Master in Chemical Engineering

Treatment of Contaminated Groundwater by Reverse Osmosis

Master Thesis

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July 2008

Acknowledgements

I would like to thank Doc. Dr. Ing. Martin Kubal for the opportunity to to hold a master's thesis in the area of groundwater treatment, for the orientation and suggestions for improvement throughout the work.

I would like to thank also to Ing. Marek Šír for the valuable assistance in the laboratory, the knowledge, motivation, constructive criticism, suggestions and support throughout the laboratory work and writing.

Abstract

This research deals with the utilization of reverse osmosis technology for treatment of contaminated groundwater. The studied landfill is situated in the south of Czech Republic, and it was a serious source of groundwater pollution: chlorinated hydrocarbons, pesticides, nitrites, nitrates, chlorides, heavy metals and other substances.

This thesis has as aim the study of remediation process efficiency, the success of methods for analytical analysis of nitrite and nitrate and the comparison between the spiral wound module (used in the remediation area) and the plate and frame model (used in laboratory experiments). The experiments leading to the optimization of the separation process (quality of permeate) were carried out. The real samples from the given locality were always used.

The remediation process it was conclude during this period, so it was also possible examine the success of these technologies in studied case.

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Notation and Glossary

S	Inlet Flow
P	Permeate Flow
R	Concentrate Flow
$\dot{n}_S$	Molar Flow of Inlet
$\dot{n}_P$	Molar Flow of Permeate
$\dot{n}_R$	Molar Flow of Concentrate
$x_{S\,i}$	Molar Fraction of Compound i in Inlet Flow
$x_{P\,i}$	Molar Fraction of Compound i in Permeate Flow
$x_{R\,i}$	Molar Fraction of Compound i in Concentrate Flow
Θ	Permeability
V_0	Initial Volume
V_R	Volume of Concentrate
J_i	Product Flow Through the Membrane
P_A	Permeability of Solvent A
δ_M	Thickness of Membrane
Δp	Pressures Differential
$\Delta\pi$	Osmotic Pressures Differential
π	Osmotic Pressure
C_i	Concentration of Dissolved Compounds i
R	Universal Gas Constant
T	Temperature
J_j	Salt Flux across RO Membrane
B	Permeability constant
C_{jS}	Salt concentration on Inlet Flow

C_{jP}	Salt concentration on Permeate Flow
R	Rejection Coefficient
ρ_i	Density of compound solvent i
C_{ip}	Concentration of compound i in Permeate
C_{io}	Concentration of compound i in Inlet Flow in boundary layer
J_v	Permeate flux
K	Mass transfer coefficient
C_{ib}	Concentration of compound i in Inlet Flow before boundary layer
S	Observed Retention
M	Concentration Polarization
µC	Conductivity of Concentrate
pH C	pH of Concentrate
µP	Conductivity of Permeate

List of Acronyms

MST	Membrane Separation Technologies
RO	Reverse Osmosis
CF	Concentration Factor
TDS	Total Dissolved Solids
UF	Ultrafiltration
EDR	Electrodialysis
AAS	Atomic Absorption Spectrometric
AES	Atomic Emission Spectrometric
TC	Total Carbon
TOC	Total Organic Carbon
TIC	Total Inorganic Carbon

POC	Carbon Volatile Organic Compounds
NPOC	Carbon Non-volatile Organic Compounds
DOC	Dissolved Organic Carbon Compounds
ECD	Electron Capture Detector
PE	Polyethylene

1 Introduction

Removing contaminants from groundwater is now a very important issue in the field of environmental burdens. Membrane separation processes are a very efficient method for remediation of this kind of pollution. Reverse osmosis technologie presents highly efficiency of separation, strongly reduce the level of contamination, often significantly shorten the period of remediation and become economically accessible, which was the main disadvantage in the past.

The studied locality is situated in the south of Czech Republic in Nový Rychnov near Pelmřimov city, and it was a serious source of groundwater pollution: chlorinated hydrocarbons, pesticides, nitrites, nitrates, chlorides, heavy metals and other substances. In the past this landfill was a granite quarry, which the anticipated impermeable, tectonically intact bedrock make it the appropriate location for storage of hazardous industrial waste with a possible capacity of 700 m^3.

Figure 1- Localization of landfill

The existence of the landfill caused the contamination in the soil and groundwater that are threatening sources for drinking water and a river localized near. The remediation work carried out in this area was the first registered by the competent authorities of the state administration as a long-term accident on groundwater. Reverse osmosis technology was used there, and represents a good option for the removal of contaminants from the groundwater in short time.

Figure 2- Landfill of Nový Rychnov

Figure 3 – Technologies used in Nový Rychnov for groundwater remediation

The technologies instaled consists of several steps, pre-treatment units, and in the last the reverse osmosis module. This work focuses on the evaluation of the remediation process, and specifically, for these purposes has been chosen this location, where are the redevelopment of work underway for some time, so it's more easy at this time to discuss about the remediation success.

It was used some samples collected in this landfill for laboratory tests with the purpose of test the best conditions and the separation efficiency of the main groundwater contaminants. The pilot-scale laboratory reverse osmosis module is the type of plate-and-frame module but stills provide a good comparison with the spiral wound type.

The aim of this thesis is study the efficiency of the unit installed in the Nový Rychnov landfill, comparing with the results obtained in the pilot scale laboratory reverses osmosis unit.

2 State of Art

2.1 Membrane Separation Technologies

In recent years, membranes and membrane separation technologies have grown from a simple laboratory tool to an industrial process with considerable technical and commercial impact. Nowadays they have several applications: produce potable water from the sea by reverse osmosis, clean industrial effluents and recover valuable constituents by electrodialysis, fractionate macromolecular solutions in the food and drug industry by ultrafiltration, remove urea and other toxins from the blood stream by dialysis in an artificial kidney, release drugs such as scopolamine, nitro-glycerine, etc.

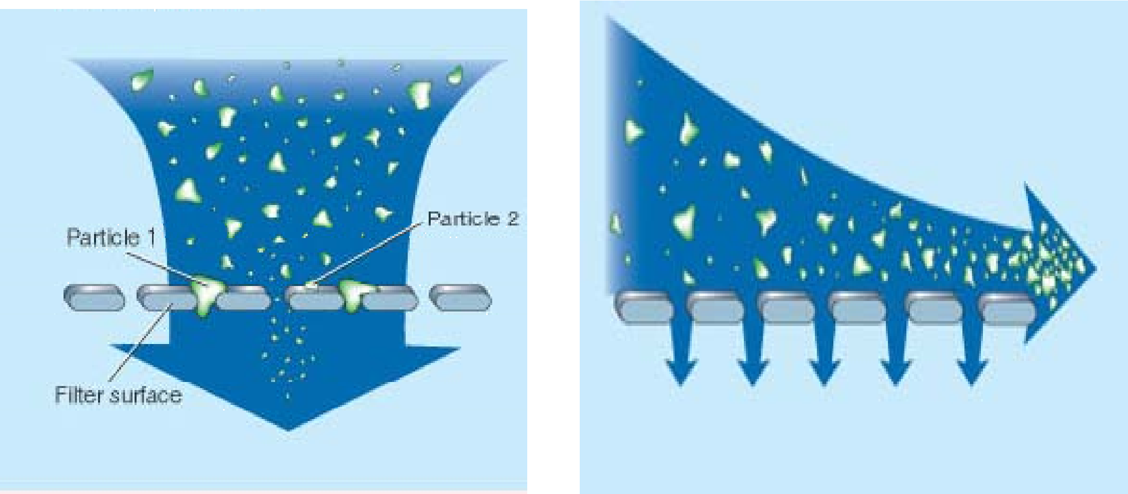
Although membrane processes may be very different in their mode of operation, in the structures used as separating barriers, and in the driving forces used for the transport of the different chemical components, they have several features in common which make them attractive as a separation tool. In many cases, membrane processes are faster, more efficient and more economical than conventional separation techniques.

There are five types of membrane processes which are commonly used in water treatment:

- Micro filtration
- Ultrafiltration
- Nanofiltration
- Reverse Osmosis
- Electrodialysis

Through these processes dissolved substances and/or finely dispersed particles can be separated from liquids. All five technologies rely on membrane transport, the passage of solutes or solvents through thin, porous polymeric membranes.

A membrane is defied as an intervening phase separating two phases forming an active or passive barrier to the transport of matter. Membrane processes can be operated as: **(1) Dead-end filtration** and **(2) Cross-flow filtration**.



(1) (2)

Figure 4- **(1)** Dead-end filtration and **(2)** Cross-flow filtration

Dead-end filtration refers to filtration at one end. A problem with these systems is frequent membrane clogging. Cross-flow filtration overcomes the problem of membrane clogging and is widely used in water and wastewater treatment. The membrane itself is a polymeric coating or extrusion with inverted conical shaped pores. Material passing through the membrane passes unimpeded through the membrane structure, therefore eliminating accumulation of material within the filter (Cheremisinoff, 2002). Some contaminants slowly accumulate on the membrane surface, forming a thin film, during normal operating conditions. This fouling process is normal and causes the filtration rate to slowly decrease with time. The following tables will give you a basic appreciation for the technologies. Table 1 provides a comparison of the factors that affect the performance of the five technologies and Table 2 provides a comparison of membrane structures. Between these two tables, you should get an idea of the operating conditions, membrane structural types, the driving forces involved in separation, and the separation mechanisms.

Table 1- Important factor for the performance of membrane processes (adapted from Cheremisinoff, 2002)

Technology	Driving Force	Influencing Factors			
		Size	Diffusivity	Ionic Charge	Solubility
Microfiltration	**Pressure**	+++	-	-	-
Ultrafiltration	**Pressure**	+++	-	+	-
Nanofiltration	**Pressure**	+++	+	+	-
Reverse Osmosis	**Pressure**	+	+++	+	+++
Electrodialysis	**Electrical**	+	+	+++	-

Table 2- Compares membrane structures (adapted from Cheremisinoff, 2002)

Technology	**Structure**	**Driving Force**	**Mechanism**
Microfiltration	Symmetric microporous (0,02-10µm)	Pressure, 1-5atm	Sieving
Ultrafiltration	Asymmetric microporous (1-20nm)	Pressure, 2-10atm	Sieving
Nanofiltration	Asymmetric microporous (0.01-5nm)	Pressure, 5-50atm	Sieving
Reverse Osmosis	Asymmetric with homogeneous skin and microporous support	Pressure, 10-100atm	Solution diffusion
Electrodialysis	Electostatically charged membranes (cation and anion)	Electrical potential	Electrostatic diffusion

2.2 Mass Balance for MST

We will consider that S will be the inlet flow, P the permeate flow and R the concentrate flow. So the global mass balance is:

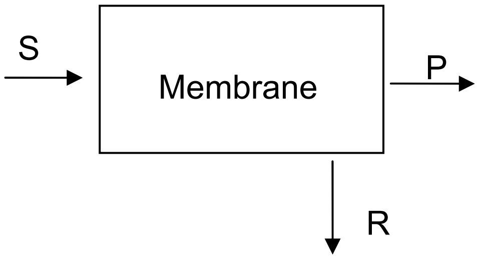


Figure 5: Membrane Flows

$$\dot{n}_S = \dot{n}_P + \dot{n}_R \qquad (2.1)$$

$$\dot{n}_S x_{Si} = \dot{n}_P x_{Pi} + \dot{n}_R x_{Ri} \qquad (2.2)$$

Where the x_S, x_P, x_R ,are used for the molar fraction of each contaminant i.

Permeability, Θ, can be calculated:

$$\Theta = \frac{\dot{n}_P}{\dot{n}_S} \qquad (2.3)$$

We cal also define concentration factor (CF) that is the ratio between the initial volume of water the volume of concentrate.

$$CF = \frac{V_0}{V_R} \qquad (2.4)$$

2.3 Reverse Osmosis

Reverse osmosis is a process which uses a membrane under pressure to separate relatively pure water (or other solvent) from a less pure solution. When two aqueous solutions of different concentrations are separated by a semi-permeable membrane, water passes through the membrane in the direction of the more concentrated solution as a result of osmotic pressure. If enough counter pressure is applied to the concentrated solution to overcome the osmotic pressure, the flow of water will be reversed. Water molecules can form hydrogen bonds in the RO membrane and fit into the membrane matrix. The water molecules that enter the membrane by hydrogen bonding can be pushed through under pressure. Most organic substances with a molecular weight over 100 are sieved out, i.e., oils, pyroxenes and particulates including bacteria and viruses. Salt ions, on the other hand, are rejected by a mechanism related to the valence of the ion. Ions are repelled by dielectric interactions; ions with higher charges are repelled to a greater distance from the membrane surface. Monovalent ions such as chloride ions will not be rejected as efficiently as, for example, divalent sulphate ions. The nominal rejection ratio of common ionic salts is 85 - 98% (Baker, 2004).

The product flow through the membrane is defined as (Strathmann, 1995):

$$J_i = \frac{P_A}{\delta_M}\left[\Delta p - \Delta \pi\right] \qquad (2.5)$$

Where Δp is the difference pressures and $\Delta \pi$ is a value of osmotic pressure differential, P_A is the permeability of membrane for clean solvent A and δ_M is the thickness of membrane. Osmotic pressure is usually calculated from the Van´t Hoff equation.

$$\pi = C_i RT \qquad (2.6)$$

This equation is valid only for small concentration of dissolved components i (up to 1 by weigh percentage).R is the universal gas constant and T the temperature.

As a rule of thumb, the product water flow with constant net applied pressure will increase about 3% for each degree centigrade increase in feedwater temperature. Salt flux through the membrane is also directly proportional to temperature and the ratio of salt flux to water flux is essentially constant at different temperatures. For some of the newer composite membranes, the water and salt permeation coefficients also vary as a function of pH (Porter *et al*, 1989).

The salt flux, J_j, across a reverse osmosis membrane is described by the equation (Baker, 2004):

$$J_j = B(C_{jS} - C_{jP}) \qquad (2.7)$$

Where B is the salt permeability constant and C_{jS} and C_{jP}, are respectively, are the salt concentrations on the feed and permeate sides of the membrane.

The concentration of salt in the permeate solution C_{jP} is usually much smaller than the concentration in the feed C_{jS}, so equation 10 can be simplified to

$$J_j = BC_{jS} \qquad (2.8)$$

We can consider that the water flux is proportional to the applied pressure, but the salt flux is independent of pressure. This means that the membrane becomes more selective as the pressure increases. Selectivity can be measured in a number of ways, but conventionally, it is measured as the salt rejection coefficient R, defined as (Baker, 2004):

$$R = 1 - \frac{C_{jP}}{C_{jS}} \times 100 \qquad (2.9)$$

The salt concentration on the permeate side of the membrane can be related to the membrane fluxes by the expression:

$$C_{jP} = \frac{J_j}{J_i} \times \rho_i \qquad (2.10)$$

where ρi is the density of water (g.cm^{-3}). By combining equations 5 to 12, the membrane rejection can be expressed as:

$$R = \left[1 - \frac{\rho_i \times B}{A \times (\Delta p - \Delta \Pi)}\right] \times 100 \qquad (2.11)$$

Where A is equal to $\frac{P_A}{\delta_M}$.

