl + Pt, that reduced the permeate flux almost a 20%. While during a continuous filtration is goes higher to 33,33 %.

Nevertheless, in this project we are looking for retaining Pt complexes. The membrane is not having the behavior expected for filtrations of 40 minutes, where if we consider the fouling to be an eighth of the total (240 min), i.e. 3,33% of decrement of the permeate flux. This value can be considered as non-fouling at all. While for long filtrations of at least 190 minutes is can be seen to appeared a decreased of the permeate flux of the 33%.

Fouling means, among other things, a decrement in permeate flux because of smaller pores size. The longer the filtrations take place, the higher the fouling is. For these reason the Platinum is going to be easily retained by the membrane when the fouling is higher. If taking a look at the behavior of the platinum concentration in permeate and retentate in long filtration (Fig. 20) it can be easily seen that Pt concentration in permeate stabilize before heading 100 minutes of filtration and it continues to be in same value for the next 100 minutes, while the Pt concentration of the retentate start increasing faster than before.

4. Discussion

After conducting the experiments, it can be concluded that this type of filtration with the membrane used does manage to reach a more concentrated solution of platinum. As expected, the higher the pressure and temperature are, the faster the filtration runs. The volume of permeate for the same filtration time increases the higher the temperature and pressure are.

No apparent differences have been found in the filtrate due to the increment of the acidity; the membrane is theoretically manufactured to withstand acid solutions. However, some discrepancies have been found regarding the pore size. The manufacturer indicates that the product has an approximate pore size of 150-200 Da, which would be more than enough to slow the passage of a platinum compound such as Platinum (II) Chloride (265.99 Da). It is also indicated that the membrane has 98% rejection at $MgSO_4$, while experimental value was 74% (section 6.1.). This means that it is more likely that the pore size will be larger for this membrane than it theoretically should be. For this reason, platinum appears in the filtrate.

Regarding the addition of another metal compounds, as can be read in the section 3, tests have been carried out with solutions containing only platinum and solutions that also contain another metal, such as copper. In tests with platinum, for the best conditions, feed concentration increases up to double in less than an hour; while for the solution with copper the increment of the concentration is 1.7 times the initial one. Therefore, the external metal is interfering and makes the platinum takes longer to concentrate.

On the other hand, a slight stability in the concentration of platinum in the permeate is observed in some tests. For this reason, a longer filtration duration has been carried out in order to see its behavior. In Fig. 20 it is seen how the platinum concentration in the permeate is clearly stabilized, while on the retentate it begins to grow rapidly. This could be due to an increment in the fouling. Actually, there is a 33% decrease in permeate flow, which apparently is being beneficial to retain platinum complexes.

The concentration reached in the long filtration in the retentate can not be compared with the previous ones since when making a filtration of this duration it has been necessary to increase the volume of the feed almost three times. When having more volume, it takes more time to concentrate the dissolution if the rest of the conditions are maintained

On balance, there are advantages and disadvantages that affect the recovery of the platinum catalyst by nanofiltration.

The first disadvantage is that the membrane is not fulfilling the expectations, this supposes that the increment of the concentration of platinum is taking longer. In addition, the control of temperature and pressure are complicated. If the solution is left filtering without anyone supervising, the pressure would increase to not recommended values. The equipment is not prepared to withstand very high pressures, which obligates someone to watch out the unit carefully during running tests. On the other hand, the cell is held by screws and the pipes of the solutions are hooked to the cell by snap fit, what does not guarantee that they will support extreme conditions. In fact, during the experimental process the pressure increased a lot and there were leakage zones of the solution, having to stop the leakage happened several times.

Another thing to keep in mind is that in the middle of this project it was necessary to make a change of unit. At the beginning it was used a membrane that did not retain the catalyst at all, when theoretically it should. The rejection percentage of experimental $MgSO_4$ did not even reach 50%. It was concluded that the membrane had deteriorated with the pass of time appearing some cracks, despite only being two years old. With the purchase of a new one with same characteristics, a greater rejection and better results were obtained. But still They have never become the expected ones. In spite of this, the membrane manages to isolate the platinum compounds and reach a more concentrated solution. The fouling is being beneficial to the filtration, since it makes the pores smaller and facilitates the retention. This is useful for several hours experiments, however if It is wanted to perform the experiment for days, the fouling could become harmful.

