New process of drinking water production in the 21st century

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Fluidized-IEX
Ca-verwijdering

Marmer
filtratie
+ GAC
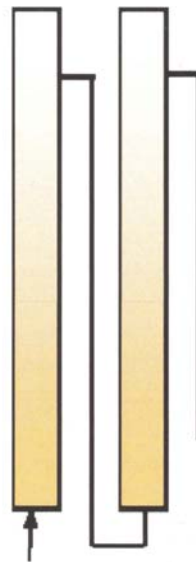
Ultrafiltratie

Nanofiltratie

Department of Water Management
Sanitary Engineering Section

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Partner for progress

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New process of drinking water production in the 21st century

Master of Science Thesis

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Abstract

With the development of industry, many new micro pollutants are found in the water sources for drinking water. For instance endocrine disrupting compounds, pharmaceuticals, personal care products, MTBE are reported. However, the conventional water treatment has limited removal efficiency for these components. Therefore, in order to deal with these substances, we introduce a new treatment concept: fluidized Ion exchange---UF---NF---GAC adsorption. With this treatment concept, we obtain a double barrier (UF-NF) for particles and microorganisms; double barrier (NF-GAC adsorption) for the micro pollutants and natural organic matter. The main problem of this concept is the membrane fouling, so we use fluidized cation exchange system to remove an important fouling factor in membrane filtration---calcium. Experiments are performed to demonstrate the positive effect of calcium removal on the prevention of membrane fouling, check the effectiveness of treatment concept on target substances, and set up the model of fluidized IEX system. The results showed that both monovalent and multivalent ions on the membrane surface are crucial fouling factors, and Fluidized IEX system is a good pretreatment for membrane filtration. The treatment concept was good in removing target substances, except the polar ones with molecule weight smaller than 100 Da. For the modeling of fluidized IEX system, pH is an important parameter, which determines the exchange capacity.

Keyword: NOM, pharmaceuticals, nanofiltration, ultrafiltration, monovalent, multivalent

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1. Introduction

In order to keep the confidence of consumers on the drinking water quality in 21st century, the water companies in the Netherlands launched a Q21 project to reach an impeccable quality in the tap water. Considering the treatment system at this moment, there are still four quality problems in the tap water: 1. Biological stability; 2. Particle concentration; 3. Polar and non-polar micro pollutants; 4. Pathogen microorganisms. Therefore, a new treatment concept was introduced, Fluidized Ion EXchange-Ultrafiltration-Nanofiltration-GAC adsorption. By applying this process, we can set up double barriers for the remaining four quality problems, because the UF-NF can form a double barrier for the particles, pathogens and the natural organic matter; while the NF-Adsorption are double barrier for the micro pollutants. The problem of this process is whether the membrane filtration steps can work stable. In traditional treatment concepts with a combination of ultrafiltration and nanofiltration severe NOM-fouling is expected on the ultrafiltration and scaling limits the recovery in the nanofiltration. In the new treatment concept we use ion exchange as pretreatment step to prevent these problems.

Divalent cation (Ca^{2+}, Mg^{2+}, Ba^{2+}) has been proved to be dramatic fouling factor for membrane filtration [1,2,4]. Under the same condition, such as initial permeate flux (permeation drag), cross flow velocity, pH and ionic strength, feed water without divalent ion gives less fouling because we know that natural organic matter is the major foulant, while the presence of divalent ion binds the acidic functional groups of NOM, and then form a compact layer on the membrane surface. In addition, the bridging between Ca^{2+} and negatively charged NOM groups further enhance the compactness of fouling layer [3]. That is the influence of divalent ion reacting with functional groups of NOM on membrane fouling. However, in NF, with the increase of concentration, more divalent ion accumulate on the surface of membrane, which will lead to the excess of saturation concentration followed by scaling---precipitation of divalent ion.

So, before we consider using membrane system to produce high quality drinking water, we must remove the divalent ions from the feed water. Although softening can remove part of Ca^{2+} from feed, and significantly reduce organic fouling in ultrafiltration [6], but it cannot remove completely. In that case, IEX is a good choice. Because of the high-preferred selectivity on Ca^{2+}, Mg^{2+}, and Ba^{2+} for acidic cation resin, the divalent ions are remained by IEX.

Because the canal water is going to be used as feed water, the particles in it can easily clog the IEX resin bed due to the small size of resin. The IEX-column cannot be backwashed as a rapid sand filter because of the low density of the resin. In order to solve this problem, fluidized IEX bed will be used, the fluidized bed is not supposed to clog with suspended solids.

After fluidized IEX, multivalent ion-free water will be transported to UF-NF. The set up of two steps membrane system is to install double barriers for particle, microorganism (bacteria, pathogen, and virus) and colloidal substance. UF can remove bacteria, virus, colloidal substance and all other particles with higher 10000 Da molecule weight, while NF can remove salts, organic micro pollutants and all other molecules with a molecule weight of 200 or more.

Because of the pretreatment of IEX, the fouling potential for UF reduces. NF is easy to be blocked by particle substance due to its small pore size. Therefore, UF, as a pretreatment of NF, reduces dramatically the fouling potential of NF due to its removal of colloidal particle substance, which has been demonstrated to be an important fouling factor on membrane. The scaling in the NF will be also minimal for the absence of divalent ion in the feed. In this order, double membrane barriers can remove microorganism, particles and colloidal substance efficiently. At the same time, fouling potential for both membrane units can be minimized by the removal of fouling factor under optimized pretreatment order.

Permeate of NF will be treated by adsorption of GAC, which absorbs organic micro pollutants, odor, taste and color producing compounds. Then, the micro pollutants also meet double barriers in the whole process---NF & GAC adsorption. Because almost all DOC are removed in NF, the pre-loading of GAC adsorption will be dramatically reduced. Therefore the adsorption filter can be run for a longer time before breakthrough of organic micro pollutants occur.

However, that is just the ideal situation. No one knows what will really happen in the practice. Until now the UF and NF fouling research was performed on laboratory scale. Therefore the objectives of this thesis project are:
1. Prove the consistent negative influence of calcium on membrane (UF) in bench scale by comparing water after ion exchange and normal raw water
2. Prove ion exchange is a good pretreatment for membrane system and provide the most important process parameters.
3. IEX-UF system will be connected with NF-Activated carbon adsorption, as a complete treatment process for future. Because of the optimized order, we expect this process can produce stably high quality drinking water with longer run time and less chemical cleaning, demonstrate the treatment stability with load fluctuation. What's more, the recovery of the NF can be higher at the same condition than other NF operations without divalent ion removal, and then reduce the investment of NF installation.
4. If the system works properly, we can spike different micro pollutants to check the removal of these compounds.
5. Set up a rough model for the fluidized IEX system

2. Theory & Literature

2.1 Natural organic matter (NOM)

2.1.1 Definition

NOM is organic matter originating from degraded plants and animals present in natural (untreated or raw) waters, for example, in lakes, rivers and reservoirs. NOM is composed of six major groups: humic substances, hydrophilic acids, carboxylic acids, amino acids, carbohydrates, and hydrocarbons.

2.1.2 Influence on fouling

NOM has been proved to be the major foulant of membrane, but which part of NOM plays the most important role is interesting for us. According to the previous research, Boksoon Kwon [8] has found that NOM can be divided into colloidal NOM and non-colloidal NOM, while each fraction can be subdivided into hydrophilic, transphilic and hydrophobic NOM. In another method, NOM was divided into humic substance (over 50% DOC), which contains aromatic and alphatic components with mainly carboxylic and phenolic functional groups [9], and non-humic substance composed of transphilic acids, proteins, amino acids and carbohydrates (20-40% DOC) [10, 11]. For both classifications, macromolecule particles are demonstrated to be the crucial foulant at the beginning of membrane fouling. For example, A.L.Zydney at al., 1999 [12] found that macromolecule humic acid particle is the major foulant. The similar result---fouling are caused by larger NOM particles, is also reported respectively by Fan at al., 2001 and Howe & Clark et al., 2002. [13, 14]

Therefore, for the fouling of ultrafiltration, macromolecule NOM plays a significant role. Since the colloidal NOM are normally macromolecule, we can view colloidal NOM as major foulant. Because of the big size of macromolecule, they at the beginning of fouling block the pores of membrane. After that, the adsorption of the fouling mechanism starts, small foulant particles will dominant the pores of membrane by adsorption, which lead to further compactness of fouling layer. The above-mentioned characterizations are not the all classifications of NOM. According to classification of Leenheer [15], NOM was divided into colloidal organic matter (remained in 3.5kDa membrane), hydrophilic organic matter, transphilic organic matter and hydrophobic organic matter.