The rejection differs from that of other inorganic and organic dissolved solids, and membrane manufacturers will provide information and rejection data that are available for their specific membrane. Table 3 shows typical results for a composite membrane when tested on a multicomponent solution. The rejection of the divalent ions such as calcium and sulphate is much better than the rejection of the monovalent ions such as sodium and chloride. If salt passage is defined as product concentration divided by the feed concentration, or one minus rejection, then it can be seen that the salt passage for the divalent ions is about one-fifth of the salt passage for the monovalent ions (Porter *et al.*, 1989).

Table 3- Typical results for ions rejections

Ion	Rejection, %
Calcium	99.62
Sodium	98
Potassium	97.4
Bicarbonate	96.2
Sulphate	99.8
Chloride	98.2
Nitrate	96.4
TDS	98.4

2.4 Concentration Polarization

Reverse osmosis is a cross-flow process and, as in any dynamic hydraulic process, the fluid adjacent to the membrane moves slower than the main stream. While the main stream flow may be turbulent, the layer next to the membrane surface is laminar. This thin, laminar flow film is called the boundary layer. When water permeates through the membrane, nearly all of the salt remains behind in the boundary layer next to the membrane. The salt must then diffuse across the boundary layer and back into the bulk stream. This results in a boundary layer with a salt concentration which is more concentrated than the bulk stream.

The effect has been termed concentration polarization, and it is schematized in the follow figure (Rousseau, 1987):

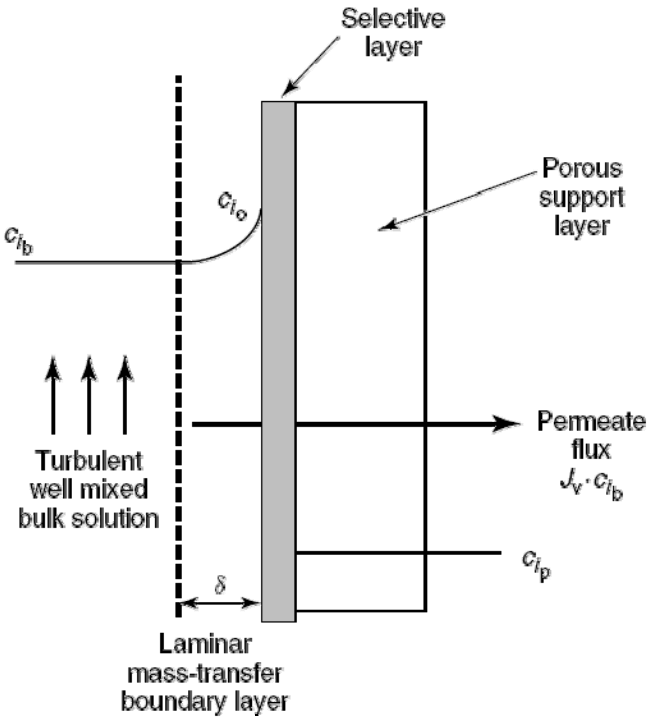


Figure 6- Concentration polarization

Figure 6 shows the concentration profile in stagnant boundary layer. Longitudinal mass transport within the boundary layer is assumed negligible, so mass transport within the film is one-dimensional. In the steady state the solute flux is constant throughout the film and equal to the solute flux through the membrane.

A material balance for the solute in a differential element gives the equation (Belfort *et al.*, 1984):

$$C_{ip} J_v = C J_v - D \frac{dC}{dy} \tag{2.12}$$

The first equality refers to the product condition with the boundary conditions:

$C = C_{ib}$ at $y = 0$

$C = C_{io}$ at $y = \delta$

Integration of equation gives:

$$\frac{(C_{io} - C_{ip})}{(C_{ib} - C_{ip})} = \exp\left(\frac{J_v}{K}\right) \qquad (2.13)$$

Where the mass-transfer coefficient k is defined by $\frac{D}{\delta}$

Equation 15 can be rearranged to give a relation between the observed retention:

$$S = 1 - \frac{C_{ip}}{C_{ib}} \qquad (2.14)$$

And finally the concentration polarization:

$$M = \frac{C_{io}}{C_{ib}} = 1 - S + S\exp\left(\frac{J_v}{K}\right) \qquad (2.15)$$

The concentration polarization can be calculated from the measurement of the concentrate and the permeate flux, when the mass-transfer coefficient for the given reverse osmosis module is known. This model contains many simplifying assumptions known to be incorrect, but the effects of these assumptions on the film-theory predictions are often found to be small. The film model is applicable in turbulent flow beyond the entrance region and in other flow situations resulting in a constant concentration along the membrane surface. It has, however, been used in laminar flow to give average M values over a membrane area, using the appropriate value for K.

Concentration polarization cannot be eliminated, but it can be minimized by decreasing boundary layer thickness. This is done by increasing the flow rate across the membrane surface or introducing turbulence promoters into the feed/reject stream. In order to achieve optimum performance, most membrane manufacturers will recommend a minimum feed rate to or from their elements and a maximum recovery in order to minimize the effects of concentration polarization (Belfort *et al.*, 1984):

2.5 Fouling

The definition is not precise but normally is concerned with a long-term flux decline and, eventually, retention decrease as a result of accumulation of some fouling material. Because another similar processes (gel formation, membrane compaction and membrane hydrolysis), sometimes is hard to distinguish fouling problems. The main difference between fouling and the other processes is that the fouling layer is formed by a different mechanism and is more closely to the membrane surface.

Fouling may be caused by a variety of compounds. These foulants may be classified as: (Belfort *et al.*, 1984)

- Dissolved organics, including humic substances, biological slimes and macromolecules.
- Dissolved inorganic, including inorganic precipitates such as $CaSO_4$, $CaCO_3$, $Mg(OH)_2$, $Fe(OH)_3$, and other metal hydroxides.
- Particulate matter.

2.6 Membrane Modules

The tubular RO membranes are among the oldest use industrially. Subsequently the development of plate and frame; spiral wound and hollow fine fiber modules were made giving higher effective membrane area per unit volume of module space. All these have different hydrodynamic characteristics, leading to the advantages and disadvantage in there various applications, as show in table 4.

Table 4- Comparison of different types of module configurations (adapted from Tiwari *et al.*, 2003)

Technical Parameters	**Spiral Wound**	**Hollow Fine Fibber**	**Plate and Frame**	**Tubular**
Compactness (m^2/m^3)	++	+++	+	-
Ease of cleaning: **--Insitu** **--Back Flush**	+++ -	- +	+ -	++ -
Degree of pretreatment required	+	-	+	+++
Pressure Drop	++	+	-	+++
Dead Volume (m^2/m^3)	+	+++	+	-
Cost of module	+++	++	+	-
Recovery per element (%)	10-25	30-60	2-3	0.2-2

3 Technical Description

3.1 Description of Reverse Osmosis Technologies used in Nový Rychonv

This was the first reverse osmosis spiral module implemented in Czech Republic to treatment of contaminated groundwater. In this section is presented a brief resume of this technology.

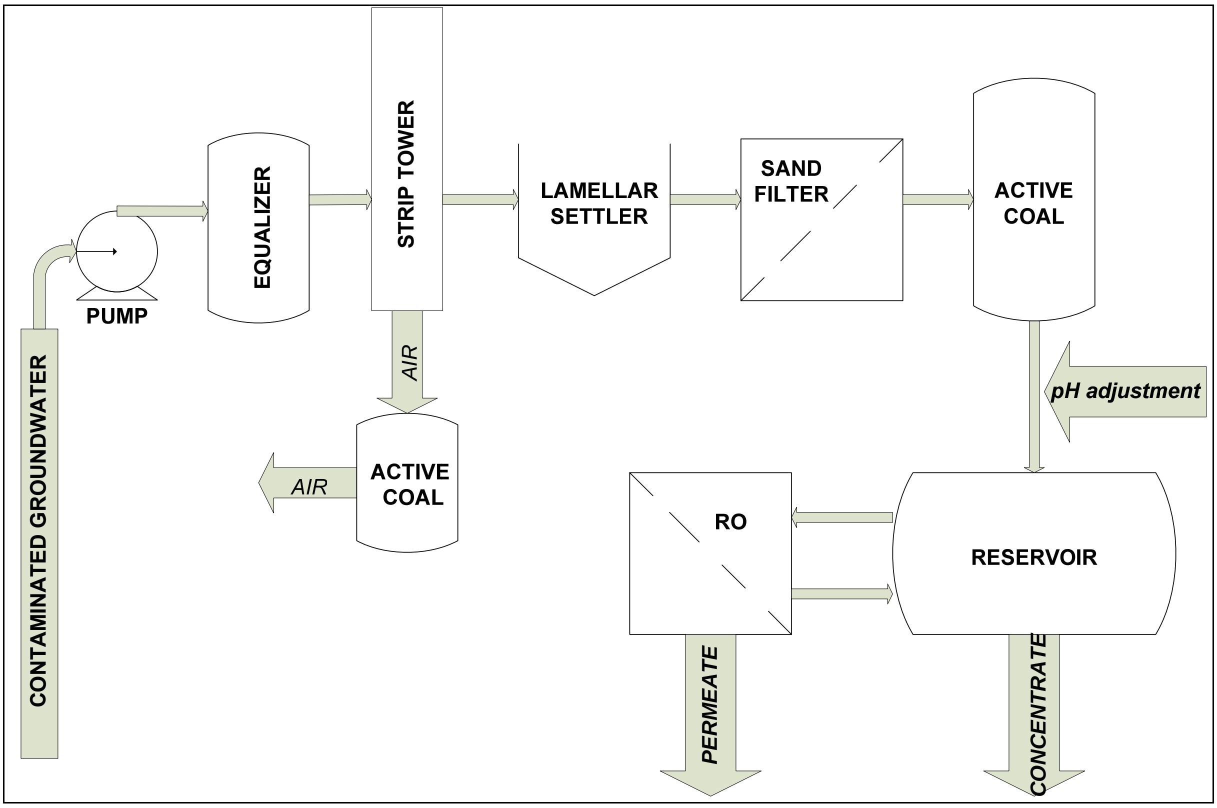


Figure 7- Nový Rychnov reverse osmosis installation

Water is pumped from the remediation of several boreholes, which are located in landfill area, using submergible pumps. The contaminated water is sucked through a pipe into the equalization tank with a capacity of 10 m^3.This storage serves to offset any concentration fluctuations and to ensure equitable flow for the next technological steps. The first water treatment process is the stripping column. Stripping column is used for the removal of volatile organic compounds. The water trickles through the small particles of the fill in the column to the tank. The air (flow 960 m^3.h^{-1}) comes through the column in contra-flow direction.

Then this air with volatile contaminants flows through the tank with activated carbon, when these contaminants are sorbed. If the sorption capacity of carbon is depleted it has to be replaced.

The following step is the separation of solid particles, such as sand particles. The sludge from this step is collected and then it is treated as hazardous waste. The elimination of non-volatile organic substances is very effective with sorption in activated charcoal. In order to avoid scaling hydrochloric acid is added in the pipeline for activated charcoal, which regulates the pH of the solution to slightly acidic.

Schedule of RO equipment is evident in Figure 11. The RO is carried out in a spiral wound module, the operating pressure is 30 bars and the station works in batch mode. This is the optimum pressure found to have lower energy consumption with cycle operation time acceptable. This creates two flows: permeate, which is deposited again in the landfill surroundings, and the second is the concentrate. Concentrate goes back into the tank, which is continuously deposit for water storage, and a progressive deposit for concentrate flow in order to achieve the prescribed conversion (90%). When the conversion is achieved the concentrate is removed to a treatment unit outside the landfill.

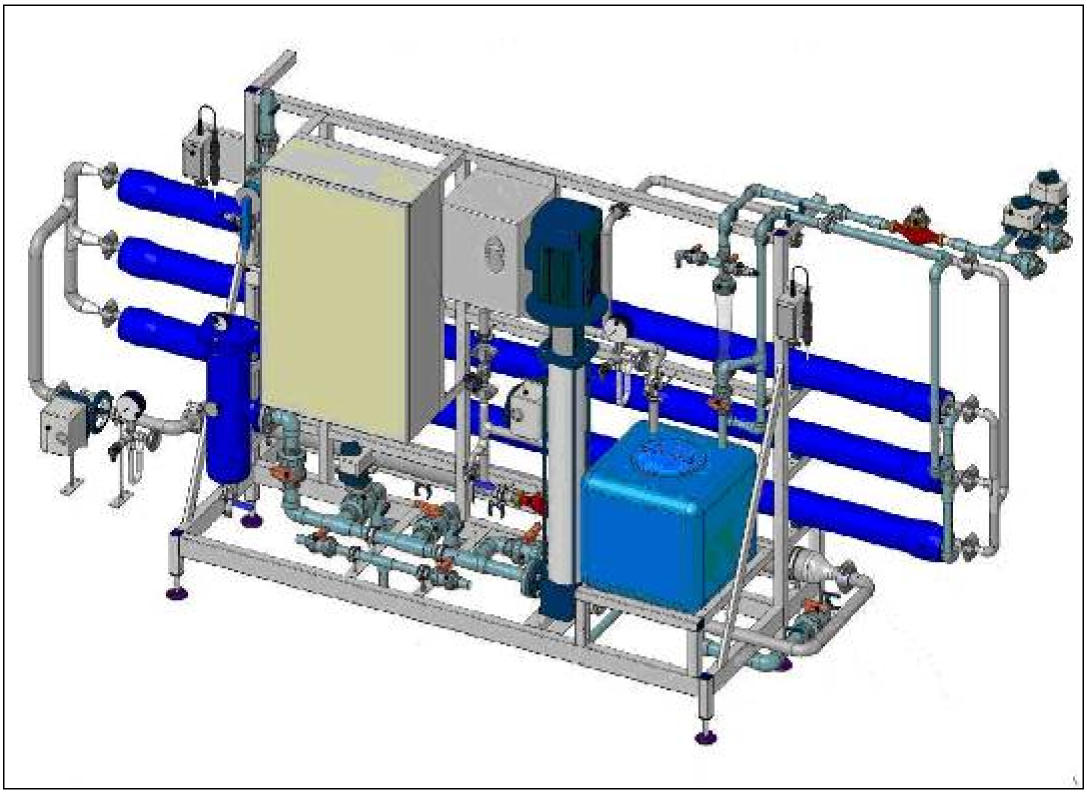


Figure 8- Osmosis Reverses Module with spiral wound configuration

The details about the most relevant units in the technologies used in Nový Rychnov and the boreholes localization map is in Annex 2.

3.2 Reverse Osmosis Module

In the laboratory tests we use a modified version of Plate and Frame modules with single central bolt tie rod in disc tube, LAB M20, that was developed by Danish Sugar Corporation and ROCHEM Company. This module has a total area of 0,348 m^2 divided for twenty membranes HR98PP - ALFALAVAL (DSS). These thin film composite membranes (acitve layer polyamide, suporte layer polysulfone) can be used in a wide range of pH (1-13) and have rejection higher than 96% (1). Working pressure in the system is assured by a piston pump and the unit operates in the range of 0-80 bar pressure. Membrane module is necessary to cooling during the process. It is built exchanger liquid-liquid, which is cooled with tap water, from which water is then drained into the sewer system. It is necessary to maintain piston pumps during the operations wet, which is another supply of tap water.