In conclusion, although it is being reached the desired goal that is to obtain a more concentrated solution of the catalyst, there are conditions that are holding back better results. The equipment, especially the membrane, is limiting that greater metal insulation can be achieved. If what is being looked for is to recover all the metal, then this method is useless. If it is indifferent that there is some of the metal that can not be concentrated and is lost in the permeate, then filtration with this equipment could be carried out for several hours in order to obtain a more concentrated solution.

5. References

[1] **Daniel J. Miller, Sirirat Kasemset, Donald R. Paul, Benny D.Freeman, "Comparison of membrane fouling at constant flux and constant transmembrane pressure Conditions" Department of Chemical Engineering, Center for Energy and Environmental Resources, and Texas Materials Institute, The University of Texas at Austin, 200E. Dean Keeton Street, Stop C0400, Austin, TX 78712, USA**

[2] **Peter Lund, "Recovery tests from residual catalyst incl. experiments with fluidised bed operation and construction of a "proof of concept" prototype unit completed" Jun. 2017, University of Southern Denmark**

[3] **Bazzarelli F., Giorno L., Piacentini E. (2015) Porous Membranes. In: Drioli E., Giorno L. (eds) Encyclopedia of Membranes. Springer, Berlin, Heidelberg**

[4] **Lenntech-Nanofiltration-Membranetechnology, "https://www.lenntech.com/processes/pesticide/nanofiltration/nanofiltration.htm"**

[5] **User Manual, Pump P 2.1S/P 4.1S, Azura, Knuer**

[6] **Cross Flow membrane market – Grwthm Future Prospects and Competitive Analysis by 2021, "https://millioninsights.blogspot.dk/2018/04/cross-flow-membrane-market.html"**

[7] **Contributing Writer, "The effect of Solution Concentration on Conductivity" March, 2018 "https://sciencing.com/effect-solution-concentration-conductivity-5942108.html"**

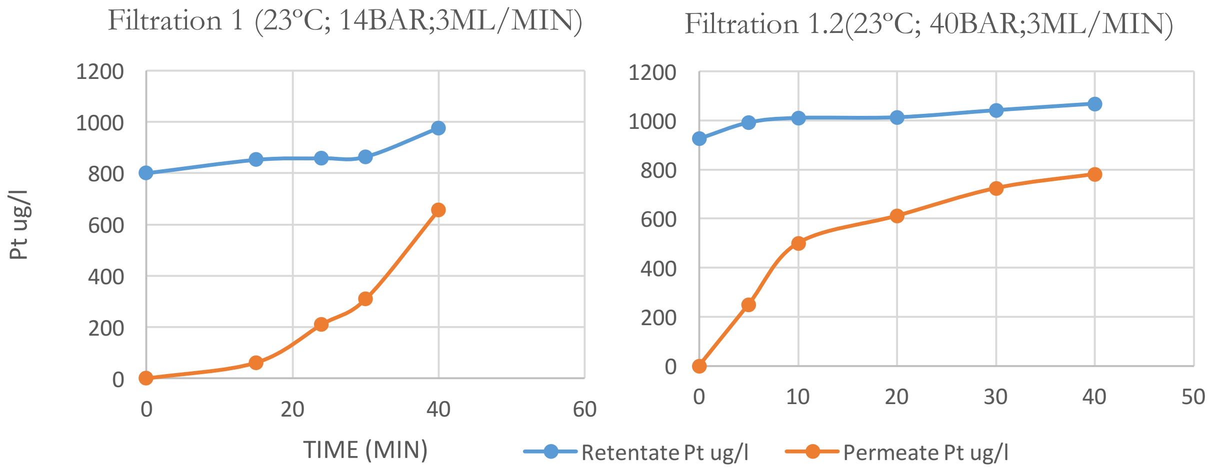
[8] **Ge osmonics, flat sheet membrane, duracid NF, TFC, NF, 305 X 305 MM "https://www.sterlitech.com/nanofiltration-nf-membrane-ymkhsp3001.html"**