Some other experiments also demonstrate that hydrophilic and hydrophobic NOM are main fouling factor [13, 16]. From the subdivision of Kwon, we know colloidal NOM contained hydrophilic and hydrophobic NOM, so it is hard to distinguish which one has bigger influence, particle size or hydrophilicity. Based on the hydrophilicity and charge of feed, Fan found that the fouling potentials of different matter were:

hydrophilic neutral>hydrophobic acids>transphilic acids>hydrophilic charged. What's more, the higher is aromaticity, the greater is the flux decline, while the aromaticity focuses on the hydrophobic and transphilic organic matter [13], it means hydrophobic and transphilic organic matter influence the fouling of membrane. However, by comparing the fouling caused by hydrophobic NOM and transphilic NOM, hydrophobic NOM gave higher flux decline. Since both hydrophilic and hydrophobic NOM contribute to the membrane fouling, for the real application, we have no need to emphasize on difference between them. Further more, because of their small size of some particles, it is useless to avoid it by pre-filtration. Perhaps, chemical properties change of membrane can give some positive effect on limiting fouling, or removing the hydrophilic & hydrophobic NOM with some chemical methods. Brian Bolto [17] proved that anion exchanger could adsorb the negatively charged NOM from feed. Although negative charged has the least fouling potential according to the Fan et al.2001, it is also an indication for us to find the practical way to separate the hydrophilic & hydrophobic from feed water from charge or other chemical aspects.

Some scientists also think colloids are the major class of foulants in membrane processes, and did some researches on colloidal fouling [19-24]. It seems there is difference among the definitions of major foulant matters, but it depends on the subdivision. We know from the above-mentioned classification of organic matter: Colloidal matter contains hydrophilic, hydrophobic and transphilic matters and colloidal matter is also part of natural organic matter (NOM).

2.2 Ion exchange
2.2.1 Definition & principles

Ion exchange is a reversible chemical reaction wherein an ion attached on the immobile functional group is exchanged by a similarly charged ion in the solution phase.

An organic ion exchange resin is composed of high-molecular-weight polyelectrolytes that can exchange their mobile ions by taking up similarly charged ions from the surrounding medium. The maximum quantity of exchanges per unit of resin is determined by the distinct number of mobile ion sites on each specific resin.

There are four kinds of resin in total: strong acid cation resin; weak acid cation resin, strong base anion resin and weak base anion resin. Each type of resin has its own specific application, strong acid resin used for deionization and softening, and weak acid resin can be used for the same purpose, but it is easy to be influenced by the pH of feed water. The advantage of weak acid cation resin is lower requirement of regenerant solution. Base anion resins are used to convert the acid solution to pure water and remove the natural organic matter, and it is the same for the weak base anion resin as weak acid resin, easily influenced by the pH. In order to make the operation more convenient, weak acid cation resin is applied in this experiment.

Weak Acid Cation Resins. In a weak acid resin, the ionizable group is a carboxylic acid (COOH), instead of the sulfonic acid group (SO_3H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated.

The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Therefore, the pH value determines partly resin capacity. Figure 1[25], shows that a typical weak acid resin has limited capacity below a pH of 6.0, making it unsuitable for removing ions from the solution.
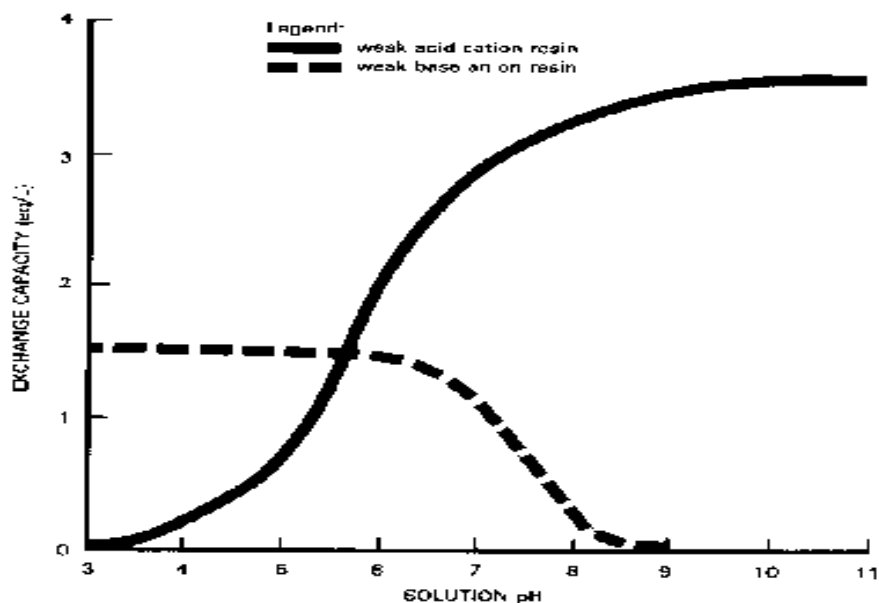
SOURCE: Adepted from Schweitzer. P. A., *Handbook of Separation Techniques for Chemical Engineers*, New York NY, McGraw-Hill, 1979.

Figure 2.1. Exchange capacity of weak acid cation resin and weak base anion resin versus pH

2.2.2 Ion selectivity

The ion exchange reaction is reversible. The degree the reaction proceeds to the right will depend on the resins preference, or selectivity. The selectivity of a resin for a given ion is measured by the selectivity coefficient. K, which in its simplest form for the reaction

R-A++B+=R--B++A+ (3)

It is expressed as: K = (concentration of B+ in resin/concentration of A+ in resin) X (concentration of A+ in solution/concentration of B+ in solution)[25].

The selectivity coefficient reflects how the ions exchange between two phases when a resin in the A+ form is placed in a solution containing B+ ions. Table 1[25] gives the selectivity's of strong acid and strong base ion exchange resins for various ionic compounds. It should be pointed out that the selectivity coefficient is not constant but varies with changes in solution conditions. It does provide a means of determining what to expect when various ions are involved. As indicated in Table 1, strong acid resins have a preference for calcium and other divalent ions over hydrogen. For the weak acid cation resin, if there is enough alkalinity in the solution, the resin also behaves with more or less the same preference as strong acid cation exchanger.

Strong acid cation exchanger	Strong base anion exchanger
Barium	Iodide
Lead	Nitrate
Calcium	Bisulfite
Nickel	Chloride
Cadmium	Cyanide
Copper	Bicarbonate
Zinc	Hydroxide
Magnesium	Fluoride
Potassium	Sulfate
Ammonia / Sodium	
Hydrogen	

Table 2.1 Selectivity of Ion Exchange Resins, In Order of Decreasing Preference

2.2.3 Regeneration

After certain time of adsorption, the resin will become exhausted so that the regeneration should be applied to bring back the adsorption capacity of resin. For the weak acid cation resin, it has the highest affinity to hydrogen ions. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. Almost complete regeneration can be accomplished with stoichiometric amounts of acid.

Regeneration procedure

1. Since the low upwards flow velocity of experiment (3.18m/h), the column is backwashed to remove suspended solids collected by the bed during the service cycle and to eliminate channels that may have formed during this cycle. The back-wash flow fluidizes the bed, releases trapped particles, and reorients the resin particles according to size.

During backwash the larger, denser panicles will accumulate at the base and the particle size will decrease moving up the column. This distribution is called stratification and prevents migration of loaded large particles from the bottom of the column to the top of the column. This stratification is remaining during operation.

2. The resin bed is brought in contact with the regenerant solution. In the case of the cation resin, acid elutes the collected ions and converts the bed to the hydrogen form. A slow water rinse then removes any residual acid.

3. The bed is brought in contact with a sodium hydroxide solution to convert the resin to the sodium form. Again, a slow water rinse is used to remove residual caustic. The slow rinse pushes the last of the regenerant through the column.

4. The resin bed is subjected to a fast rinse that removes the last traces of the regenerant solution and ensures good flow characteristics.

5. The column is returned to service.

2.3 Membrane filtration

2.3.1 Ultrafiltration

2.3.1.1 Definition & principles

Membrane filtration is a treatment, which separates the compounds from the feed water by the physical way in a semi permeable membrane. Ultrafiltration is one kind of membrane filtration, able to remove colloidal substances, microorganisms or compounds with molecular weight above 200 kDa.