(1) > 96 % NaCl rejection based on 0,2% solution, 16-40 bar, 25 °C.

This module includes:

- Module plate and frame.
- Piston pump.
- Barometer.
- Valves for pressure control.
- A vessel for inlet and concentrate with a volume of 15 l.
- Tubes in polyethylene (PE) for permeate.
- Tubes in PE for recycling of concentrate stored in the vessel.

Figure 9: RO module - DSS Labstak M20

There were made several tests, where the pressure was varying and the temperature was constant. During the experiences it was measured proprieties like temperature, pH and conductivity of inlet water, permeate and concentrate. During the tests we measured also, each 2 l of permeate, the time necessary for collect this volume, the conductivity and the temperature of permeate and concentrate. We measured also the time to collect 100 ml of permeate.

After the experiments the cleaning of module is an essential step for keep the equipment working with a good performance. Usually the membrane was cleaned only by tap water, but sometimes to provide a deep cleaning or when the inlet solution had a very high concentration in pollutants it was added to the water Ultrasilu solution. The solution is left circulate for a period of approximately 10 minutes. Thereafter, the whole system is cleaned again with tap water. Sometimes was added also a solution of HCl, with a pH of about 2, for a period of 10 to 15 minutes. To stabilize the pH after this solution it was used tap water again.

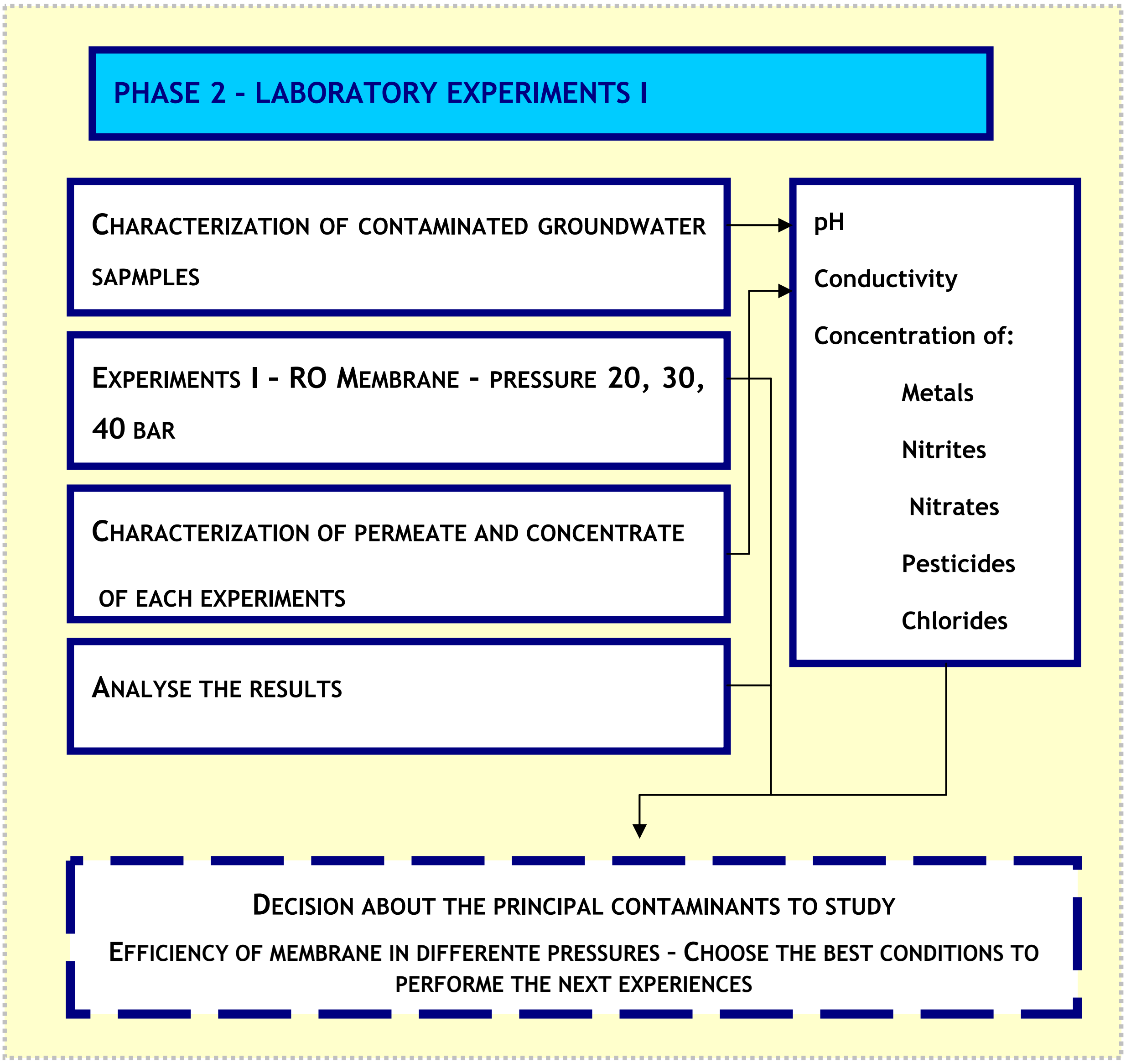
The schedule bellow will make a resume about the way that the entire project was prepared and also described how techniques were used for samples analysis:

PHASE I - PREPARATION PHASE

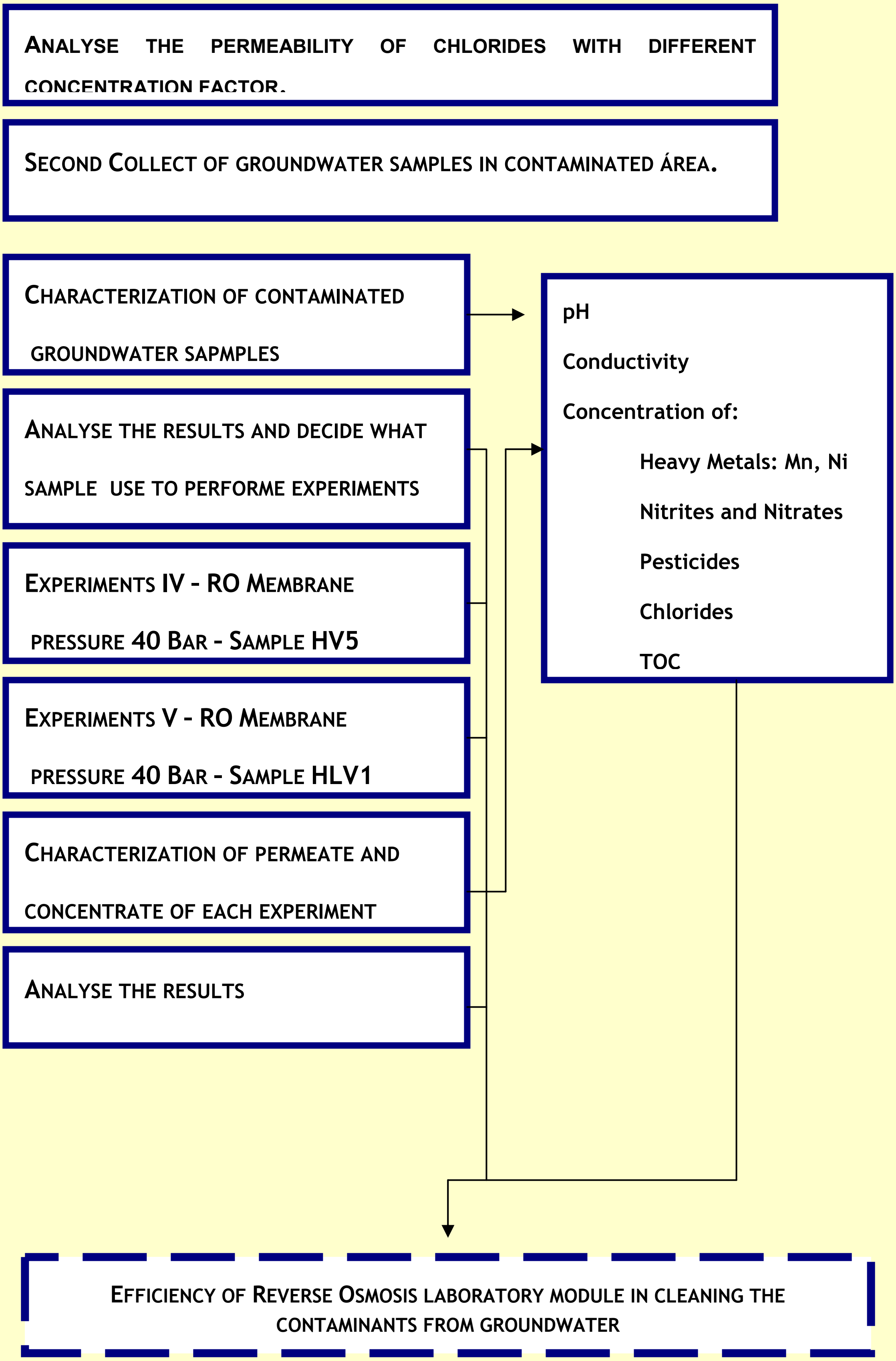
DEFINITION OF THE GOALS

THEORETICAL BACKGROUND

COLLECT GROUNDWATER SAMPLES IN CONTAMINATED



PHASE 3 - LABORATORY EXPERIMENTS II



ANALYSE THE PERMEABILITY OF CHLORIDES WITH DIFFERENT CONCENTRATION FACTOR.

SECOND COLLECT OF GROUNDWATER SAMPLES IN CONTAMINATED ÁREA.

CHARACTERIZATION OF CONTAMINATED GROUNDWATER SAPMPLES

ANALYSE THE RESULTS AND DECIDE WHAT SAMPLE USE TO PERFORME EXPERIMENTS

EXPERIMENTS IV - RO MEMBRANE PRESSURE 40 BAR - SAMPLE HV5

EXPERIMENTS V - RO MEMBRANE PRESSURE 40 BAR - SAMPLE HLV1

CHARACTERIZATION OF PERMEATE AND CONCENTRATE OF EACH EXPERIMENT

ANALYSE THE RESULTS

pH

Conductivity

Concentration of:

- Heavy Metals: Mn, Ni
- Nitrites and Nitrates
- Pesticides
- Chlorides
- TOC

EFFICIENCY OF REVERSE OSMOSIS LABORATORY MODULE IN CLEANING THE CONTAMINANTS FROM GROUNDWATER

4 Results Discussion

In this chapter it will be present and discuss the results obtained in the different phases of the project work. Obviously, it is going start with phase II, because it was in this phase that the experimental work started.

4.1 Laboratory experiments I

After collect the groundwater sample in the field, without any RO pre-treatment, the experiments in laboratory started. The groundwater collected it was a mix of several control boreholes that exists in the quarry area. The first step it was made an analysis to know the chemical composition of the sample to have a better idea about the type and concentration of contaminants. Then, it was collected more samples, also a mixed of several boreholes from the quarry and it was started the experiments in the membrane.

4.1.1 Characterization of contaminated groundwater sample

It was made a complete chemical analysis, to have a better idea about what were the principal contaminates and them concentrations. **The pH measured it was 7,0 and the conductivity of the sample was 1,88 mS.cm^{-1}.** The heavy metals **manganese and nickel were present in groundwater in concentrations higher** than the limits established for groundwater(table A4.1) The determination of nitrate it was made by spectrophotometric method at wavelength 200 nm, but later it was discovered that are some interferences at this wavelength that affect the result. For determination of nitrite at this phase there were made some experiences to try a novel method for the spectrophotometric determination with barbituric acid (Aydın, 2004) but there were no satisfactory results. Although the results for the determination of these anions are not satisfactory, the determination of these contaminates are still a fundamental parameter to analyse, because there are some information's about this area that tell us that these are one of the most dangerous and higher concentrated contaminants. About the analysis of the pesticides it was not found any of these compounds which concentration exceed the limits established (table A4.2). These limits were established in previous studies and they are the goals to achieve in the end of the project.The concentration of **chlorides it was also bellow the limits (286 mg.L^{-1})** and the concentration of **sulphates it was higher than normal limits for groundwater 665 mg.L^{-1}.** It was also measured the TOC level with **TIC concentration 31,33 mg.l^{-1}**, **NPOC concentration 9,18 mg.l^{-1}** and **TC concentration 40,54 mg.l^{-1}.**

4.1.2 Experiments I – RO Module

For these experiences we use two different types of water. The samples were a mix of several boreholes situated in the quarry and they were collected with a week of difference. We use the first groundwater collected (GW1) for the experiments using the pressures of 20 and 40 bar, and the second (GW2) for the experiment using the 30 bar pressure. Although the samples were collected in different period they have a similar chemical composition, so it will be compared the effect of pressure in efficiency of process separation. Like it was explained before, in each RO module experience, for every 2l of permeate collected, it was measured the time necessary for collect this volume, the conductivity and the temperature of permeate and concentrate. We measure also the time to collect 100mL of permeate. The tables with these results are in Annex 5 and they allow the calculus of important parameters to study the efficiency of membrane: **conductivity of permeate vs. conductivity of concentrate**, **permeability** and **driving force**.

Beyond the sample of groundwater was the same, for the experiments 20 and 40 bar it was also used the same inlet volume, 20l. For the experiment using a pressure of 30 it was used less volume of inlet water, 15l. It is still possible to discuss the efficiency of separation at the same concentration factor during the experiment.