6. Appendix

6.1. Problems with the first membrane

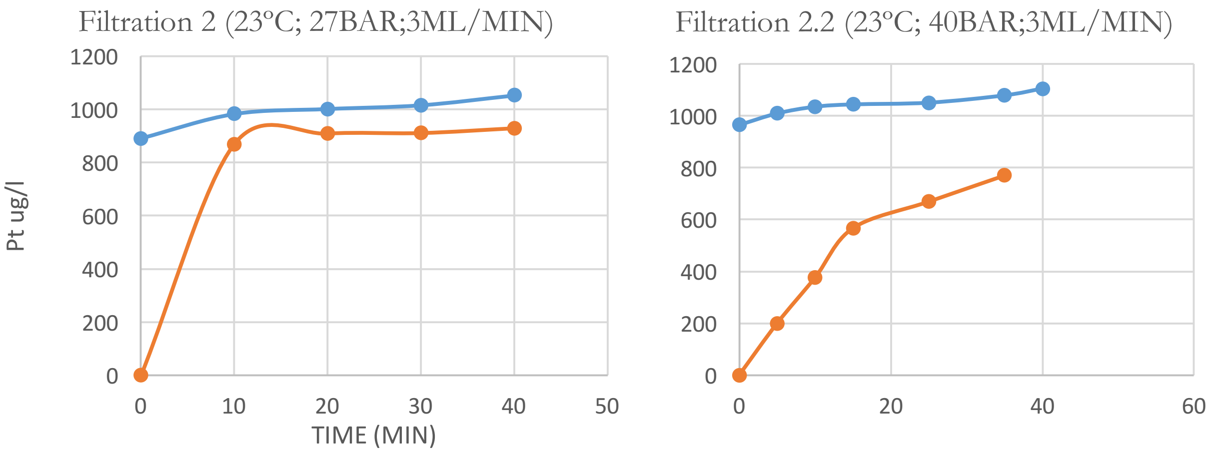
During the development of the project there was a change of membrane. After first experiments with platinum solutions it was found that membrane wasn't retaining platinum complexes at all.

As can be seen in Figures A.1, A.2 and A.3 the concentration in the retentate and the permeate was too similar, even thought the retentate was still over. These filtrations only took 40 minutes and it can be clearly seen that concentration is increasing very slowly for the retentate but very quickly for the permeate, so probably after less than an hour it might be the same.
These filtrations were repeated for low and medium pressure in order to assure that there was no error in the first try


Filtration 1 (23ºC; 14BAR;3ML/MIN)

Filtration 1.2(23ºC; 40BAR;3ML/MIN)

Figure A.1. Graphic of Pt concentration vs. Time for filtration 1 and 1.2


Filtration 2 (23ºC; 27BAR;3ML/MIN)

Filtration 2.2 (23ºC; 40BAR;3ML/MIN)

Figure A.2. Graphic of Pt concentration vs. Time for filtration 2

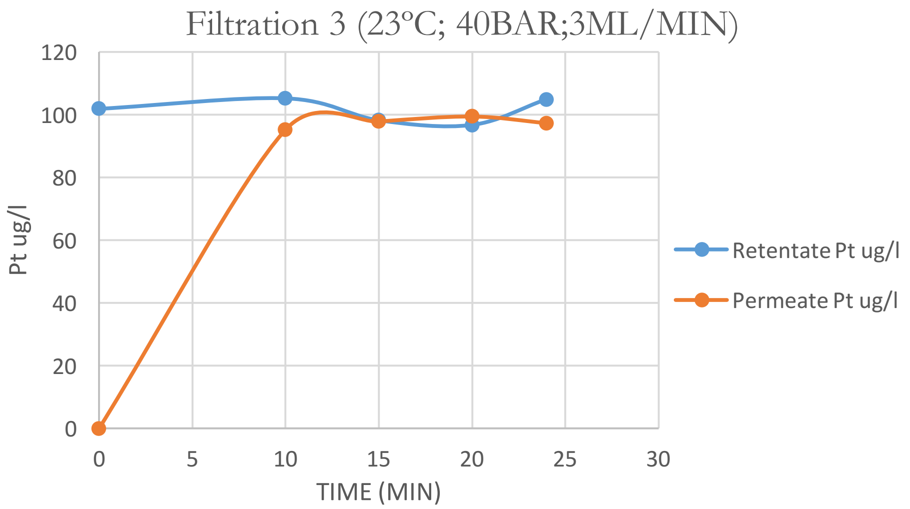


Figure A.3. Graphic of Pt concentration vs. Time for filtration 3

After these filtrations a rejection test with $MgSO_4$ was made. The membrane was supposed to have a rejection of the 98%.