Mass balance

For the dead end filtration:

$$Q_f = Q_p$$

Where: Q_f = feed flow rate [m3/h]
$\quad\quad$ Q_p = permeate flow rate [m3/h]

For a filtration run, the mass balance becomes:

$$Q_f = Q_p + Q_{bw}$$

Where: Q_{bw} = backwash flow rate [m3/h]

The recovery of ultrafiltration is the ratios between permeate flow and feed flow. During the filtration time, the recovery is 100%, but taking the backwash into account, the recovery becomes:

$$\gamma = \frac{V_p - V_{bw}}{V_p}$$

Where: V_p = volume of permeate
$\quad\quad$ V_{bw} = volume of permeate for backwash

Kinetics

Flux is an important parameter in membrane filtration. It is defined as the volume of permeates got per square meter in one hour.

$$J = \frac{Q}{A_{mem}} = \frac{TMP}{\nu \cdot R_{tot}}$$

Where: J $\quad\quad$ = flux [m3/(m2.h)]
$\quad\quad$ Q $\quad\quad$ = volume of flow [m3/h]
$\quad\quad$ A_{mem} $\quad$ = membrane surface area [m2]
$\quad\quad$ TMP $\quad$ = Trans membrane pressure [Pa]
$\quad\quad$ ν $\quad\quad\quad$ = Dynamic viscosity [Pa/s]
$\quad\quad$ R_{tot} $\quad\quad$ = Total resistance [m]

TMP is the pressure difference across the membrane, which determines the flux production. Temperature is another influence factor for the ultrafiltration under a certain TMP. One degree higher temperature can lead to 3 more percentages flux at the same pressure, so in order to compare the membrane performance under different temperature, the flux should be normalized for a fixed temperature by the following formula:

$$J_{cor} = J_{real} \frac{(42.5 + T_{ref})^{1.5}}{(42.5 + T_{real})^{1.5}}$$

Because of the same reason, in order to compare the different installation with different applied TMP, the flux should also be normalized for a fixed pressure. Since there is a linear relationship between flux and pressure, the normalized flux for pressure is:

$$J_{norm} = J_{cor} \cdot \frac{P_{ref}}{P_{real}}$$

Dead end filtration
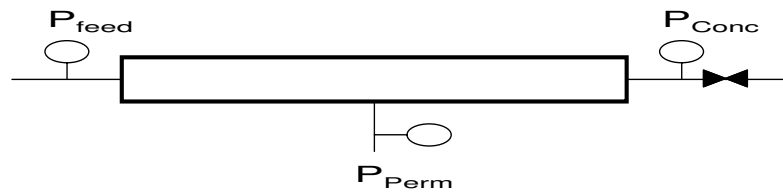
$$TMP = \frac{P_f + P_c}{2} - P_{permeate} = P_f - \frac{\Delta P_{hydr}}{2} - P_{permeate}$$

Because it is dead end filtration, hydraulic head loss in ultrafiltration is very small and neglectable, the TMP becomes:

$$TMP = P_f - P_{permeate}$$

2.3.1.2 Fouling mechanism

During the filtration, more and more particles are rejected by the membrane and then increase the membrane resistance because rejected particles block the pores of membrane or form a cake of suspended substances on the membrane surface. IUPAC [International Union of Pure and Applied Chemistry] defines the fouling as follow:1) deposition of suspended or dissolved matters on the membrane; 2) in front of the pores; 3) in the membrane pores. Therefore the fouling is defined into different mechanisms:

- Membrane resistance
- Pore blocking
- Adsorption in the pores
- Cake resistance
- High concentration of dissolved substances near the surface

Besides the particle size and hydrophilicity, a lot of other factors influence the fouling potential: such as applied pressure, cross flow velocity (NF), ionic strength, PH and calcium concentration. Hong S and Elimelech M [4] have proved that the higher ion strength of feed water is, the easier the membrane is fouled. Compared with low PH, high PH can produce less fouling. In the same report, Calcium concentration has been demonstrated a significant fouling factor, which complies with the research of Victor Ausgusto Yangali Quintanilla (UNESCO-IHE). [5]

Song also investigated the effect of ionic strength on the fouling. He found fouling potential is a good description of the fouling properties. [20] And if we use it to simulate the permeate flux, it can give extremely simulation to the measured permeate flux. After that, Singh and Song found that under the same colloids concentration, the higher is ionic strength, the higher is fouling potential. [18]

In the research of influence of various monovalent cations and calcium ion on the colloidal fouling potential done by Song [27], he also found the appearance of calcium could be a significant fouling factor.

The reason for the fouling with calcium probably is the formation of organic-Ca^{2+} bridging. However, how the organic-Ca^{2+} interacts with the negative charged membrane need better understanding. Perhaps the calcium cation acts as a bridge to connect the negative charged organic matter and negative charged membrane surface.

Besides the effect of calcium on the fouling potential mentioned in Ultrafiltration fouling mechanism, song also found there is a maximum fouling potential with the increment of ionic strength for divalent cations. In the experiment, membrane has maximum fouling potential with calcium under 0.003m ionic strength. Because the turbidity measurement showed that the aggregate occurs at 0.003 m ionic strength, concentration of salt at that case is the critical coagulation concentration (CCC). If the salt concentration is below CCC or peak in the fouling potential, fouling potential increases with divalent ionic strength, and the fouling potential decreases with over ionic strength due to the forming of aggregates [27]. Aggregate like the foulant with macromolecule, will produce more porosity, resulting less compact layer. Therefore, if aggregate forms, the fouling potential will be reduced.

For the monovalent cation, there is also maximum fouling potential with the effect of ionic strength. Na+: 0.45M; K+: 0.49M. Because it is much higher than the used ionic strength of monovalent cation, the fouling potential of monovalent cation didn't give the maximum fouling potential, and it has been increasing with the increment of ionic strength.

We must know that the effect of divalent ion is influenced by the permeate flux too. At the high flux 40-60l/m2h, Ca concentration and the flux itself have significant influence on the flux decline during about 50h operation, while at the moderate flux (20l/m2h), flux decline decrease slower [1,3]. However, for the real application, it is meaningless to use low flux, so although the divalent ion concentration has no influence on low flux process, we cannot skip its severe effect on high flux, which is the desired result we need.

Apart from the maximum ionic strength, for a given pressure, there exists an associated critical filtered volume [28]. Below the critical volume, fouling is reversible by rinsing, whereas above this critical volume a significant part of fouling is irreversible.

However, seidel and Elimelech et al.2002 said permeation drag (controlled by applied pressure) and divalent ion binding to NOM are the major cause for the observed rapid flux decline. Because the permeation drag acts on the transported NOM molecules, make them overcome the electrostatic repulsion between the NOM and the membrame, thus resulting in NOM deposition [23, 26]. At the same time, divalent

ions, such as calcium, magnesium, bind the acidic functional groups of NOM, which result in a compact fouling layer due to negatively charged property of membrane. In addition, the compactness of fouling layer will be further enhanced by bridging between calcium ion and negative charged NOM groups.

2.3.2 Nanofiltration
2.3.2.1 Definition & principles

Nanofiltration is one of the membrane filtration processes. This process is used to remove salts, organic micro pollutants and all other molecules with 200 molecule weight or more. Because of theirs small size of pores, the membrane can be easily fouled by very small substances.

Mass balance

The flow balance in nanofiltration system is:
$$Q_f = Q_c + Q_p$$

Where: Q_f = feed flow [m^3/h]
  Q_c = concentrate flow [m^3/h]
  Q_p = permeate flow [m^3/h]

It is also the case for the dissolved particles in water.
$$Q_f \cdot C_f = Q_c \cdot C_c + Q_p \cdot C_p$$
Where: C_f = concentration of dissolved material in feed water [g/m^3]
  C_c = concentration of dissolved material in feed water [g/m^3]
  C_p = concentration of dissolved material in feed water [g/m^3]

Recovery

Recovery is the ratio between permeate and the feed. The bigger is the recovery, the less concentrate produced during the membrane filtration.
$$\gamma = \frac{Q_p}{Q_f} \cdot 100\%$$
Where: γ = recovery

Kinetics

TMP
Water cannot pass through the membrane without any external power. Normally, we provide pressure for the need of membrane filtration. Beause of the high resistance of nanofiltration membrane, the pressure has to be high enough to overcome it. Besides the membrane resistance, the hydraulic loss along the membrane and the osmotic pressure difference among feed, concentrate and permeate also give extra resistance to the membrane filtration required overcoming. The pressure difference over the

membrane is the term called TMP---Trans Membrane Pressure, united in bar (10^5 kpa). By subtracting the pressure difference between both sides of the membrane, TMP is the real pressure applied on the filtration.

$$TMP = P_v - \overline{\Delta \pi} - \frac{1}{2}\Delta P_{Hydr} - P_p$$

Where: P_v = pressure of feed [Pa]

ΔP_{Hydr} = hydraulic pressure loss [Pa]

$\Delta\prod$ = osmotic pressure difference [Pa]

P_p = pressure of permeate [Pa]

Hydraulic pressure loss is the pressure difference between feed and concentrate.

$$\Delta P_{Hydr} = P_v - P_c \; ; \quad \text{then the TMP become:}$$

$$TMP = \left(\frac{P_v + P_c}{2} - P_p\right) - \left(\frac{\pi_v + \pi_c}{2} - \pi_p\right)$$

Osmotic pressure difference

Osmosis is a natural process which water flow tries to make the dissolved substances averaged by diluting the high concentration water with low concentration water. Because the remained particles cannot pass through the membrane, in order to get the balance, osmosis will make the water molecule outside flow into the membrane, and then it needs the driving force---osmotic pressure ---to reach the goal.