Table 7 - Characteristics of the flows from the experiments in RO module

Pressure (bar)	Temperature (°C)	V inlet (l)	pH			Conductivity		
			Inlet	Concentrate	Permeate	Inlet $(mS.cm^{-1})$	Concentrate $(mS.cm^{-1})$	Permeate $(\mu S.cm^{-1})$
20	20	20	7,3	8.0	6,3	1,24	8,10	115
30	20	15	6,5	7,7	5,7	1,75	8,12	123,1
40	20	20	7,3	7,9	5,9	1,24	8,07	219

There are three parameters that give important information about the efficiency of the process separation:

1. Conductivity of Permeate vs. Conductivity of Concentrate

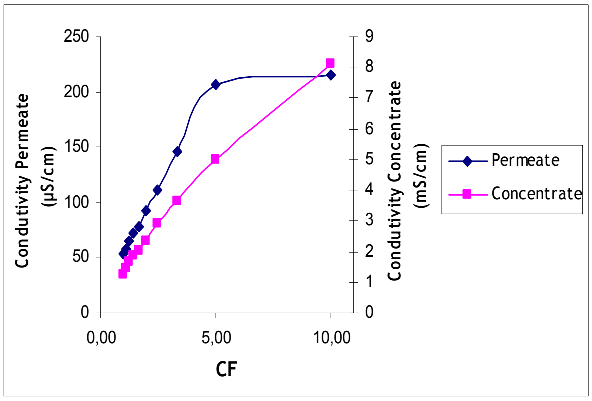


Figure 10 – Pressure 20 bar – Conductivity of Permeate vs. Conductivity of Concentrate

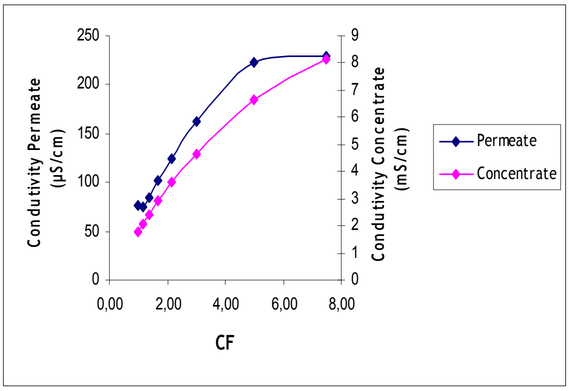


Figure 11 – Pressure 30 bar – Conductivity of Permeate vs. Conductivity of Concentrate

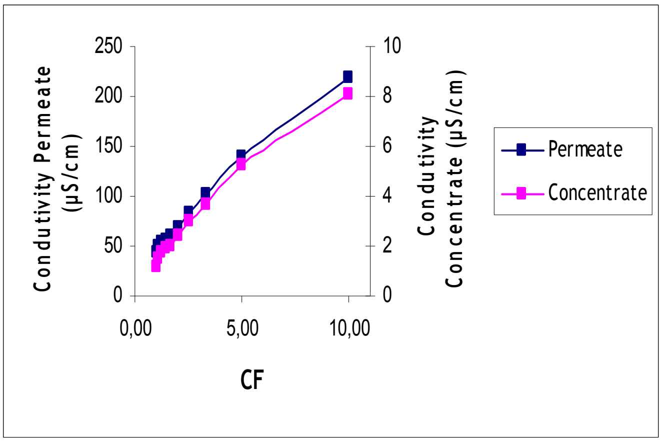


Figure 12 – Pressure 40 bar – Conductivity of Permeate vs. Conductivity of Concentrate

If the conductivity gives us the idea about the amount of solids in the water (an increase of 1 mS.cm-^{1} means an increase of 1 g.l^{-1} in concentration of solids), by analyse of this graphs it is showed that in the end of the experiment we will obtain similar values for conductivity of permeate and concentrate in all the experiments.

For the pressure of 20 bar the graph shows that the values of conductivity of permeate stabilizes in 200 µS.cm^{-1}, while for a pressure of 40 bars it's increasing till the end of the experience. So it was expected a higher value of conductivity for the mix of permeate of 20 bar experiment. This not happen (see table 7) due experimental errors in the determination of this conductivity.

2. Permeability

This is the most important parameter to analyse, because it gives the information about the general permeability of membrane during the experience and can be calculated like:

$$Permeability = \frac{Conductivity_{Permeate}}{Conductivity_{Concentrate} \times 1000} \times 100 \qquad (4.1)$$

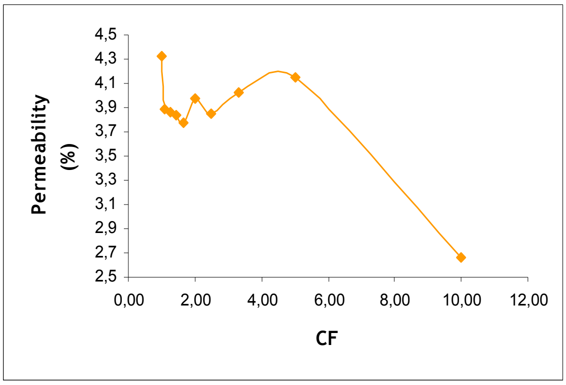


Figure 13- Pressure 20 bar - Permeability of membrane during the experience

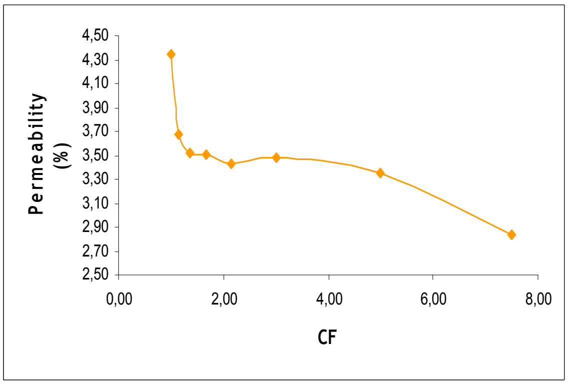


Figure 14- Pressure 30 bar - Permeability of membrane during the experience

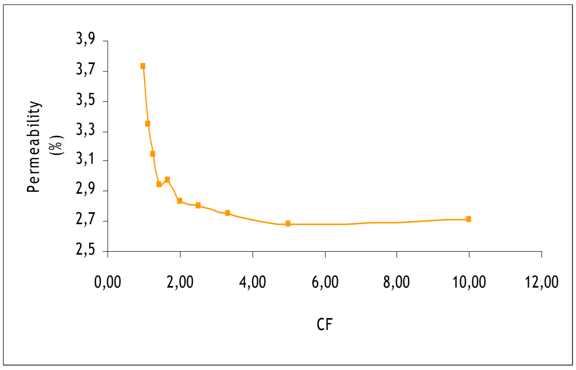


Figure 15 – Pressure 40 bar – Permeability of membrane during the experience

By the analysis of graphs the lowest permeability is achieved with the 20 bar experiment, but the 40 bar pressure allows a constant lower value of permeability during all the experiment. So this experiment confirms that lower permeability's are achieved with high pressures.

3. Driving Force

The "driving-force" of membrane refers to the flux of liquid that flows per unit of membrane area. For calculate this factor we measure the time necessary to take 100ml of permeate, the flowrate of permeate along the experiment in the membrane.

$$X = \frac{Flowratepermeate}{MembraneArea} \tag{4.2}$$

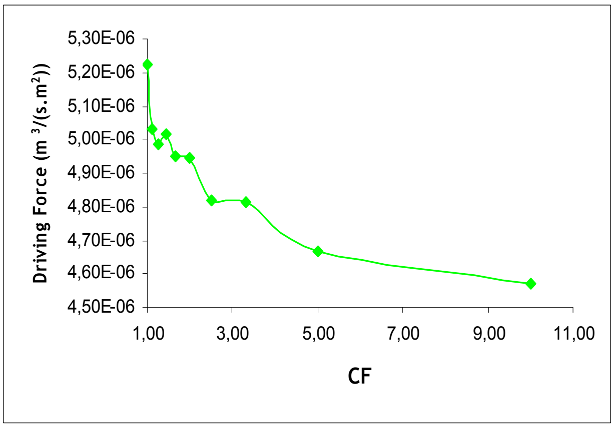


Figure 16 – Pressure 20 bar – Driving Force of membrane during the experience

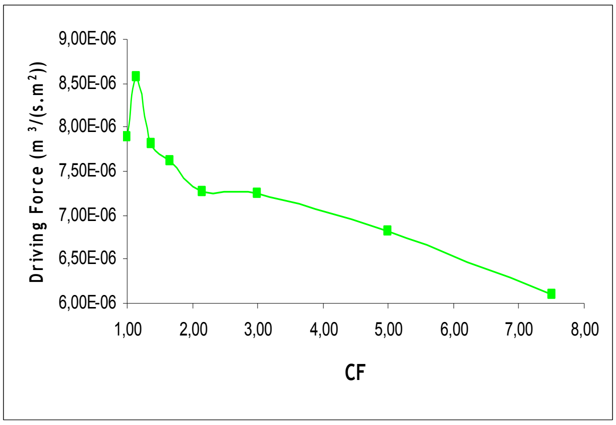


Figure 17 – Pressure 30 bar – Driving Force of membrane during the experience

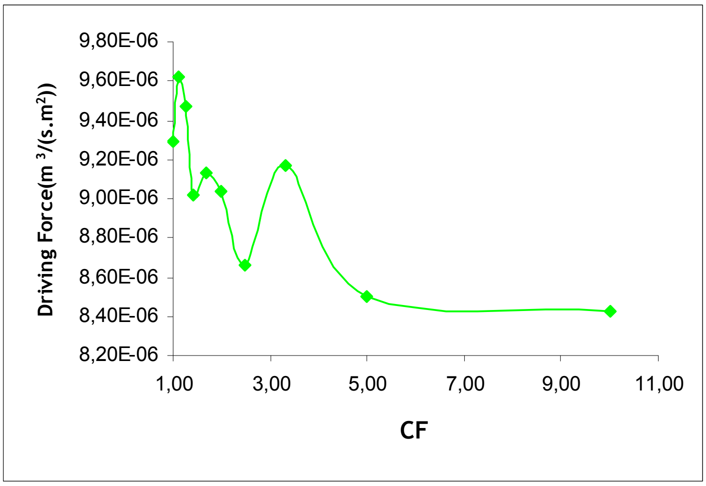


Figure 18 – Pressure 40 bar – Driving Force of membrane during the experience

We can see that the driving force tends to decrease during the experiment due the variation of osmotic pressure that is caused by the increasing of the quantity of ions. The piston pump keeps the work pressure constant so if the osmotic pressure is increasing its normal that the driving force decreases:

$$DrivingForce = p - \pi \qquad (4.3)$$

Like it was expected the experiment with higher pressure work, 40 bars, has higher values of driving force, which will make the experiment quicker.

The next step was the chemical analysis of the flows from the experiences and checks the efficiency of separation for each contaminant. For calculate this parameter we calculate first the efficiency of separation of each compound i:

$$Permeability = \frac{C_i Permeate}{C_i Inlet} \times 100 \qquad (4.4)$$

And the efficiency of separation is:

$$Efficiency = 100 - Permeability \qquad (4.5)$$

- **Metals Analysis**

Table 5- Efficiency of separation for the most representative metals

Working Pressure	Sample	Concentration k^+ (mg.l^{-1})	Efficiency (%)
	GW1	97,27	
20 bar	Permeate	8,41	91,35
	Concentrate	607,49	
40 bar	Permeate	6,54	93,28
	Concentrate	542,26	
	GW2	105,02	
30 bar	Permeate	7,26	93,08

	Concentrate	401,34	

Working Pressure	Sample	Concentration Na^+ (mg.l^{-1})	Efficiency (%)
	GW1	5,73	
20 bar	Permeate	1,66	71,02
	Concentrate	6,38	
40 bar	Permeate	0,87	84,81
	Concentrate	6,77	
	GW2	8,50	
30 bar	Permeate	1,07	87,42
	Concentrate	7,46	

Working Pressure	Sample	Concentration Ca^{2+} (mg.l^{-1})	Efficiency (%)
	GW1	87,56	
20 bar	Permeate	4,85	94,46
	Concentrate	812,88	
40 bar	Permeate	3,32	96,21
	Concentrate	827,85	
	GW2	120,10	
30 bar	Permeate	5,72	95,24
	Concentrate	879,02	

Working Pressure	Sample	Concentration Mg^{2+} (mg.l^{-1})	Efficiency (%)
	GW1	25,16	
20 bar	Permeate	1,60	93,65
	Concentrate	313,60	
40 bar	Permeate	1,4	94,44
	Concentrate	296,24	
	GW2	41,57	
30 bar	Permeate	1,63	96,08
	Concentrate	239,52	

Working Pressure	Sample	Concentration Mn^{2+} (mg.l^{-1})	Efficiency (%)
	GW1	4,27	
20 bar	Permeate	0,21	95,05
	Concentrate	27,96	
40 bar	Permeate	0,18	95,90
	Concentrate	27,58	
	GW2	5,70	
30 bar	Permeate	0,21	96,25
	Concentrate	23,95	

Membrane Pressure	Sample	Concentration Ni^{2+} (mg.l^{-1})
	GW1	0,06
20 bar	Permeate	0
	Concentrate	0,68
40 bar	Permeate	0
	Concentrate	0,66
	GW2	0,07
30 bar	Permeate	0
	Concentrate	0,36

How it was expected the divalent metals are higher efficiency of separation than the monovalent metals. The efficiency of separation for each metal doesn't vary much for different pressure works. Sodium has low efficiency of separation because is monovalent ion and as also a very low molecular weight. Nickel is also present in the samples, but it's not possible calculate the exactly efficiency of separation because the concentration on permeate is not detectable, so it's estimated that nickel has an efficiency of separation similar of the other metals.

- **Nitrite, Nitrate and Sulphate Analysis.**

At this point of the project it was being made some tests to improve the analytical method for determination of nitrite and nitrate. So the analysis of these compounds will be discussed in later experiments.

About the sulphate analysis it was decided that it's not a very important compound for this study case, so it's not going to be analysed in this or further experiments.

- **Pesticides Analysis**

Both the samples analysed has already a pesticides concentration very low (below the limits established and in the most of compounds bellow the detection limit 0,0004 mg.l^{-1}), so it's obvious that the RO was a successful method for separate this low concentration. The results for both determinations are in Annex5.

- **Chloride Analysis**

Table 6- Efficiency of separation for chlorides

Working Pressure	Sample	Concentration Chlorides (mg.l^{-1})	Efficiency (%)
	GW1	177,03	
20 bar	Permeate	16,05	90,93
	Concentrate	1292,08	
40 bar	Permeate	17,79	89,95
	Concentrate	1267,98	
	GW2	262,95	
30 bar	Permeate	18,22	93,07
	Concentrate	1335,47	

The efficiency of separation of chlorides is a very important parameter to deduce de global efficiency of separation, because chlorides are small ions that can pass trough the membrane very easily. This factor can also explain the high permeability verified. However the efficiency of separation is very similar for the three experiments, and we can conclude once more, that the pressure doesn't have a high influence on the separation process.

- **TOC Analysis**

Table 7- Efficiency of separation for NPOC

Working Pressure	Sample	TIC ($mg.l^{-1}$)	Concentration NPOC ($mg.l^{-1}$)	Efficiency NPOC (%)
	GW1	50,19	11,55	
20 bar	Permeate	5,92	0,05	99,56
	Concentrate	347,92	77,51	
40 bar	Permeate	5,22	0,11	99,01
	Concentrate	359,45	72,13	
	GW2	46,25	9,74	
30 bar	Permeate	6,04	0,47	95,13
	Concentrate	257,83	44,16	

The NPOC are almost all represent by the pesticides, so this determination is essential to deduce the efficiency of separation of this compounds. By the analysis of the table 8 it's possible to verify that the efficiency is very similar for the 20 and 40 bar pressure experiment, that are using the same sample, which make the pressure a not very important parameter for this separation.

After the end of these three experiments and the analysis of the results it was concluded that the optimum pressure work is 40 bars, because provides the best efficiency of separation ally to less time necessary to finish one experiment in the reverse osmosis module.

4.2 Laboratory experiments II

4.2.1 Variability of chloride concentration with concentration factor

The goal of this experiment it was study the permeability of membrane for chlorides. The samples were collected in RO module installed in Nový Rychnov. The samples from permeate and concentrate were collected during one cycle of operation of the RO module, so we can study how the concentration of chlorides is varying along the concentration factor. Then and using the Mohor method we determined the chloride concentration in the samples. It was also measured the conductivity of both samples.

The obtained results are in the Annex5. In following graphs it will be represented the principal conclusions for this analysis.