$$\% \, Rejection = \frac{Feed \ Conductivity - Permeate \ Conductivity}{Feed \ Conductivity} \cdot 100 \qquad [Ec \ 3.]$$

Feed Conductivity	Conductivity
10,9 mS/cm	6,29 mS/cm

%Rejection = 42,29%

This $MgSO_4$ rejection value is not even close to the theoretical one. So it can be conclude that membrane had been deteriorated.

With the purchase of the new membrane a new Rejection test was done obtaining:

Feed Conductivity	Conductivity
24,9 mS/cm	6,29 mS/cm

%Rejection = 74,73 %

This rejection still doesn’t achieve the theoretical 98%, but afterwards the project was developed with this membrane

6.2. Values of the graphics presented in section 3.2., "Blank Experiments".

Table A.1. Data from Figure 8 and 9

	Pressure (bar)		
Feed flow (ml/min)	11 to 16	22 to 27	38 to 45
1	1	2,8	6
2	1	3,4	5,2
3	1,2	3,2	6
4	1,7	3,6	5,7
5	1,6	3	6
6	1,5	3,3	5
7	1,3	3	5,2

Table A.2. Data from Figure 10

PRESSURE 12-16 BAR	PERMEATE VOLUME (ML)		
Feed Flow (ML/MIN)	40-42 ºC	53-55 ºC	63-65 ºC
1	2,75	3,8	4,2
2	3	3,4	4
3	2,8	3,2	4
4	3	3,5	4
5	2,5	3	3,8
6	3	3,3	3,5
7	3,2	4	4,3

Table A.3 Data from Figure 11 for low pressure and low T

Pressure 20-25	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,071	0,085
2	0,117	0,123
3	0,083	0,123
4	0,087	0,105
5	0,071	0,081
6	0,071	0,087
7	0,079	0,087

Table A.4 Data from Figure 11 for high pressure and low T

Pressure 45-52	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,105	0,123
2	0,11	0,117
3	0,079	0,098
4	0,069	0,093
5	0,074	0,107
6	0,085	0,093
7	0,074	0,079

Table A.5. Data from Figure 11 for low pressure and high T

Pressure 20-25	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,065	0,117
2	0,095	0,102
3	0,079	0,129
4	0,06	0,093
5	0,071	0,107
6	0,059	0,105
7	0,058	0,120

Table A.6. Data from Figure 11 for high pressure and High T

Pressure 45-52	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,078	0,117
2	0,093	0,107
3	0,062	0,117
4	0,059	0,105
5	0,056	0,135
6	0,066	0,100
7	0,065	0,110

Table A.7. Data from Figure 12 for low pressure and low T

Pressure 20-25	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,708	0,776
2	0,692	0,813
3	0,933	1,000
4	0,912	0,977
5	0,933	1,000
6	0,871	0,977
7	0,741	0,933

Table A.8. Data from Figure 12 for high pressure and low T

Pressure 38-48	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,692	0,794
2	0,724	0,813
3	0,708	0,776
4	0,708	0,912
5	0,741	0,933
6	0,794	0,955
7	0,759	0,977

Table A.9. Data from Figure 12 for low pressure and high T

Pressure 20-25	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,741	1,000
2	0,776	0,794
3	0,871	0,912
4	0,759	0,891
5	0,871	1,000
6	0,776	0,955
7	0,851	1,000

Table A.10. Data from Figure 12 for high pressure and high T

Pressure 38-48	[HCl] (MOL/L)	
Feed Flow (ML/MIN)	[HCL] PERMEATE	[HCL] RETENTATE
1	0,813	0,977
2	0,813	0,871
3	0,794	0,977
4	0,832	1,000
5	0,891	0,955
6	0,912	0,955
7	0,851	0,933