Osmotic pressure is given in the following formula:

$$\pi = \sum \frac{R \cdot T \cdot c_i \cdot z_i}{M_i}$$

Where: $\prod$ = osmotic pressure [Pa]

R = gas constant [J/K.mol]

T = temperature [K]

C_i = concentration of ion [g/m^3]

M_i = molecular weight of ion [g/mol]

Z_i = valency of ion [-]

TCF for $\prod$

$$TCF = \frac{273 + T_{act}}{273 + T_{ref}}$$

Where: TCF = temperature correction factor for $\prod$ [-]

T_{act} = actual temperature [℃]

T_{ref} = reference temperature [℃]

Normalized osmotic pressure

$$\pi_{normalized} = EGV * factor(EGV \rightarrow TDS) * factor(TDS \rightarrow \pi) * TCF$$

Where: EGV = conductivity [μs/cm]

Because the osmotic pressure also influenced by the temperature, it should be normalized if it is going to be used for the calculation of normalized Mass Transfer Coefficient (MTC).

Osmotic pressure difference
Osmotic pressure difference is the difference between permeate and the average osmotic pressure of feed and concentrate.

$$\overline{\Delta \pi} = \frac{\pi_{feed} + \pi_{concentrate}}{2} - \pi_{permeate}$$

Where: $\prod_{feed}$ = osmotic pressure of feed [Pa]
$\prod_{concentrate}$ = osmotic pressure of concentrate [Pa]
$\prod_{permeate}$ = osmotic pressure of permeate [Pa]

MTC (Mass Transfer Coefficient)
$$MTC = \frac{Q_p \cdot TCF_{MTC}}{A_{mem} \cdot TMP}$$

Where: Q_p = discharge of permeate [m^3/s]
A_{mem} = area of membrane [m^2]
TMP = trans membrane pressure [kPa]
TCF_{MTC} = temperature correction factor for MTC [-]

Normalization
Because the performance of membrane is influenced by the temperature, in order to compare the membrane fouling situation under different temperature, the MTC should be normalized to 20 degree centigrade.

TCF_{MTC}

$$TCF_{MTC} = e^{U \cdot \{\frac{1}{273+T_{act}} - \frac{1}{273+T_{ref}}\}}$$

Where: TCF_{MTC} = temperature correction factor for MTC [-]
U = membrane dependent constant [-]

2.3.2.2 Fouling mechanism

The fouling phenomenon of nanofiltration includes particle fouling, concentration polarization, scaling and biofouling. For NF, besides the fouling mechanisms mentioned in UF section: pore blocking, cake layer formation under the bridge effect of calcium, hydrodynamic interaction leads to the accumulation of NOM; divalent ions and bicarbonate, which will result in the chemical interaction, accelerating the

fouling by precipitation of dissolved ions. Because of the exceeding solubility, inorganic salts will precipitate on the surface of the membrane. That is what we call scaling. Scaling can occur when the concentration of salts in feed is too high, like running under a high recovery or the concentration polarization happen in the membrane. Under high recovery, just small amount of water is discharged as concentrate from the membrane system, so large amount of salts are accumulated in the membrane leading to the high salt concentration in the bulk flow, so the scaling starts when the concentration is high enough. Concentration polarization is a phenomenon that the transport of salts due to convection to the membrane is larger than the transport of salts from the membrane by diffusion. In that case, although the salt concentration in bulk flow is below the saturation concentration, the salt concentration near the membrane surface is above the solubility because of the salt accumulation caused by convection. However, concentration of salts is not the only factor for the scaling occurs, scaling also depends on many factors, like pH, temperature and the presence of other ions.

Super saturation is defined by the saturation index SI:

$$SI = log\left(\frac{IP}{Ksp}\right)$$

Where: SI   =saturation index [-]

K_{sp}=solubility product salt [mol/l]

IP =ion product [mol/l]

The solubility product K_{sp} is the temperature dependent. The value of ion product of a salt is determined by the ion strength, pH and the ion affinity.

Scaling can be prevented by increasing the cross flow velocity (eliminate concentration polarization), reducing ion concentration with pretreatment or dosing anti-scalants. High cross flow velocity can prevent the exceeding of solubility, but it takes high-energy consumption.

Lee, Cho and Elimelech also found the flux decline appeared to be more severe in the presence of divalent cations during their research of salt rejection in RO&NF [7]. They thought that is due to: 1) the higher rejection of salt, which lead to the high osmotic pressure; 2) thicker, denser colloid cake layer caused by decrease electrostatic repulsion between colloidal particles in presence of divalent cations.

Silica is one of the most abundant minerals naturally occurring on earth and a major species of colloids found in aquatic environments. [29] By observing the fouling layer on the membrane, we found that silica is also an important fouling factor for the nanofiltration. In the past, scientists thought due to short-range repulsive force formed by immobilized liquid layer brought by ions attached to surface, so silica colloid has high stability. The repulsive force inversely related with the size of attached cations: cesium<potassium<sodium<lithium. More recently, repulsive force was attributed to a gel layer or hydrated silica hairs approximately 1nm thick that is formed on silica surface on exposure to water. The layer forming the repulsive force was thought to contain silicic and silanol groups, which lead to the steric-like repulsive force between

particles. [30] it is the existence of repulsive force that makes the silica colloidal substance on membrane less compact.

However, experiment results showed changes in repulsion between silica are not highly sensitive to changes in solution, such as pH and ionic strength. It is contrary to hypothesis.

It is the same as Abenbdroth research; Song proved fouling potential is in sensitive to the type of salts and generally affected by ionic strength adsorption of alkali metal from lithium to cesium differ less than 20%. [27, 31]

While Vivian found lithium preferentially adsorbs at the silica interface, forming an impervious layer [32]. Song thought the reason for higher fouling potential perhaps is: lithium ions screen the silica hairs that formed on silica surface and form the impervious layer, then prevent hairs from interacting with each other and therefore particles can be pushed closer together, which lead to more compact cake layer and hence higher fouling potential value.

The above researches [4, 7, 27] have demonstrated that the divalent ions, such as calcium, barium, magnesium, are the scaling ions. If we can remove completely the divalent ions before nanofiltration, there should not be any scaling happen in the membrane system. In that case, we can improve the recovery of the NF, and then more flux can be produced at the same condition as previous recovery setting. It is important for the cost reduction due to less membrane area needed for the same flux requirement. What's more, because the reduction of scaling, less chemical will be used for the membrane cleaning; the frequency for chemical cleaning can be reduced and the production time increases.

Actually, it is possible in our concept; the fluidized IEX column and ultrafiltration are able to handle the fouling factors by removing divalent ions in fluidized IEX column and rejecting most of particles (organic and inorganic) with high molecule weight in ultrafiltration, then the pore blocking, scaling, biofouling can be limited. In addition with the recycling of concentrate, concentration polarization can be prevented under high cross flow velocity in membrane.

2.4 GAC adsorption
2.4.1 Definition
GAC adsorption is a treatment process used to remove the dissolved organics (both low and high molecular weight), taste & odour compound, pesticides, detergent, overall organics (DOC, TOC, KMnO4 number, UV-abs) and biodegradable organics (AOC, BDOC). In general, non-polar substances are better adsorbed than polar, and substances with double bounds are better adsorbed than substances with single bounds.

Activated carbon is a substance with a high carbon concentrate (e.g. pit-coal, turf). Under high temperatures this material is carbonated where the carbon is partially transformed into carbon monoxide and water. This is how the carbon gets its open structure. The internal surface area of the activated carbon is several times larger than the external surface area. Hence, a large part of the absorbed substances is adsorbed inside the carbon. The dissolved organic matter can be removed from water by filtration through a bed of activated carbon.