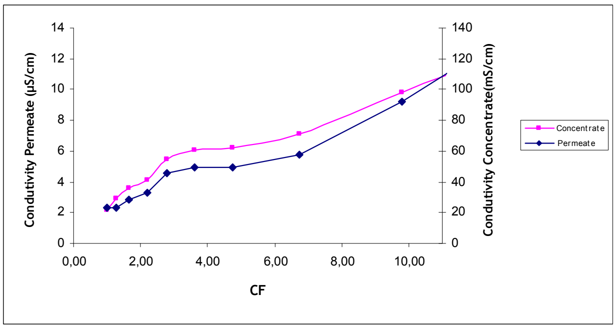


Figure 19- Conductivity of permeate and concentrate along the experiment in Nový Rychnov

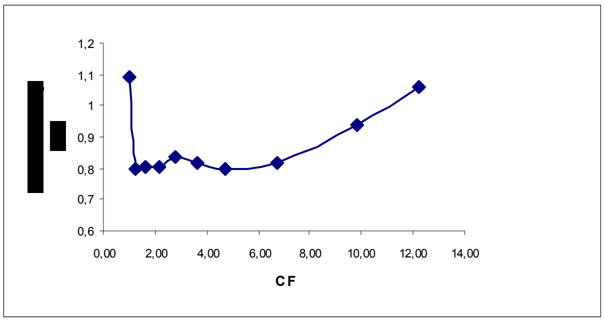


Figure 20- Permeability along the experiment in Nový Rychnov

Like it was refereed before chlorides are small ions that can pass through the membrane very easy, so this experiment is important to establish a comparison between the two different models: the spiral wound (in Nový Rychnov) and the plate and frame model (in laboratory). Theoretically the spiral wound model has a four times higher efficiency of separation, and by the analysis of the graph 24 it's possible to verify that the permeability for chlorides in this module is approximately 1%, which is a excellent performance of separation for this compound. So this performance aloud to conclude that performances with efficiency in the order of 90% obtained in the laboratory experiments means efficiency of separation in Nový Rychnov installation of 99%. It was verified also lower values for the conductivity of permeate and concentrate than the obtained in the laboratory witch confirms the high efficiency of separation of spiral wound model.

4.2.2 Characterization of contaminated groundwater samples – part II

For this second round of experiences, it was collected groundwater samples for several boreholes, to try to see how the contamination is disperse on the contaminated area. It is important to reefer also, that these samples were collected in the end of the remediation, so these contaminants concentrations correspond to the values achieved with the remediation process.

- **Conductivity and pH measurement**

Table 8- Conductivity and pH

	HV1	HV4	HV5	HV11	HV15	HV17	HV19	HLV1	HLV4	HLV5
Conductivity ($mS.cm^{-1}$)	0,619	1,2	0,944	4,56	3,87	1,43	1,32	4,96	7,19	1,54
pH	6,3	8,8	7,2	7,4	8,1	8,3	8,1	7,6	7,9	8,4

Analysing the table 11 it was verified a higher conductivity for the samples that were taken from the landfill (HLV samples).These results were expected because the quarry it was the local for the deposit of contaminants. There are also high levels for the samples HV11 and HV15 that belong to boreholes that are about 100 m from the quarry. These high levels can be explained by the dispersion of contamination (favoured by the type and breaks on soil) going in the direction of these boreholes.

- **Metals Analysis**

Table 9- Concentration of Ni^{2+} and Mn^{2+} in groundwater samples

	HV1	HV4	HV5	HV11	HV15	HV17	HV19	HLV1	HLV4	HLV5
Concentration Ni^{2+} ($mg.l^{-1}$)	0,14	0,13	0,09	0,17	0,12	0,06	0,14	0,38	0,26	0,33
Concentration Mn^{2+} ($mg.l^{-1}$))	1,46	2,43	2,76	19,38	28,16	3,59	12,48	14,99	16,57	12,58

The concentration limit for these heavy metals is 1 mg.l^{-1} (Annex1). So by the analysis of the table 12 all the samples taken are beyond the limits for manganese. Once more the higher concentrations belong to the samples that were taken from the landfill.

- **Nitrates and Nitrites Analysis**

  It was the first time during the entire project that it was possible analyse the behaviour of concentration of these anions. It was determined the concentrations in different days during one week, to check if these concentrations remain constant (Annex 5). These concentrations can vary due factors like: oxidation of NO_2^- to NO_3^-, because the water is stored in normal vessels and exposed to the air (the samples were stored in fridge and kept in dark). It can be due the presence of bacteria that can transform NO_2^- to NO_3^-, the *Nitrobacter*. To check all the possibility it was also analysed samples that were stored in normal conditions and to check if the analytical method is correct some samples were analysed by liquid chromatography.

It was verified that concentration for nitrate remains constant during the 10 days of analysis, so it is possible to conclude that this analytical method is quite precise and the nitrate concentration can be measured at least ten days after collect the sample without variation of nitrate concentration. Comparing with the liquid chromatography analysis, it was verified that for some sample the results obtained were very different, and this can be explained because these samples concentration were out of liquid chromatography concentration range and should be diluted before. The other samples measured correctly by liquid chromatography show results quite similar with the analytical method, which indicate that this is a good method for the determination of nitrate. In spite of it were being analysed only two samples that were stored in normal conditions, the results are consistent and show that the normal storage doesn’t have influence on the nitrate concentration.

It was verified that the analytical method used for the determination of nitrite provide very accurate results. The concentration remains quite constant for 12 days, even if the samples were stored in normal conditions (Annex 5). The results for comparing with the liquid chromatography analysis are not so good. The reason can be the very low level of detection for these compound and all the samples analysed were out of the detection range and should be more diluted. The other reason can be the interferences with chlorides, because chlorides in high concentration disturb this measurement.

- **Pesticides Analysis**

Table 10- Pesticides Concentration

	Concentration of Pesticides (mg.l^{-1})							
	HLV1	**HLV5**	**HV1**	**HV4**	**HV5**	**HV11**	**HV15**	**HV19**
Total Concentration	0,126	0,227	0,566	0,074	0,342	0,013	0,019	0,011

Analysing Table 10 it is possible to verify that the samples HV1, HV5 and HLV5 have more high concentration in pesticidades. The more high concentrated pesticide is α-HCH (Annex 5).

- **Chlorides Analysis**

Table 11- Chlorides Concentration

Concentration	**HV1**	**HV4**	**HV5**	**HV11**	**HV15**	**HV17**	**HV19**	**HVL1**	**HVL4**	**HVL5**
Chloride (mg.l^{-1})	58,73	158,50	144,35	452,87	753,60	206,62	244,83	742,98	1167,55	189,64

It was verified very high concentrations of chlorides especially in the samples that were collected in the landfill. It was also verified concentrations higher than the limit of 300 mgl.l^{-1} in the samples HV11 and Hv15.

- **TOC Analysis**

Table 12- TIC an NPOC Concentration

Concentration (mg.l^{-1})	**HV1**	**HV4**	**HV5**	**HV11**	**HV15**	**HV17**	**HV19**	**HVL1**	**HVL4**	**HVL5**
TIC	69,99	64,33	54,44	37,41	22,62	70,28	25,84	194,03	158,71	111,52
NPOC	19,80	4,85	11,43	6,44	6,84	8,38	3,67	26,21	20,71	14,90

There are high concentrations of NPOC and TIC compounds in the samples taken from the landfill like it was expected.

4.2.3 Experiments II- RO Module

- **Sample HV5**

For this experiment it was used the sample which has high concentration of pesticides to study the behaviour of membrane in this cases. The results are in Annex4.

Table 13- Characteristics of the flows from the experiments in RO module with HV5

Pressure (bar)	Temperature (°C)	V inlet (l)	pH			Conductivity		
			Inlet	Concentrate	Permeate	Inlet ($\mu S.cm^{-1}$)	Concentrate ($mS.cm^{-1}$)	Permeate ($\mu S.cm^{-1}$)
40	24	20	6,8	7,5	7,6	944	5,49	66

It was analysed the same three parameters that were used before to study the efficiency of the process separation:

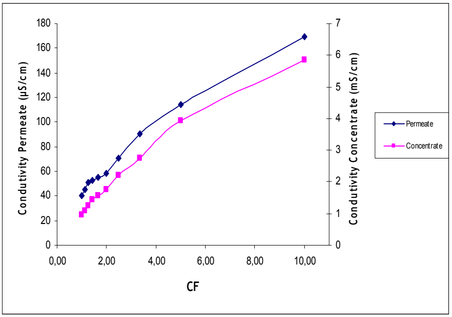


Figure 21 – Sample HV5 – Conductivity of Permeate vs Conductivity of Concentrate

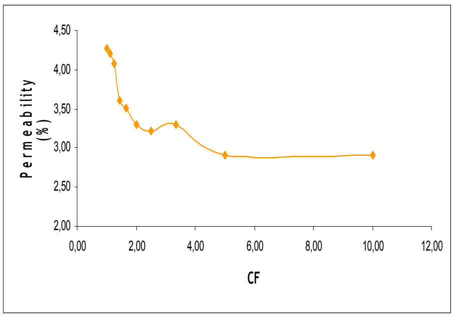


Figure 22 – Sample HV5 – Permeability of membrane during the experience

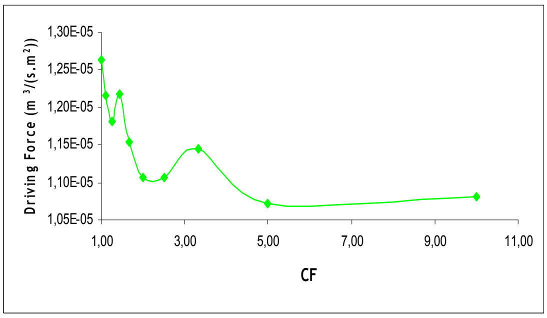


Figure 23 – Sample HV5 – Driving Force of membrane during the experience

The values for conductivity of permeate and concentrate grows as it was expected and the final values of conductivity for the mix of permeate and concentrate are also expected and consistent with the graphs. The permeability of membrane is around 3% which is a result expected for the pressure working of 40 bars. The driving force graph has also the expect behaviour, is decreasing with the concentration factor and the driving force for this process separation has values a little higher than the normal for 40 bar pressure. This situation has become the experiment quicker than the expected.

The next step was the chemical analysis of the flows from the experiences and checks the efficiency of separation for each contaminant.

- **Metals Analysis**

Table 14- Efficiency of separation for Mn^{2+}

Working Pressure	**Sample**	**Concentration Mn^{2+} ($mg.l^{-1}$)**	**Efficiency (%)**
	HV5	2,76	
40 bar	Permeate	0,18	97,64
	Concentrate	27,58	

The efficiency of separation for this metal is the expected according to global efficiency verified in the graph from figure 23.

- **Nitrites and Nitrates Analysis**

Table 15- Efficiency of separation for nitrates

Working Pressure	**Sample**	**Concentration NO_3^- ($mg.l^{-1}$)**	**Efficiency (%)**
	HV5	107,76	
40 bar	Permeate	16,22	84,95
	Concentrate	531,02	

Table 16- Efficiency of separation for nitrites

Working Pressure	Sample	Concentration NO_2^- ($mg.l^{-1}$)	Efficiency (%)
	HV5	7,85	
40 bar	Permeate	2,12	72,99
	Concentrate	55,62	

The efficiency of separation for these compounds is lower than the expected. This can happen due different reasons: high permeability from the membrane to this compounds, oxidation of nitrite due the exposition of air along the entire experiment which made vary the concentration of these anions, or experimental errors.

- **Pesticides Analysis**

Table 17 - Efficiency of separation for pesticides

	Concentration $mg.l^{-1}$			
	HV5	**Concentrate**	**Permeate**	**Efficiency**
α-HCH	0,1716	0,4481	0,0009	99,47
HCB	<0,0004	<0,0004	<0,0004	-----------
ß- HCH	0,0992	0,0758	0,0007	99,32
γ-HCH	0,0630	0,0744	0,0008	98,74
heptachlor	0,0017	0,0516	0,0006	67,90
4,4´DDE	0,0021	<0,0004	<0,0004	-----------
2,4´DDD	<0,0004	<0,0004	<0,0004	-----------
4,4DDD	<0,0004	<0,0004	<0,0004	-----------
2,4DDT	0,0009	<0,0004	<0,0004	-----------
4,4´DDT	0,0021	<0,0004	<0,0004	-----------

The efficiency of separation for pesticides is high. Only the compound heptachlor as lower efficiency than expected due is lower concentration, almost out of calibration range, which increase the error deviations. These compounds have the similar structures so it is expected that they have the same efficiency of separation.

- **Chlorides Analysis**

Table 18 - Efficiency of separation for chlorides

Working Pressure	Sample	Concentration Chlorides (mg.l^{-1})	Efficiency (%)
	HV5	144,35	
40 bar	Permeate	10,61	92,65
	Concentrate	410,41	

The efficiency of separations for chlorides it was expected to be lower than general efficiency of process because these are very small ions.

- **TOC Analysis**

Table 19 - Efficiency of separation for NPOC

Working Pressure	Sample	Concentration TIC (mg.l^{-1})	Concentration NPOC (mg.l^{-1})	Efficiency NPOC (%)
	HV5	54,44	11,43	
40 bar	Permeate	3,00	3,17	72,27
	Concentrate	199,90	57	

The efficiency for NPOC is also very low, maybe because permeate has a very high concentration in NPOC due cleaning problems or calibration curve not expected responses.

- **Sample HLV1**

For this experiment it was used the sample which has high concentration of pesticides, nitrites, nitrates and chlorides to study the behaviour of membrane in this cases. The results are in Annex5.