6.3. Values of the graphics presented in section 3.3., "Filtrations of Pt solutions".

Table A.11. Data from Figure 13 and 14 for 25-30 °C, 6-8 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,0465
10	0,062	1,0625
25	0,151	1,306
40	0,2715	1,4515

Table A.12. Data from Figure 13 and 14 for 25-30 °C, 11-12 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,061
10	0,076	1,2665
25	0,147	1,377
40	0,3025	1,4805

Table A.13. Data from Figure 13 and 14 for 25-30 °C, 20-22 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,0465
10	0,1005	1,255
25	0,373	1,402
40	0,384	1,552

Table A.14. Data from Figure 13 and 14 for 35-40 ºC, 6-7 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,071
10	0,0915	1,26
25	0,232	1,3055
40	0,4235	1,4755

Table A.15. Data from Figure 13 and 14 for 35-40 ºC, 13-15 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,051
10	0,2615	1,3255
25	0,312	1,426
40	0,4085	1,7755

Table A.16. Data from Figure 13 and 14 for 35-40 ºC, 19-20 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,045
10	0,327	1,2515
25	0,336	1,5625
40	0,385	1,9155

Table A.17. Data from Figure 15 and 16 for 25-30 ºC, 4-5 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,061
10	0,0555	1,0735
25	0,1275	1,2865
40	0,2515	1,471

Table A.18. Data from Figure 15 and 16 for 25-30 ºC, 11-12 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,033
10	0,065	1,2265
25	0,1765	1,4015
40	0,3115	1,489

Table A.19. Data from Figure 15 and 16 for 25-30 °C, 20-25 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,065
10	0,116	1,276
25	0,369	1,381
40	0,3965	1,529

Table A.20. Data from Figure 15 and 16 for 35-40 °C, 2-3 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,06
10	0,12	1,2415
25	0,2365	1,3215
40	0,317	1,4595

Table A.21. Data from Figure 15 and 16 for 35-40 °C, 10-15 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,051
10	0,2795	1,351
25	0,323	1,4045
40	0,356	1,726

Table A.22. Data from Figure 15 and 16 for 35-40 °C, 22-23 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	1,051
10	0,3325	1,225
25	0,3355	1,6
40	0,366	1,945

Table A.23. Data from Figure 17 and 18 for 25-30 °C, 6-7 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	0,4115
20	0,092	0,481
40	0,1028	0,5852

Table A.24. Data from Figure 17 and 18 for 25-30 °C, 12-13 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	0,4065
20	0,117	0,481
40	0,139	0,6006

Table A.25. Data from Figure 17 and 18 for 25-30 °C, 21-23 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	0,4125
20	0,115	0,493
40	0,1185	0,616

Table A.26. Data from Figure 17 and 18 for 35-40 °C, 4-5 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	0,4085
20	0,095	0,4845
40	0,1205	0,6415

Table A.27. Data from Figure 17 and 18 for 35-40 °C, 11-13 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	0,4115
20	0,118	0,566
40	0,1265	0,655

Table A.28. Data from Figure 17 and 18 for 35-40 °C, 19-22 BAR

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	0,406
20	0,1265	0,5805
40	0,131	0,6835

Table A.29. Data from Figure 19

Cu Concentration (mg/L)	25-30 °C; 6-7 bar	25-30 °C; 12-13 bar	25-30 °C; 21-23 bar	35-40 °C; 4-5 bar	35-40 °C; 11-13 bar	35-40 °C; 19-22 bar
Permeate	57,4	52,7	58,2	60,2	50,37	53,2
Retentate	63,3	68,05	66,9	63,9	65,3	64,9

Table A.30. Data from Figure 20

Time (min)	Pt in Permeate (mg/L)	Pt in Retentate (mg/L)
0	0	0,4115
20	0,096	0,5115
50	0,1265	0,53
70	0,1455	0,539
100	0,137	0,56
130	0,1295	0,5715
160	0,131	0,616
190	0,131	0,691