2.4.2 Principles
2.4.2.1 Equilibrium
There is equilibrium during the adsorption process. The concentration of adsorbed matter in the bulk flow determines the maximum loading capacity of the carbon. The higher concentration is in the bulk flow, the higher loading capacity. The relationship between the loading capacity and the concentration in the bulk flow follows adsorption-isotherm:

$$q_{max} = \frac{X}{m} = K \cdot C_s^{\ n}$$

Where: qmax = loading capacity [g/kg]
      Cs = equilibrium concentration [g/m3]
      X = adsorbed amount of compound [g]
      m = mass of activated carbon [kg]
      K = Freundlich constant [(g/kg).(m3/g)n]
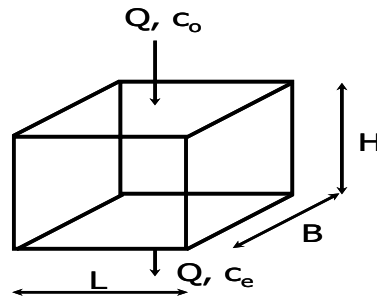   n = Freundlich constant [-]

2.4.2.2 Kinetics
The kinetics equation is as follow:

$$\frac{\delta c}{\delta t} = -u \frac{\delta c}{\delta y} - K_2 \cdot (c_0 - c_s)$$

This equation consists of a convection term: $u \dfrac{\delta c}{\delta y}$, and removal term: $K_2 \cdot (c_0 - c_s)$

2.4.2.3 Mass balance

According to the above figure, the mass balance equation is:

$$\frac{\delta q}{\delta t} = -\frac{v}{\rho}\frac{\delta c}{\delta y}$$

Where: v = filtration rate [m/h] = Q/BL

q = loading [g/g]

ρ = density of carbon [g/m3]

2.4.2.4 Solution s for the basic equations

Based on mass balance and kinetics, when a stationary situation is assumed, the effluent concentration of activated carbon filter can be calculated by using Bohart-adams equation.

$$\frac{c_0}{c_e} = 1 + \exp\{K_2 \cdot EBCT \cdot (1 - \frac{BV \cdot c_0}{q \cdot \rho})\}$$

EBCT = $\dfrac{V}{Q}$ = empty bed contact time [h]

BV = $\dfrac{Q \cdot T}{V} = \dfrac{T}{EBCT}$ = bed volume [m3/m3]

T = filter run time [h]

V = volume of filter [m3]

BV = amount of water filtered per filter bed volume

2.4.2.5 Regeneration

After certain time of filtration, the carbon bed should be regenerated because the carbon bed is saturated by the adsorbed organic compounds. It can be done by taking out the carbon from the bed and heat it up to 1000 degree, which leads to the degradation of adsorbed substances in the pores of activated carbon.

2.5 FeCl$_3$ coagulation

2.5.1 Coagulants

Coagulation is the process leading to the destabilization of negatively charged particles by dosing coagulant. After dosing coagulant, the destabilized particles incorporate into flocs, which have bigger size. Because of the big diameter, it is easy to block in front of the membrane pores, instead of in the pores. What's more, the foulant layer on the membrane surface will be less compact since there are more spaces among the big diameter flocs. The blockage in front of the pores and less compact foulant layer can be removed easily by the backwash, and that is why coagulation is used as pretreatment of membrane filtration.

In the Netherlands, iron chloride (FeCl$_3$) is frequently used as coagulant. Alternatively, aluminum sulfate (Al$_2$(SO$_4$)$_3$) can be applied. FeCl$_3$ is easy to dissolve in water, with 27.9mol/l solubility product (Ksp). Therefore, 162 g FeCl$_3$ can be dissolved in one liter of water, which means 56 mg/l Fe^{3+} and 106 mg/l Cl$^-$.

2.5.2 Coagulation mechanisms

There are three different mechanisms for coagulation process:
- Electrostatic coagulation
- Adsorptive coagulation
- Precipitation coagulation

For the electrostatic coagulation, positively charged ions approach negatively charged colloids, and then leads to the destabilization of colloidal substance and form removable flocs. During adsorptive coagulation, particles are adsorbed to positive charged hydrolysis product FeOH$_2^+$ and FeOH^{2+}. The last mechanism, precipitation coagulation, colloids are incorporated in neutral (iron) hydroxide flocs. In the real application, the above-mentioned mechanisms cannot be distinguished clearly, because they normally occur in parallel.

2.5.3 Coagulation as pretreatment of membrane filtration

As mentioned in the coagulants section, the coagulation can make the particles near the membrane surface bigger and result in a more effective backwash. That is why some real scale membrane installations in the Netherlands adapt the iron coagulation as the pretreatment. Although the coagulant can reduce the fouling in the membrane, it doesn't mean the higher concentration of coagulant dosing, the better fouling prevention. According to the research carried out by S.G.J.Heijman and G. Amy, it is clear that the fouling can be reduced if the coagulant is at low concentration, but the remaining fouling increases again at the higher concentration. They have found that, in the mini-scale experiment, there is an optimum coagulation concentration at about 2.5 mg Fe per liter [35].

2.6 Experiences of existing membrane plant

In order to produce high quality drinking water, some membrane treatment pilot plants have been built and provided us some valuable information about which treatment extent a specific membrane can reach. Some pre-treatment steps are also suggested to limit the fouling and improve the performance of membrane.

Colloidal aggregate are the initial foulant on the membrane, which catalyze fouling by lower molecular weight humic components [12]. Therefore, pre-coagulation, filtration is necessary to remove the big colloidal particles. However, according to their research, there are four fouling modes on the membrane: 1) cake formation; 2) complete pore blocking; 3) standard blocking; 4) intermediate blocking. Prefiltration of large NOM aggregate has no effect on the mode of fouling and only limited effect on its rate of development for smaller MWCO membranes. So the small MWCO membrane fouled in a cake formation mode (predominant).

Pilot plant experiment conducted by I.Mijatovic [33] showed that it is necessary to employ membranes with small cut-off, because experiment results reflected UF membrane can not remove the organic matter well. Compared with the conventional treatment steps (flotation-rapid filter-ozonation-slowfilter), UF didn't improve much. However, rejection of organics by UF can be increased by addition of coagulation ($FeCl_3$) in feed water.

NF, rather than UF should be used for removal of NOM, because most of organic molecules have low molecule weight. A similar full-scale process has been applied in France and the performance is promising. [34]

What's more, NF membrane with low inorganic rejection showed very good removal of NOM with negligible tendency towards scaling, so it is good to remove the inorganic matter before the nanofiltration. Colloids are also potential foulant for NF, because the conventional treatment cannot completely remove colloidal matter from the water.