Table 20- Characteristics of the flows from the experiments in RO module with HLV1

Pressure (bar)	Temperature (°C)	V inlet (l)	pH			Conductivity		
			Inlet	Concentrate	Permeate	Inlet ($\mu S.cm^{-1}$)	Concentrate ($mS.cm^{-1}$)	Permeate ($\mu S.cm^{-1}$)
40	25	20	7,6	6,9	7,2	4,79	24,3	461

It was analysed the same three parameters that were used before to study the efficiency of the process separation:

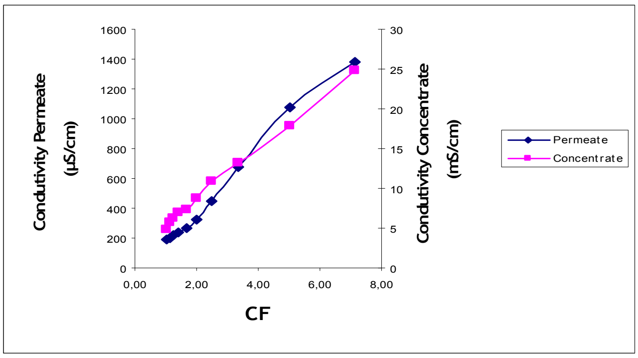


Figure 24 – Sample HLV1 – Conductivity of Permeate vs. Conductivity of Concentrate

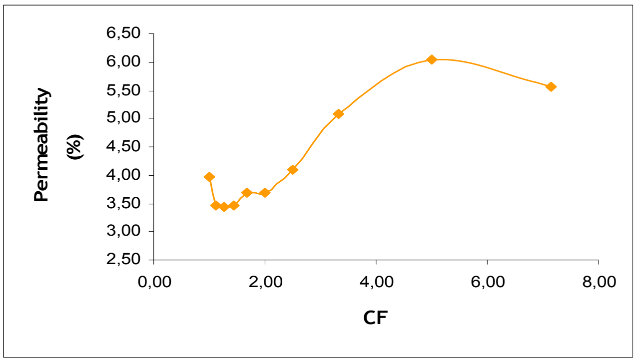


Figure 25 – Sample HLV1 – Permeability of membrane during the experience

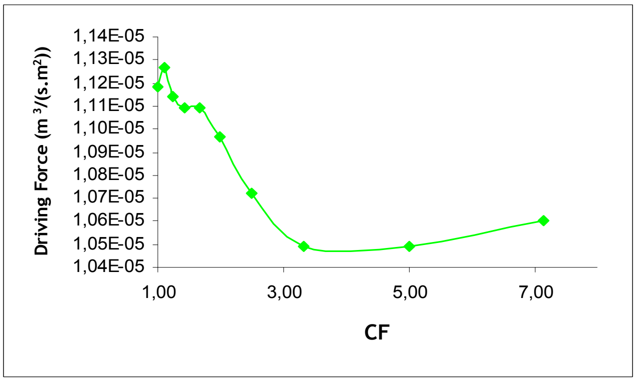


Figure 26 – Sample HLV1 – Driving Force of membrane during the experience

The values for conductivity of permeate and concentrate grows as it was expected and the final values of conductivity for the mix of permeate and concentrate are also expected and consistent with the graphs and with the high values of conductivity of inlet water. This situation was responsible for the precipitation of some compounds and for the clogging of membrane which caused the interrupt of the experiment at concentration factor 7.

The driving force graph has also the expected behaviour, was decreasing with the concentration factor and the driving force for this process separation has values a little higher than the expected for 40 bar pressure.

The next step was the chemical analysis of the flows from the experiments and checks the efficiency of separation for each contaminant.

- **Metals Analysis**

Table 21- Efficiency of separation for Mn^{2+}

Working Pressure	Sample	Concentration Mn^{2+} ($mg.l^{-1}$)	Efficiency (%)
	HLV1	14,99	
40 bar	Permeate	0,13	99,13
	Concentrate	41,71	

Although the clogging of membrane the efficiency of separation for this metal is very high.

- **Nitrites and Nitrates Analysis**

Table 22- Efficiency of separation for nitrates

Working Pressure	Sample	Concentration NO_3^- ($mg.l^{-1}$)	Efficiency (%)
	HLV1	725,31	
40 bar	Permeate	263,92	63,61
	Concentrate	4009,32	

Table 23- Efficiency of separation for nitrites

Working Pressure	Sample	Concentration NO_2^- ($mg.l^{-1}$)	Efficiency (%)
	HLV1	137,89	
40 bar	Permeate	7,77	94,37
	Concentrate	637,53	

For nitrate the efficiency of separation stills very low. In this experiment the efficiency for nitrite is higher and close to the efficiency expected for these compounds.

- **Pesticides**

Table 24- Efficiency of separation for pesticides

	Concentration $mg.l^{-1}$			
	HLV1	**Concentrate**	**Permeate**	**Efficiency**
α-HCH	0,1023	0,6384	0,0362	64,59
HCB	<0,0004	<0,0004	<0,0004	------------
ß- HCH	0,0099	3,9978	0,0020	80,18
γ-HCH	0,0104	0,8967	0,0007	92,80
heptachlor	0,0006	0,0015	0,0001	79,86
4,4´DDE	<0,0004	<0,0004	<0,0004	------------
2,4´DDD	<0,0004	<0,0004	<0,0004	------------
4,4DDD	<0,0004	<0,0004	<0,0004	------------
2,4DDT	0,0008	<0,0004	<0,0004	------------
4,4´DDT	0,0017	<0,0004	<0,0004	------------

The efficiency of separation for pesticides is lower than the expected, and there big deviations between the compounds with same structure. This situation happens maybe because this experiment has some experimental problems due the clogging of membrane.

- **Chlorides**

Table 25- Efficiency of separation for chlorides

Working Pressure	Sample	Concentration Chlorides ($mg.l^{-1}$)	Efficiency (%)
	HLV1	742,98	
40 bar	Permeate	33,25	95,52
	Concentrate	2052,05	

This sample has a very high concentration in chlorides, but the efficiency of separation for these compounds is very high and over the expected.

- **TOC**

Table 26- Efficiency of separation for NPOC

Working Pressure	Sample	Concentration TIC ($mg.l^{-1}$)	Concentration NPOC ($mg.l^{-1}$)	Efficiency NPOC (%)
	HLV1	194,01	26,21	
40 bar	Permeate	6,44	2,27	91,34
	Concentrate	870,00	92,20	

The efficiency for NPOC is higher than the expected, because of lower efficiency of pesticides. This contradiction in results can be explained by the experimental errors associated to this experiment.

5 Conclusions

Nový Rychnov landfill was a serious source of groundwater pollution: chlorinated hydrocarbons, pesticides, nitrites, nitrates, chlorides, heavy metals and other substances. In laboratory experiments it was proved that reverse osmosis technologies can be very highly efficient in this kind of separations and very effective in reduce the level of contamination in the studied landfill.

It was studied the efficiency of separation of chlorides in Nový Rychnov module, to allow the comparison with the module used in the laboratory experiments. Chlorides are small ions that can pass easy through the membrane, so the study of them permeability is essential to have an idea about the global permeability of membrane. It was verified that in the spiral wound module (Nový Rychnov) the efficiency of separation is around 99%, and in plate and frame module the (laboratory experiments) it was obtained efficiencies around 90%. If it was used the same type of membrane and for the obtained results for permeability's in laboratory, it is possible to conclude that reverse osmosis has high efficiency of separation for almost all contaminants.

It was also verified that variations of pressure (between 20 and 40 bar) doesn't have influence in efficiency of separation but only in the time of a cycle operation. So the fact that it's being used 30 bars in Nový Rychnov module and 40 bars in laboratory module it is only for optimise the work conditions and should not affect the comparison between the efficiency obtained for the both modules.

Another important parameter studied was the analytical analysis and the efficiency of separation for nitrites and nitrates. It was verified that the analytical methods used for these determinations provide very accurate results. The efficiency of separation for these compounds is lower than the expected. This can happen due different reasons: high permeability from the membrane to this compounds, oxidation of nitrite due the exposition of air along the entire experiment which made vary the concentration of these anions, or experimental errors.

It was collected groundwater samples for several boreholes (Characterization of contaminated groundwater samples – part II), to try to see how the contamination is disperse on the contaminated area. Analysing the results it was verified a higher level of contamination for the samples that were taken from the landfill (HLV samples).These results were expected because the quarry was the local for the deposition of contaminants. There are also high levels for the samples HV11 and HV15 that belong to boreholes that are about

100 m from the quarry. These high levels can be explained by the dispersion of contamination (favoured by the type and breaks on soil) going in the direction of these boreholes.

These samples were collected and analysed in the end of the remediation, so these contaminants concentrations correspond to the values achieved with the remediation process. It is possible to conclude that reverse osmosis technologies has very effective results in contaminants separation from groundwater, but analysing the results it was verified that some levels were not achieved which can be explained by the short time of work of the installation.

6 Assessment of work

6.1 Objectives Achieved

It was study with success the efficiency of separation for the main contaminants in groundwater. After some attempts it was found efficient methods for analytical analysis of nitrite and nitrate. It was also conclude with achievement the comparison between the spiral wound module and the plate and frame model and the efficiency of remediation process in the studied landfill.

6.2 Other Work done

It was the first time in this institute that the nitrite and nitrate anions were analysed in groundwater. During the first experiments to try to analyse them concentrations in groundwater it was found that them concentrations could vary due: oxidation of NO_2^- to NO_3^-, because the water is stored in normal vessels and exposed to the air (the samples were stored in fridge and kept in dark); the presence of bacteria that can transform NO_2^- to NO_3^-, the *Nitrobacter.* To eliminate this last option it was realized some microbiological tests to test the presence of these bacteria, but it was no found them presence.

6.3 Limitations and future work

It can be conclude that osmosis reverse technologies is very successful in the treatment of contaminated groundwater, but there some limitations: in this case it was verified that this technologies request longer time than 2 years to achieve the goals for the decontamination of groundwater. These remediation process have normally sponsors (in case studied European Union), so it is recommend more studies about the remediation areas to determine more precisely the time and the effective cost of such process.

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ANNEX

Annex 1 Table of Health Risk Limits for Groundwater and Toxicological Endpoints

Table A1.1- Table of Health Risk Limits for Groundwater and Toxicological Endpoints (adapted from Seagrant, 2008)

Chemical or Substance	Health Risk Limit (µg.l^{-1})	Toxicologic Endpoint
Acetone	700	Kidney
Arsenium	5	
Alachlor	4	Cancer
Anthracene	2000	----
Atrazine	20	Cardiovascular system
Barium	2000	Cardiovascular system
Benzene	10	Cancer
Beryllium	0.08	Cancer
Cadmium	4	Kidney
Chlorobenzene	100	Liver
Chromium III	20	-----
Chromium VI	100	-----
Cyanide, free	100	Endocrine system, nervous system
Cupper	100	-----
Boron	600	Male reproductive system
Ethylbenzene	700	Kidney, liver
Heptachlor	0.08	Cancer

Hexachlorobenzene	0.2	Cancer
Chemical or Substance	**Health Risk Limit (μg l^{-1})**	**Toxicologic Endpoint**
Manganese	100	Nervous system
Nickel	100	------
Nitrate (as nitrogen)	10,000	Hematologic system
Lead	5	------
Polychlorinated biphenyls (PCBs)	0.04	Cancer
Potassium	20000	-----
Selenium	30	------
Silver	30	------
Sodium	500	-----
Zinc	2000	------

Annex 2 Details about the most relevant units in the technologies used in Nový Rychnov and the boreholes localization map

Stripping column

This unit provides the separation of volatile substances due a gas flowing (air, smoke or gas water vapour) through the column. The column is filled with small components (Raschigs, Palls rings…), which serve to improve the contact between the liquid and gaseous phase. The volatile substances, which can be removed, are:

- Organic compounds: aliphatic and aromatic volatile hydrocarbons, chlorinated compounds, phenols and derivatives, certain pesticides.

- Inorganic compounds in their non dissociated form: ammonia, sulfan, carbon dioxide, hydrogen cyanide.

The desorption rate of organic compounds is determined by its volatility and solubility in water. The stripping by air is possible to use for chlorinated hydrocarbons. It is necessary to trap these compounds to avoid the air pollution.

Sand Filter

This is the key process of pretreatment of water before the RO, and it works like an in-depth filtration. For this type of filtration is used a sand filter bed. For successful filtering the follow parameters are critical: the size of grains of sand, uniformity and distribution, bed depth and the flow speed of fluids (Isaias, 2001).

Sedimentation

Sedimentation is used for the separation of suspended particles with diameter between 10 to 50 μm. The speed of the fall of particles is determined primarily by its density, size and shape. The effectiveness of sedimentation tank doesn’t depend on the depth, but on the surface. Efficiency is increased, when in the sedimentation tank are put diagonally oriented plates - strips. Such a settling tank is then called multiplates tank. The construction of slats used plastic, steel or aluminium plates.

Activated Carbon Filter

Activated carbon is the most frequently used adsorbent. The adsorption it applied mainly in intermolecular force, but also in chemical bonds. The activated carbon adsorbs especially organic compounds and the important factors for this adsorption are the size of molecules, relative molecular mass, its shape, and polarity. The porous structure of this material is essential for achieve the inner surface from 400 to 1500 $m^2.g^{-1}$.

Adjusting pH

This is a very important step to avoid scaling of HCO_3^- and CO_3^{2-} compounds in the pipes and fouling in the RO membrane. Usually some hydrochloric acid is added, which regulates the pH of the solution to slightly acidic. The main form of ammonia in acid solution is $NH4^+$ form that can be also removed by adjusting the pH. In alkali solution the ammonia is mainly in NH_3 form, which can pass through the membrane easily.

Boreholes Localization Map

The next map is useful to have a better idea about the disposition of boreholes in the remediation area.

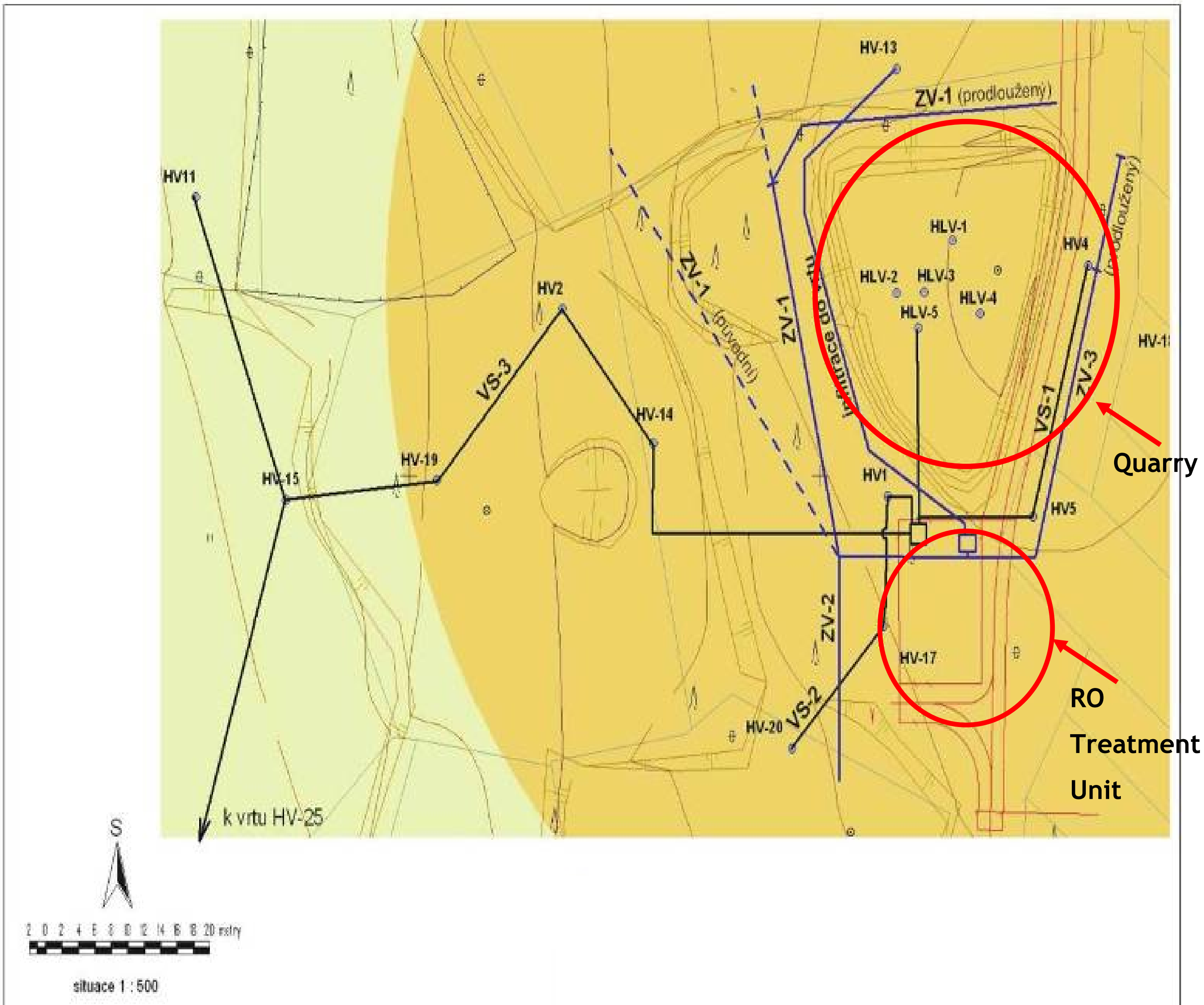

Figure A2.1- Map of the boreholes localization in Nový Rychnov

In previous studies about this problem it was established some limits to achieve in the end of the remediation. These limits are:

Table A2.1– Limits to achieve in the end of remediation for the different boreholes

Boreholes: HV-1, HV-2, HV-4, HV-5 (distance of 50 m from the landfill):

Contaminant	**Limit concentration ($mg.l^{-1}$)**
sum of chlorinated hydrocarbons (i.e. 1,2 cis-DCE, TCE a PCE)(1)	1,5
Pesticides: α, β, γ, δ, ε – HCH, hexachlorbenzen, heptachlor a o,p – DDT, p,p - DDT)	0,1
Chlorides	400
Nitrates	300

Levels to achieve at the end of the remediation in a distance of 100 m from the landfill:

Contaminant	**Limit concentration ($mg.l^{-1}$)**
sum of chlorinated hydrocarbons (i.e. 1,2 cis-DCE, TCE a PCE) (1)	1,0
Pesticides: α, β, γ, δ, ε – HCH, hexachlorbenzen, heptachlor a o,p – DDT, p,p - DDT)	0,05
Chlorides	350
Nitrates	250

(1) The chlorinated hydrocarbons weren't study in this project because the equipment that allows them detection was not available.