3. Experiment materials and methods

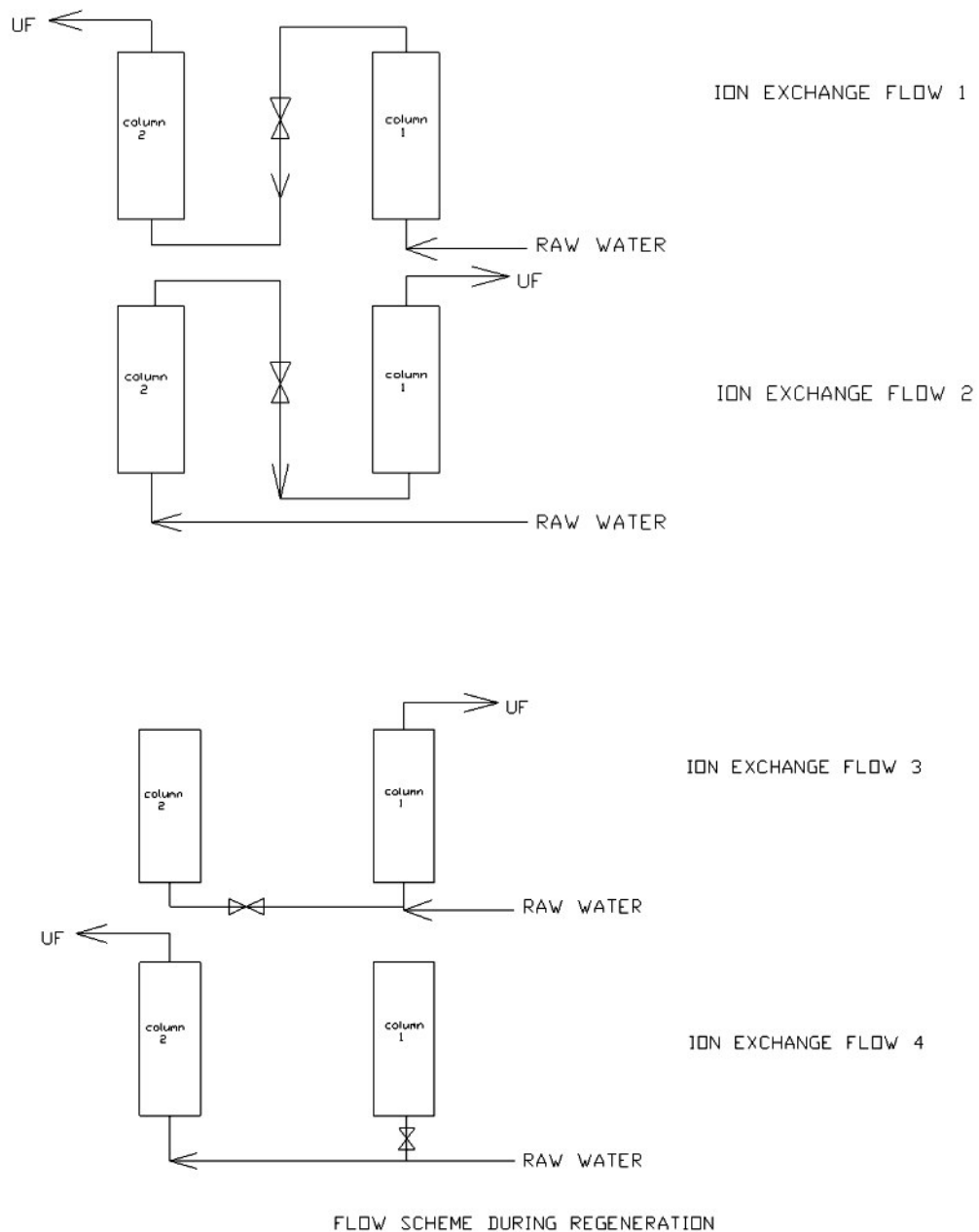## 3.1 Experiment materials
3.1.1 Fluidized IEX system
    1.   Flow scheme, flow mode

In order to make sure the particles in the canal water will not clog the resin bed like normal filtration process, fluidized Ion Exchange system was used in this project. During the exchange process, released hydrogen ion will react with the bicarbonate ion and form CO_2 bubbles, which will lead to the extra bed resistance if we used filtration flow mode. Because of the high calcium concentration of canal water, one Ion Exchange (IEX) column is not enough to guarantee the complete calcium removal, and then two IEX columns in series is important to give the promising performance. In that case, when we regenerate the first IEX column, the second one can still be used. Because the second column is a polishing column, it has enough capacity to handle the canal water in few hours. After the regeneration of the first column, it will be put after the original second column as a polishing column, and we can always have a less saturated column at the end then.
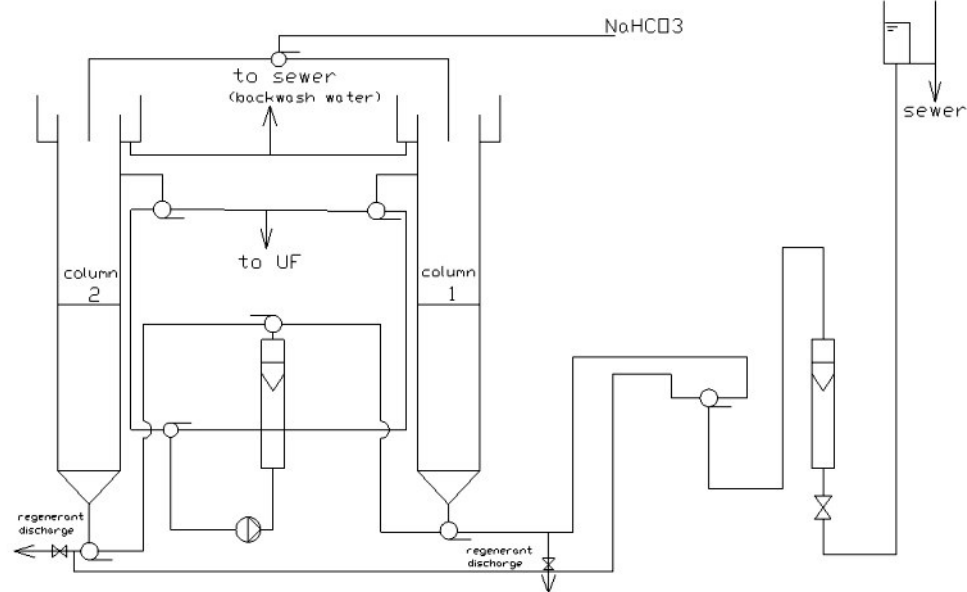
As shown in the above figure, Schie water is taken from the high level reservoir by gravity, and then pass through the IEX system in upwards flow. From the top of the column, $NaHCO_3$ will be dosed in the effluent of the first column so that the second column can work properly. The effluent of the first column will be pumped by a little pump to overcome the resistance of second column. In order to change the flow mode, we can simply change the direction of three-way valves. There are four flow modes in this system in total.

When both columns are not yet saturated, they will be used in two orders: column 1-column 2; column 2-column 1. The regenerated column is always the last column in the system. There are also two flow orders during the regeneration as figure x. In that case, only one column is in function.

ION EXCHANGE FLOW 1

ION EXCHANGE FLOW 2

ION EXCHANGE FLOW 3

ION EXCHANGE FLOW 4

FLOW SCHEME DURING REGENERATION

2. Resin

There are two kinds of acidic cation resin for divalent ion exchange: 1. strong acid cation resin; 2. weak acid cation resin. Compared with the strong cation resin, weak acidic resin is better, because it need fewer chemicals for regeneration than the strong acidic resin.

The weak acidic cation resin used in this experiment is the Amberlite IRC86 produced by ROHM&HAAS Company. This kind of resin is good to use in low salt background, which matches with the situation in this experiment. The capacity of this resin is 4,1

eq/l. the detail of this kind resin is presented at the following table.

Resin characteristics		
Functional group	COO^-	
Delivery form	H^+	
Total capacity	≥4.1 mol/l (H^+ form)	
Moisture salary	47 until 53% (H^+ Form)	
Thick	1.17 until 1.195 (H^+ Form)	
Debris weight	790 g/l	
Harmonious mittel	580-780 micro meter	
Equivalence coefficient	≤1.8	
Fine particle share	< 0.3: 2% max	
Volume porches ring	$H^+ \rightarrow Na^+$: 100%	
Max. temperature	120℃	
Least layer high	700 mm	
Specific load	5 until 70 BV/h	
Max. speed	50 m/h	
Regeneration	HCL	H_2SO_4
Concentration	2 until 5	0.5 until 0.7
Specific load	2 until 8	15 until 40
Quantity	104 until 110%	
Distorted	2 BV under regeneration condition	
Wash out	2 until 4 BV work condition	

3.1.2 Ultrafiltration
1. Flow scheme
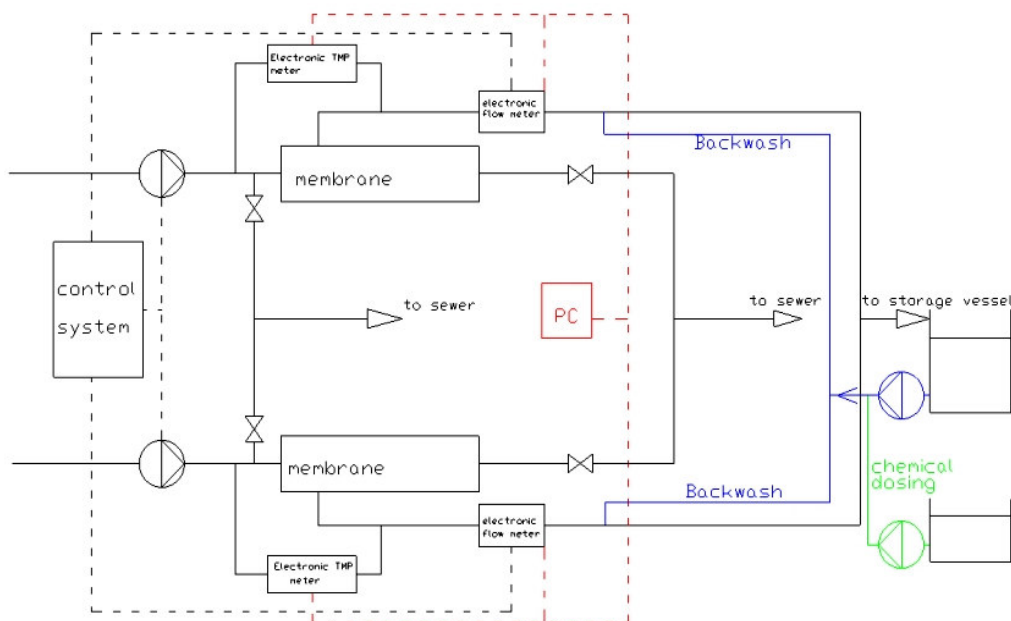
The equipment for ultrafiltration is an integrated installation. There are two feed pump on the installation, so parallel experiment is possible. However, permeate of both membranes are collected in the same permeate vessel, and during backwash permeate is taken from the bottom of vessel. Chemical is dosed on-line when the Enhanced Chemical Backwash starts.