Annex 3 Description of analytical methods used in laboratory experiments

The measurement of conductivity

Conductivity solution is caused by the movement of particles in homogeneous electric field and is one of the fundamental properties of the solution and its unit is $S.m^{-1}$.

Setting specific conductivity is a normal part of the analysis of water. It immediately estimates the ion concentration of dissolved substances and the total mineralization. It depends on the concentration of ions, their hub, mobility and the temperature of the solution.

For the conductivity measurement was used digital conductometer type GHM 3430, produced by Electronic Greisinger. Conductivity monitoring consists in a pair of platinum electrodes, with constant surface area and constant distance between them. The procedure is very simple and consists only in immerse the electrodes in the sample and wait for the stabilisation of values.

The measurement of pH

Measurement of pH is one of the basic determinations, which is used for all types of water, and it is important for assessing its qualities.The pH is defined as negative common logarithm activity of hydrogen ions expressed in mol per litre. Activity is close to the value of their concentration in only a much diluted solution, otherwise the value is lower than the concentration of ions as a result of interactions.

The measurement of pH is carried out through various methods, ranging from simple methods such as the use of indicator paper, colour indicators, to the complex electrochemical methods. The most commonly used today is the determination of pH potentiometric determination through glass specific and comparative electrodes.

The pH used was digital pH meter WTW Company, the type of pH330. The device consists on a combined glass electrode. Before the measurement it was carried out a calibration curve with buffers according to the manufacturer's instructions. After stabilising the device was available to measure pH in the samples.

Determination of Heavy Metals

Determination of metals was carried out by atomic absorption (AAS) and emission spectrometric (AES) SensAA produced by GBC Scientific Equipment. The device is combined and serves as a measurement of absorption and emission spectrum. The atomizator flame is a mixture of acetylene and air. AAS method measured the concentration of Ni, Cu, Mn, Zn, Mg, Ca, Cd, As, Cr, Fe, Pb. AES method measure the concentrations of K and Na.

Before the determination of the metal in a water sample, has been properly set parameters for the instrument and the calibration has been carried out for each metal. If the measured concentrations of the metal is too high and exceeded the scope of calibration, the solution is properly diluted.

Determination of TOC (Total Organic Compounds)

The total carbon (TC) is the level of dissolved and suspended content of organic matter (TOC) and inorganic forms of carbon (TIC) in the water. Determination of TOC is based on the principle of oxidation of organic matter to carbon dioxide in the presence of catalysts. The CO_2 is then determined directly or after conversion of hydrogen in the methane flame ionization detector. The method of direct detection of CO_2 is the most commonly used in the infrared absorption spectrometry. The thermal oxidation of the total content of CO_2 is equivalent, not only, to the content of oxidizing organic pollutants, but also inorganic forms of carbon as a TIC. Almost all the TOC analyzers use a differential way of determination TC (thermal oxidation), TIC (chemical decomposition in the acidic environment) and the value of TOC is then calculated as the difference of the two values (TOC = TC-TIC). For distinguish de different forms of carbon are commonly used the following symbols: POC (carbon volatile organic compounds), NPOC (carbon non-volatile organic compounds) and DOC (dissolved organic carbon compounds. To determine the TOC (total organic carbon) was used high-temperature TOC / TNb analyser liquiTOC II, from the company Elementar Analysensysteme GmbH, which allows measurement of TC, TIC and TOC.

Determination of Pesticides

For this determination was used gas chromatograph HP 5890 from Agilent Technologies with the electron capture detector (ECD). The mobile phase used nitrogen with a capacity of 1 column ml.min^{-1}. It was used capillary column with a length of 60 m internal diameter with a thickness of 0.25 mm. As a stationary phase were used these sorbets: biphenyl (5%) and dimethylsiloxan (95%).

A volume of 250 ml each sample was extracted with 10 ml of hexane. Thus prepared samples they were analysed in the selected temperature programme, which was set up as follows: 50 ° C was maintained for 1 minute, followed by heating 25 ° C.min^{-1} until they reach temperatures of 180 ° C, the second was heating speed 1 ° C.min^{-1} to 205 ° C and a third heating rate was set at 3 ° C.min^{-1} to a temperature of 280 ° C, and then the temperature was kept for 15 minutes. The pressure was set at 140 kPa. Each sample had a volume of 1 µl. The detector used was an ECD, which is suitable for the detection of halogenated substances such as pesticides.

Products:

Hexane, p.a, Lachema

Equipment:

Gas chromatograph HP 5890 from Agilent Technologies with the electron capture detector (ECD).

Technical:

A volume of 250 ml each sample was extracted with 10 ml of hexane. Thus prepared samples they were analysed in the selected temperature programme, which was set up as follows: 50 ° C was maintained for 1 minute, followed by heating 25 ° C.min^{-1} until they reach temperatures of 180 ° C, the second was heating speed 1 ° C.min^{-1} to 205 ° C and a third heating rate was set at 3 ° C.min^{-1} to a temperature of 280 ° C, and then the temperature was kept for 15 minutes. The pressure was set at 140 kPa. Each sample had a volume of 1 µl.

Example of calculation:

The equipment gives the follow information about one sample:

Table A3.1 - Information provide from Gas chromatograph HP 5890 from Agilent Technologies

Compound Name	Retention time	Response	Response
α HCH	20,4	159,07	158,08
HCB	20,9	1,24	4,86
β HCH	21,9	1695,30	1655,77
γ HCH	22,5	89,58	88,74
	24,0	870,63	829,87
	24,8	200,30	195,25
Heptachlor	27,8	2,42	2,82
4,4´DDE	37,7	0,11	0,16
Dieldrin	38,1	0,13	0,08
2,4´DDD	38,4	0,03	0,06
β endosulfan	40,5	6,21	5,60
4,4´DDT	43,6	0,60	0,55

Then it is make an average of the values for response and with calibration curves is determined the concentration of each compound:

(Example for α HCH)

$$\mathrm{Re}\,sponse = \frac{159{,}07 + 158{,}08}{2} = 158{,}58$$

Calibration curve: $\mathrm{Re}\,sponse = 21675 \times C - 289{,}79$ valid for concentration between 0,01-1 mg.l^{-1}.

And the concentration in 10 ml of hexane is:

$$C = 0{,}02\ mg.l^{-1}$$

For the concentration in mg.l^{-1} of sample:

$$C_{SAMPLE} = \frac{C}{10} \times 4 = 0{,}008\ mg.l^{-1}$$

Determination of Nitrate

Although we can use the liquid chromatography for this determination, we used the spectrophotometric technique for the determination of nitrate, because the first technique was not available in laboratory, and it was interesting test if the spectrophotometer method could give accurate results as liquid chromatography. The principle of spectrophotometic method is very simple: nitrates react with 2,6-dimethylphenol in presence of concentrated sulphuric acid and phosphoric acid to red product, 4-nitro-2,6-dimethylphenol, then it’s only determine the nitrate concentration measuring the absorbance in the wavelength of 340nm. For this determination we use the equipment UV-VIS Spektrofotometr, Jasco V530, Jasco Corporation.The concentration range for this method is 3-50 mg.l^{-1} for nitrate. If the nitrite concentration is very high perturbing influences can appear. To eliminate this influence we add sulfamic acid. Chlorides can also have perturbing influences if its concentration is higher than 100 mg.l^{-1}.

Products:

Acetic Acid, Penta

2,6-dimethylphenol, 99%, Audrich

Sulphuric acid, 96% p.a., Lach-Ner

Phosphoric Acid, 85%, Chemapol

Sulfamic Acid, Fluka

Sodium Nitrate, p.a., Penta

Equipment:

UV-VIS Spektrofotometr, Jasco V530, Jasco Corporation.

Technical:

First it was prepared the follow solutions:

- 2,6-dimethylphenol solution: 250 ml of acetic acid + (0,300±0,002)g 2,6-dimethylphenol
- Mixture of acids: 250 ml acid sulphuric+ 250 ml of phosphoric acid
- Sulfamic acid solution: dissolve (0,800±0,002)g of sulfamic acid in 100 ml of distilled water.
- Standard solution of sodium nitrate 1000 mg.l^{-1}.

Put 1 ml of sample (or diluted sample according in concentration range) into the small flask, add 0,1 ml of Sulfamic acid solution and mix it. Add 7 ml of acid mixture and mix it. Then add 1ml of 2,6-dimethylphenol solution, cork the flask and mix it properly. Keep it stand 10 min and measure the absorbance in glass cuvette of 2 cm at 340 nm.

Example of calculation:

The calibration curve obtained was:

$Absorbance = 0{,}0245 \times C + 0{,}1627$ for the range of concentrations 5-50 mg.l^{-1}

Then it's only substitute the absorbance obtained and calculate the concentration:

(Example sample HLV1)

$$0{,}304 = 0{,}0245 \times C + 0{,}1627$$
$$C = 7{,}25\ mg.l^{-1}$$

The sample was diluted 100 times so the real concentration will be:

$$C = 7{,}25\ mg.l^{-1} \times 100 = 725\ mg.l^{-1}$$

Determination of Nitrite

Nitrite determination can also be made with liquid chromatography, but for the same reasons presented for the determination of nitrate it was used also the spetrophotometric determination. The principle for this method is: sulphanilamide is diazotised by HNO_2 (from NO_2 in sample) to diazonium salt in medium acid reaction (when H_3PO_4 is present). This salt reacts with N-(1-naftyl)-1,2-ethylendiamin-dihydrochlorid to red azo-dye, which is measured by spectrophhotometry in the wavelength of 540nm with the UV-VIS Spektrofotometr, Jasco V530, Jasco Corporation. The concentration range for this method is 0,05-0,25 $mg.l^{-1}$ for nitrite.

Products:

Phosphoric Acid, 85%, Chemapol

Sulfanilamide, 98%, Fluka

N-(1-naftyl)-1,2-ethylendiamin-dihydrochlorid, p.a., Penta

Sodium nitrite, p.a., Penta

Equipment:

UV-VIS Spektrofotometr, Jasco V530, Jasco Corporation.

Technical:

First it was prepared the follow solutions:

- NED solution, store in darkness – this reagent is dangerous, use gloves:

Put 500 ml of distilled water into 1000 ml balloon, keep continual mixing and add 100 ml of phosphoric acid. Then add (40,0 ± 0,5)g of sulphanilamide gradually and dissolve it. Then add (2,00 ± 0,02)g of N-(1-naftyl)-1,2-ethylendiamin-dihydrochlorid and dissolve it. Add distilled water to 1000 ml.

- Standard solution of sodium nitrite 100 mg.l^{-1}, store in the darkness. Dissolve (0,4922± 0,002)g of sodium nitrite in 1000 ml. Solution is not stable for a long time.

Put 40 ml of sample (or diluted sample accord in concentration range) into 50 ml volumetric flask. Add 1 ml of NED solution. Add distilled water to 50 ml. Mix it properly. Keeps it standing 20 min and then measure the absorbance in cuvettes of 1 cm at 540 nm.

Example of calculation:

The calibration curve obtained was:

$Absorbance = 5{,}2594 \times C - 0{,}0075$ for the range of concentrations 0,05-0,25 mg.l^{-1}

Then it's only substitute the absorbance obtained and calculate the concentration:

(Example sample HLV1)

$$0{,}718 = 5{,}2594 \times C - 0{,}075$$
$$C = 0{,}14\ mg.l^{-1}$$

The sample was diluted 1000 times so the real concentration will be:

$C = 0{,}14\ mg.l^{-1} \times 1000 = 140\ mg.l^{-1}$

Determination of Sulphates

For the determination of sulphate it was used the turbidimetric method. This method is based on the fact that light is scattered by particulate matter in aqueous solution. When barium and sulphate react in water, they make the solution turbid, which means the concentration of the sulphate can be measured by using a spectrophotometer. The equation for the reaction of barium and sulphate is show below:

$$SO_4^{\ 2-}(aq) + Ba_2^{\ +}(aq) \rightarrow BaSO_4(s)$$

These solid particles can not sediment, so the analysis must be concluding in 25 minutes. The concentration range is 10-40 mg.l^{-1} for sulphate and the wavelength for analysis is 550nm .It was analysed with the UV-VIS Spektrofotometr, Jasco V530, Jasco Corporation.

Products:

Sodium sulphate, 98%, Penta

Barium Chloride di-hydrated , Lachema

Equipment:

UV-VIS Spektrofotometr, Jasco V530, Jasco Corporation.

Technical:

For the determination of sulphate it was used the turbidimetric method. Measure 50 ml of sample and then add 0,1-0,2 g of Barium Chloride di-hydrated. Then wait 5 min and measure carefully in spectrophotometer at 550 nm.

The calibration curve obtained was:

$Absorbance = 0{,}001 \times C - 0{,}0005$ for the range of concentrations 10-40 mg.l^{-1}

Then it's only substitute the absorbance obtained and calculate the concentration.