This installation can be run automatically or manually. Under the manual operation, we can check whether the equipment works properly. Because the experiment is long-term experiment, automatic operation is used normally. As shown in the figure x, the values of pressure of feed pump and the permeate flux are real-time transferred to the control system. If we set the experiment in constant flux condition, the control system will send the signals to the feed pump to increase the feed pressure when the flux decline due to the fouling on the membrane surface. The pressure and flux information are also sent to computer automatically so that the graph of TMP, flux versus time can be formed in the computer. And then we can see the TMP change tendency versus time under constant flux situation. Another way around, if we set the installation in constant pressure, the flux decline tendency can be observed.

2. Type of membrane

The membrane used for ultrafiltration in this experiment is produced by X-Flow Company. This kind of membrane is hydrophilic and composed of a blend of polyvinylpyrrolidone and polyethersulfone. It also contains glycerine for pore protection and bisulfite for prevention of microbiological growth. There are two kinds of capillary tube available: 0.8 mm and 1.5 mm, and the 0.8 mm capillary tube is used in this experiment.

The detail information of the membrane is shown in the following table:

Parameter	Unit	UFC M5	Remarks
Transmembrane pressure	kPa	-300---+300	
Molecular weight cutoff	kDa	200	on dextranes
pH feed		2---12	
Chlorine exposure	ppm.h	250000	500 ppm max.at 0-40℃
Temperature	℃	1---80	

	NaOCl	200 ppm max.at 40℃ max. and max.30minutes per day
	H₂O₂	100-200 ppm at 40℃ max.
Chemicals for cleaning	NaOH +EDTA	pH≦12+1 wt%
	HCl	pH≧1
	Citric acid	2 wt%
	Enzymatic compounds	

Which chemical should be used depends on the water quality of feed, so the optimized chemical cleaning should be determined by the optimization experiment.

3.1.3 Nanofiltration
1. Flow scheme
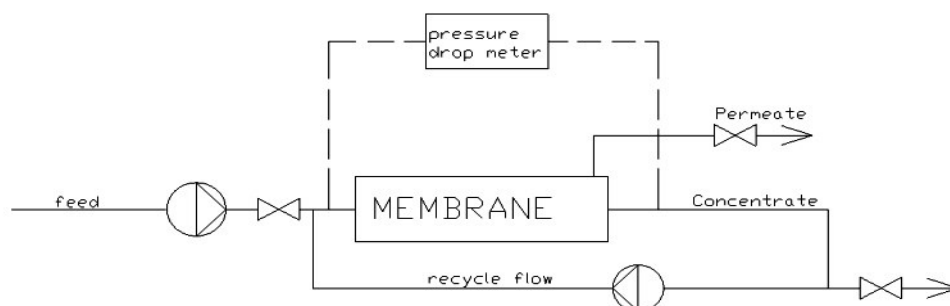
conductivity, pressure of feed, concentrate and permeate will be measured by electronic meters on line

The nanofiltration equipment is one module installation. Feed is provided by a pump with maximum pressure of 25 bar, and after the filtration, permeate is delivered to GAC adsorption, while the concentrate is discharged. By controlling the concentrate flow, we can do the experiment at different recovery. During the experiment, the pressure drop between feed and concentrate; conductivity, pressure of feed, concentrate and permeate are real-time measured and shown on the panel. In order to prevent the concentration polarization, a recycle flow is maintained to guarantee a high flow velocity in the membrane.

2. Type of membrane

Spiral wound membrane was used in this experiment. It is produced by Trisep Company, and the element type is 2540-TS80-TSF. The detailed description of the membrane is in the following table.

Membrane type	ANM aromatic polyamide advanced nanofiltration membrane
Configuration	spiral wound, fiberglass outer wrap
Recommended applied pressure	3-14 bar
Maximum applied pressure	41 bar
Recommended applied temperature	2--45
Feed water pH range	4-11 continuous
Chlorine tolerance	<0.1 ppm
Maximum turbidity	1 NTU
Molecular weight cutoff	200 Da

3.1.4 GAC adsorption

Flow scheme

The GAC adsorption works like a normal filter. Because the permeate of nanofiltration has certain pressure and the inlet point of GAC adsorption is only 2 meters high, it is not necessary to use a pump to push the water up. After this process, the effluent of adsorption is discharged in the sewer.
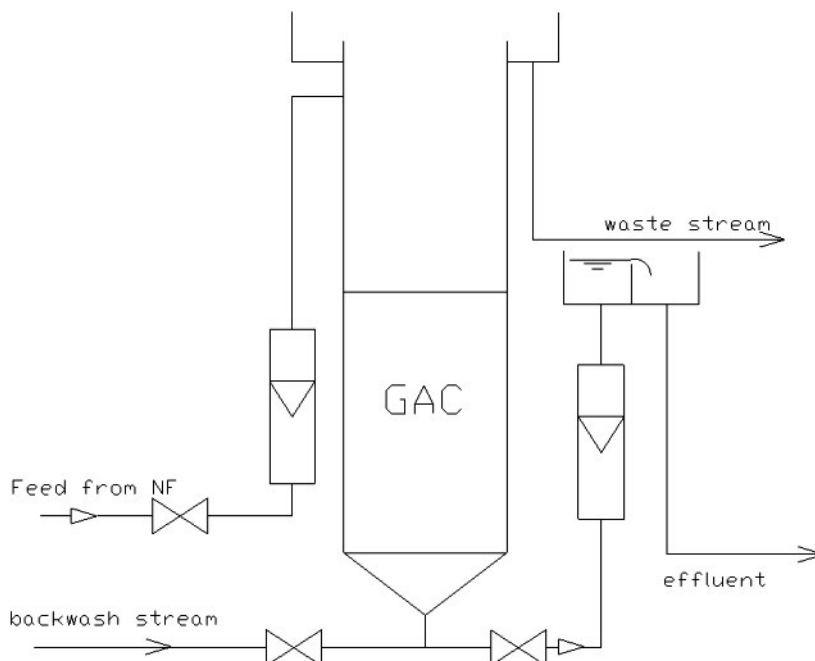
Type of carbon

The carbon used in this experiment is produced by Norit Company, and its production type is Norit Row 0.8 supra GAC, which has the following characteristics:

Iodine number	Bed density (kg/m^3)	Effective size (mm)	Uniformity coefficient	Raw material
1050	345	N/A^2	N/A^2	peat

3.1.5 Experiment solutions

➢ NaOH

It was 60% concentrated and used for the UF chemical cleaning and the pH adjustment of UF feed. The solution concentration are different for these two applications: 1) chemical cleaning: 2 mol/l; 2) pH adjustment: 0.5 mol/l.

➢ NaOCl

Used for UF chemical cleaning optimization experiment, 15% concentrated.

➢ FeCl$_3$

Used for on-line coagulation as pretreatment of UF, 197 g/l concentrated. The real concentration of FeCl$_3$ dosing solution is diluted to 3.2 g/l, and the dosing amount in the feed water is 4 mg/l.

➢ NaHCO$_3$

Used for the pH adjustment of water after the first IEX column and provision of

buffering capacity (HCO_3^-) in the second IEX column. The $NaHCO_3$ is made by dissolving the powder form into the demi water, and the concentration of solution is 0.6 mol/l. while the dosing amount in the water is 4mmol/l.