Determination of Chlorides

The determination of chlorides was made using the Mohr method. In this method the determination is made by a titulation. It consists in adding silver nitrate to the sample, in presence of the indicator potassium chromate, and wait for the end point (when the colour of solution is red-brown). Then with the obtained volume and concentration of silver nitrate the concentration of chlorides will be determined. The pH of sample should be between 6 and 8.

Products:

Silver Nitrate, p.a., Lachema

Potassium Chromate, p.a., Lachema

Technical:

First it was made a standard solution of silver nitrate of concentration approximately 0,01M. After it was determined the real concentration of this solution, it was started the analysis of chlorides. For this determination it is used 50 ml of sample, witch is added 50 ml of distilled water and 1ml of potassium chromate indicator. Then it starts the titration by adding silver nitrate to the sample. The end point will be indicated by the persistence of a red-brown color through the yellow solution for about 30 seconds.

Example of calculation:

$$C_{AgNO_3} = 0{,}011601M$$

$$V_{AgNO_3} = 32{,}20\ ml$$

At end point:

$$C_{AgNO_3} \times V_{AgNO_3} = C_{Cl^-} \times V_{Cl^-}$$

And the chlorides concentration can be calculated:

$$0{,}0011601 \times 32{,}20 = C_{Cl^-} \times 50$$

$$C_{Cl^-} = 0{,}007459\ mol.l^{-1} \times 35{,}45\ g.mol^{-1} = 0{,}286\ g.l^{-1} = 286\ mg.l^{-1}$$

Annex 4 Characterization of contaminated groundwater sample

Metals Analysis

Table A4.1 - Analysis of Metals

Spectrum	Compound Name	Concentration (mg.l^{-1})
Absorption	Arsenic	ND
	Calcium	66,09
	Cadmium	0,122
	Chromium	<2
	Cupper	<0,2
	Zinc	<0,2
	Iron	ND
	Manganese	3,25
	Nickel	0,074
	Lead	<0,1
Emisssion	Sodium	51,98
	Potassium	115

Pesticides Analysis

Table A4.2 - Analysis of Pesticides

Compound Name	Concentration ($mg.l^{-1}$)
α-HCH	0,0582
HCB	<0,0004
ß-HCH	0,0165
γ- HCH	0,0238
Heptachlor	0,0008
Heptachlor exo epoxid	<0,0004
2,4-DDE	<0,0004
α - endosulfan	<0,0004
4,4-DDE	<0,0004
Dieldrin	<0,0004
2,4-DDD	<0,0004
endrin	<0,0004
ß- endosulfan	<0,0004
4,4-DDD	0,0012
2,4-DDT	0,0009
4,4-DDT	0,0023

Annex 5 – Results from RO experiments

Experiment 20 bar

Table A5.1 - Data from collect time, conductivity of concentrate (μC) and permeate (μP), temperature of concentrate, concentration factor, permeability and efficiency (EFC).

$V_{Permeate}$ (l)	t (s)	μC ($mS.cm^{-1}$)	μP ($\mu S.cm^{-1}$)	TC (°C)	t 100ml (s)	CF	Driving Force ($m^3.s^{-1}.m^{-2}$)	Permeability (%)	Efficiency (%)
0	0	1,2	53,7	20,0	55,00	1,00	5,22E-06	4,33	95,67
2	1135	1,5	57,6	20,6	57,10	1,11	5,03E-06	3,89	96,11
4	2290	1,7	65,2	20,4	57,63	1,25	4,99E-06	3,86	96,14
6	3425	1,9	72,1	20,1	57,30	1,43	5,01E-06	3,84	96,16
8	4630	2,1	77,4	20,0	58,07	1,67	4,95E-06	3,78	96,22
10	5820	2,3	92,2	19,7	58,10	2,00	4,95E-06	3,97	96,03
12	7010	2,9	111,3	20,1	59,66	2,50	4,82E-06	3,85	96,15
14	8210	3,6	146,0	20,3	59,70	3,33	4,81E-06	4,02	95,98
16	9423	5,0	206,0	20,3	61,56	5,00	4,67E-06	4,14	95,86
18	10688	8,1	216,0	20,3	62,84	10,00	4,57E-06	2,67	97,33

Experiment 30 bar

Table A5.2 - Data from collect time, conductivity of concentrate (µC) and permeate (µP), temperature of concentrate, concentration factor, permeability and efficiency (EFC).

$V_{Permeate}$ (l)	t (s)	µC ($mS.cm^{-1}$)	µP ($\mu S.cm^{-1}$)	TC (ºC)	t 100ml (s)	CF	Driving Force ($m^3.s^{-1}.m^{-2}$)	Permeability (%)	Efficiency (%)
0	0	1,75	76	21	36,38	1,00	7,90E-06	4,34	95,65
2	726	2,05	75,3	22,2	33,5	1,15	8,58E-06	3,67	96,32
4	1462	2,4	84,6	21,9	36,78	1,36	7,81E-06	3,52	96,47
6	2311	2,9	101,6	22,6	37,75	1,67	7,61E-06	3,50	96,49
8	2973	3,61	123,6	23,1	39,5	2,14	7,27E-06	3,42	96,57
10	3744	4,66	162,3	22,8	39,7	3,00	7,24E-06	3,48	96,51
12	4522	6,66	223	22,9	42,1	5,00	6,83E-06	3,34	96,65
13	5036	8,12	230	20,7	47,15	7,50	6,09E-06	2,83	97,16

Experiment 40 bar

Table A5.3 - Data from collect time, conductivity of concentrate (μC) and permeate (μP), temperature of concentrate, concentration factor, permeability and efficiency (EFC).

$V_{Permeate}$ (l)	t (s)	μC ($mS.cm^{-1}$)	μP ($\mu S.cm^{-1}$)	TC (°C)	t 100ml (s)	CF	Driving Force ($m^3.s^{-1}.m^{-2}$)	Permeability (%)	Efficiency (%)
0	0	1,2	44,7	20,6	30,94	1,00	9,29E-06	3,73	96,28
2	607	1,5	49,9	24,1	29,87	1,11	9,62E-06	3,35	96,65
4	1215	1,7	54,1	21,4	30,34	1,25	9,47E-06	3,15	96,85
6	1851	1,9	55,7	21,1	31,87	1,43	9,02E-06	2,95	97,05
8	2490	2,0	59,8	20,7	31,47	1,67	9,13E-06	2,98	97,02
10	3121	2,4	68,0	20,8	31,81	2,00	9,03E-06	2,83	97,17
12	3772	3,0	82,8	20,8	33,17	2,50	8,66E-06	2,80	97,20
14	4425	3,7	102,0	20,6	31,35	3,33	9,17E-06	2,76	97,24
16	5112	5,2	139,6	20,5	33,82	5,00	8,50E-06	2,68	97,32
18	5800	8,1	219,0	20,3	34,12	10,00	8,42E-06	2,71	97,29

Table A5.4- Concentration of pesticide in the different flows from experiments of 20, 30 and 40 bar in RO module.

		Concentration mg.l^{-1}					
Compound	**GW1**	**Permeate 20 bar**	**Permeate 40 bar**	**Permeate 30 bar**	**Concentrate 20 bar**	**Concentrate 30 bar**	**Concentrate 40 bar**
α-HCH	<0,0004	<0,0004	<0,0004	<0,0004	0,01	0,03	0,01
HCB	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004
β- HCH	0,008	<0,0004	<0,0004	<0,0004	0,1	0,04	0,01
γ-HCH	0,002	<0,0004	<0,0004	<0,0004	0,01	0,01	0,02
Heptachlor	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004
4,4´DDE	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004
Dieldrin	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004
2,4´DDD	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004
4,4´DDT	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004

Table A5.5 - Measurements of permeate characteristics for different times of the experiment (along the concentration factor) in Nový Rychnov samples: concentration of chlorides and conductivity.

Permeate	**CF**	**Concentration** **Chlorides ($mol.l^{-1}$)**	**μ($\mu S.cm^{-1}$)**
B2	1,01	7,59E-04	23,5
B4	1,26	8,78E-04	23,2
B6	1,65	5,09E-04	28,8
B8	2,19	3,99E-04	33,2
B10	2,78	4,29E-04	45,5
B12	3,63	5,19E-04	49,4
B14	4,75	7,29E-04	49,3
B16	6,74	6,09E-04	58
B18	9,79	7,49E-04	92,1
B20	12,22	6,69E-04	125,4

Table A5.6 - Measurements of concentrate characteristics for different times of the experiment (along the concentration factor) in Nový Rychnov samples: concentration of chlorides and conductivity.

Concentrate	CF	Concentration Chlorides (mol.l^{-1})	μ (μS.cm^{-1})
B1	1,01	7,68E-04	2,15
B3	1,26	9,48E-04	2,91
B5	1,65	1,07E-03	3,59
B7	2,19	1,23E-03	4,12
B9	2,78	1,57E-03	5,44
B11	3,63	1,72E-03	6,04
B13	4,75	1,81E-03	6,2
B15	6,74	2,03E-03	7,11
B17	9,79	2,61E-03	9,81
B19	12,22	3,30E-03	11,87

Table A5.7 - Results for the permeability along the experiment from the samples from Nový Rychnov.

CF	Permeability (%)
1,01	1,09
1,26	0,80
1,65	0,80
2,19	0,81
2,78	0,84
3,63	0,82
4,75	0,80
6,74	0,82
9,79	0,94
12,22	1,06

Table A5.8 - Concentration of NO_3^- in groundwater samples

	Concentration NO_3^- ($mg.l^{-1}$)				
	Day 1 (Analytical method)	**Day 3 (Analytical method)**	**Day 3 (Liquid Chromatography)**	**Day 10 (Analytical method)**	**Day 12 Sample Normally Stored**
HV1			**71,90**	673,06	
HV4	197,63	177,22		147,43	
HV5	107,76	123,84		155,80	
HV11	1221,22	1233,88	904,46	1306,53	
HV15	700,16	865,55		910,86	702,04
HV17			**265,32**	951,43	
HV19		193,31		230,33	
HLV1	725,31	698,53	726,31	610,12	912,82
HLV4			1173,72	1201,84	
HLV5				222,12	

Table A5.9 - Concentration of NO_2^- in groundwater samples

	Concentration NO_2^- (mg.l^{-1})			
	Day 3 (Analytical method)	**Day 3 (Liquid Chromatography)**	**Day 7 (Analytical method)**	**Day 12 Sample Normally Stored**
HV1	2,88	**23,62**	2,99	
HV4	8,85		8,38	
HV5	7,85		7,45	
HV11	11,80	**151,47**	11,60	
HV15	22,03		20,64	19,95
HV17	0,10	**11,28**	0,11	
HV19	ND		ND	
HLV1	70,54	**522,44**	69,91	72,82
HLV4	104,48	**770,93**	105,94	
HLV5	7,87		7,90	

- **Pesticides Analysis**

Table A5.10- Pesticides Concentration

	Concentration of Pesticides (mg.l^{-1})							
	HLV1	**HLV5**	**HV1**	**HV4**	**HV5**	**HV11**	**HV15**	**HV19**
α-HCH	0,102	0,127	0,154	0,048	0,172	0,005	0,008	0,002
HCB	<0,0004	0,001	0,010	<0,0004	<0,0004	<0,0004	<0,0004	<0,0004
ß- HCH	0,010	0,041	0,075	0,013	0,099	0,002	0,001	0,002
γ-HCH	0,010	0,024	0,043	0,008	0,063	0,001	0,001	0,001
heptachlor	0,0006	0,001	<0,0004	0,001	0,002	<0,0004	<0,0004	<0,0004
4,4´DDE	<0,0004	0,002	0,007	<0,0004	0,002	<0,0004	<0,0004	<0,0004
2,4´DDD	<0,0004	0,002	0,010	<0,0004	<0,0004	0,001	0,001	0,001
ß-endosulfan	<0,0004	<0,0004	0,001	<0,0004	0,001	<0,0004	0,001	<0,0004
4,4DDD	<0,0004	0,005	0,037	<0,0004	<0,0004	0,001	0,002	0,001
2,4DDT	0,001	0,006	0,052	0,001	0,001	0,001	0,001	0,001
4,4´DDT	0,002	0,018	0,177	0,003	0,002	0,003	0,003	0,003
Total Concentration	0,126	0,227	0,566	0,074	0,342	0,013	0,019	0,011

Sample HV5

Table A5.11 - Data from collect time, conductivity of concentrate (μC) and permeate (μP), temperature of concentrate, concentration factor, permeability and efficiency (EFC).

$V_{Permeate}$ (l)	t (s)	μC ($mS.cm^{-1}$)	μP ($\mu S.cm^{-1}$)	TC (°C)	t 100ml (s)	CF	Driving Force ($m^3.s^{-1}.m^{-2}$)	Permeability (%)	Efficiency (%)
0	0	0,944	40,4	26,7	22,75	1,00	1,26E-05	4,28	95,72
2	547	1,08	45,4	27,4	23,64	1,11	1,22E-05	4,20	95,80
4	1000	1,25	51	27,4	24,32	1,25	1,18E-05	4,08	95,92
6	1438	1,45	52,2	27,8	23,6	1,43	1,22E-05	3,60	96,40
8	1942	1,58	55,4	27,8	24,89	1,67	1,15E-05	3,51	96,49
10	2440	1,77	58,5	27,9	25,96	2,00	1,11E-05	3,31	96,69
12	2939	2,19	70,5	28,2	25,95	2,50	1,11E-05	3,22	96,78
14	3430	2,74	90,4	28,5	25,09	3,33	1,15E-05	3,30	96,70
16	3922	3,94	114,5	28,8	26,83	5,00	1,07E-05	2,91	97,09
18	4492	5,84	169,7	28,4	26,6	10,00	1,08E-05	2,91	97,09

Sample HLV1

Table A5.12 - Data from collect time, conductivity of concentrate (μC) and permeate (μP), temperature of concentrate, concentration factor, permeability and efficiency (EFC).

$V_{Permeate}$ (l)	t (s)	μC (mS.cm^{-1})	pH C	μP (μS.cm^{-1})	TC (°C)	t 100ml (s)	CF	Driving Force (m^3.s^{-1}.m^{-2})	Permeability (%)	Efficiency (%)
0	0	4,79	7,66	190	25,7	10,56	1,00	1,12E-05	3,97	96,03
2	225	5,7	7,68	197	25,5	11,72	1,11	1,13E-05	3,46	96,54
4	470	6,27	7,68	216	25,8	13,81	1,25	1,11E-05	3,44	96,56
6	690	6,92	7,7	239	25,9	16,75	1,43	1,11E-05	3,45	96,55
8	1070	7,33	7,71	270	25,9	17,19	1,67	1,11E-05	3,68	96,32
10	1441	8,75	7,72	323	26,2	20,44	2,00	1,10E-05	3,69	96,31
12	1900	10,97	7,72	450	26,8	29,4	2,50	1,07E-05	4,10	95,90
14	2613	13,3	7,7	675	27,4	44,16	3,33	1,05E-05	5,08	94,92
16	3725	17,9	7,67	1080	27,4	71,9	5,00	1,05E-05	6,03	93,97
17,2	5290	24,8	7,09	1380	27,1	91,38	7,14	1,06E-05	5,56	94,44