➤ Spiked micro pollutants

In order to check the effectiveness of the NF-GAC process, some micro pollutants are spiked in front of the NF. The spiked pollutants are as follow:

Atrazine

A Selective triazine herbicide. Inhalation hazard is low and there are no apparent skin manifestations or other toxicity in humans. Acutely poisoned sheep and cattle may show muscular spasms, faciculations, stiff gait, increased respiratory rates, adrenal degeneration, and congestion of the lungs, liver, and kidneys. (From The Merck Index, 11th ed)
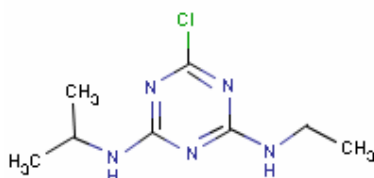
Diuron
A pre-emergent herbicide
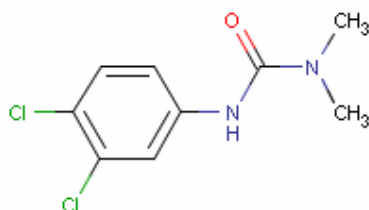
MTBE
Chemical remains on MTL because of additional testing actions (see OECD/SIDS listing)
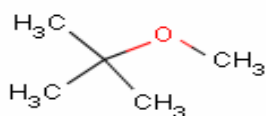
ETBE

Ethyl tertiary butyl ether (ETBE) is commonly used as a blend stock in the production of gasoline from crude oil. It is created by mixing ethanol and isobutene and reacting them with heat over a catalyst [definition from Wikipedia, the free encyclopedia]
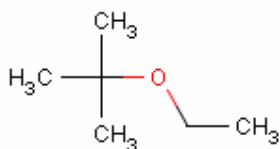
TAME

Tertiary amyl methyl ether - $(CH_3)_2(C_2H_5)COCH_3$ -- An oxygenate blend stock formed by the catalytic etherification of isoamylene with methanol.
[definition from TeachMeFinance.com]
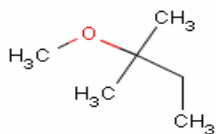
TBA

Tertiary-Butyl Alcohol (TBA) is a fuel oxygenate and is also an impurity in, and a breakdown problem of Methyl-Butyl Ether (MTBE). TBA is a significant potential groundwater contaminant due to its mobility, recalcitrant nature.
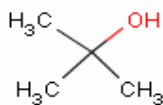
> Pharmaceuticals

| Compound	MW (g/mol)	log Kow (-)	pKa (-)	Solubility (mg/l)	Detection	Distributor
Bezafibrate	361.823	4,25 (???)	???	???	TZW 1	Sigma
Fenazon/antipyrine	188.229	0.38	1.4	51900	TZW 2	Acros
Ibuprofen	206.283	3.97	4.91	21	TZW 1	Acros
Clofibric acid	214.647	2.57	???	583	TZW 1	Acros
Terbutaline	225.286	0.9	???	213000 (???)	TZW 2	Sigma (hemisulfaat zout)
Naproxen	230.262	3.18	4.15	15.9	TZW 1	Sigma
Propyfenazon	230.309	1.94	???	3000000	TZW 2	???
Aminopyrine	231.297	1	5	54400	TZW 2	Acros
Carbamazepine	236.273	2.45	???	17.7	TZW 1	Acros
Salbutamol	239.313	0,64 (???)	???	13400	TZW 2	Sigma (duur)
Fenoprofen	242.273	3,9 (???)	7.3	???	TZW1	Sigma (calcium zout hydraat)
Pindolol	248.324	1.75	???	7880	TZW 2	Sigma
Gemfibrozil	250.336	4,77 (???)	???	???	TZW 1	Sigma
Ketoprofen	254.284	3.12	4.45	51	TZW 1	Sigma
Propanolol	259.347	3.48	9.42	61.7	TZW 2	???
Cyclophosphamide	261.087	0.63	???	40000	TZW 2	Acros (monohydraat)
Iphosphamide	261.087	0.86	???	3780 (???)	TZW 2	Hier ???
Atenolol	266.339	0.16	???	13300	TZW 2	Sigma
Metoprolol	267.366	1.88	???	16900	TZW 2	Sigma (tartraatzout)
Sotalol	272.376	0.24	???	5510	TZW 2	Sigma (HCl)
Clenbuterol	277.193	2,00 (???)	???	???	TZW 2	Sigma (HCl)
Pentoxyfilline	278.31	0.29	???	77000	TZW 1	Sigma
Diazepam	284.745	2.82	3.4	50	TZW 1	Sigma
Diclofenac	296.152	4.51	4.15	2.37	TZW 1	Sigma (Na-zout)
Bezafibrate	361.823	4,25 (???)	???	???	TZW 1	Sigma

3.2 Experiment methods

3.2.1 Experiment 1 Membrane fouling prevention
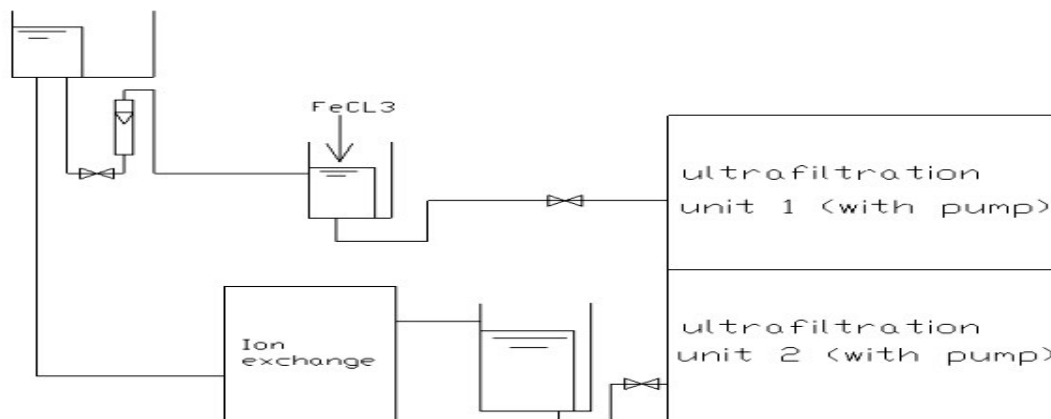
For this experiment, the focus is the effectiveness of pretreatment on the prevention of UF fouling. There are two groups of experiment carried out: short-term, and long-term.

In the first round short-term experiment (6 hours), the delft Schie canal water was used as the feed water, without any pretreatment. The water quality of canal water is rather constant during the experiment, so we have no need to prepare a batch of feed water and adjust the parameters, such as pH (8.10), conductivity (1200 μs/cm). The canal water is taken from the reservoir on the top of the laboratory by gravity, and then filled in the feed vessel with overflow. The flow rate is monitored by a flow meter and controlled by a valve. Because the UF equipment can run automatically, I just need to set the parameters: constant flux (50l/h.m^2); time interval of reading data (2 minutes); time interval between two backwashes (30 minutes); backwash time (30 seconds); forward flush (30 seconds); maximum feed pressure and maximum backwash pressure (1.5 bar); backwash flux: 2.5 times of filtration flux. After setting of each parameter, just let the equipment run automatically for 6 hours, and then stop the process and check the produced graphs. Permeate was used as backwash water during the experiment. The second round short-term experiment was carried out with on-line iron coagulation as pretreatment. In order to make a proper mixing, the FeCl$_3$ is dosed in the feed vessel. The dosing amount is about 4 mg per liter feed canal water [35]. The settings on the UF equipment were the same as the first round. In the third round experiment, fluidized ion exchange system was used. Because the ph decrease after the first IEX column, NaHCO$_3$ (4 mmol/liter) was added in the effluent of the first IEX column and provide buffering capacity for the exchange reaction of second column. For the same concern, NaOH was used to adjust the pH of water pretreated by IEX, up to around 6.3. However, the settings of UF were the same as another two round experiments with different feed water, Schie water treated with IEX and Schie

water treated with $FeCl_3$.

Under 65l/h.m^2 constant flux, the above three experiment were carried out again to demonstrate the influence of flux on the membrane fouling, and check the optimal operation flux. Based on the normal operation in the Netherlands [??], the settings for these three experiments were adjusted: time interval between two backwashes (15 minutes); backwash time (1 minute); no forward flush. All the other settings were not changed.

In the first round Long-term experiment (2 days) of 65 l/h.m^2 constant flux, the Schie canal water and Schie water treated with IEX were used, and the settings of ultrafiltration are the same, except the extra parameter: time interval between two Enhanced Chemical Backwashes (5 hours); and the demi water was used as backwash water. In order to check the effect of ion concentration in backwash water on the membrane fouling, during the last three hours running, the backwash water was changed to mixed permeate from both membrane modules.

For the same reason, when the four step process (IEX-UF-NF-GAC) started to run, the effluent of GAC was also used as backwash water. Because after NF, the effluent of GAC just contains some monovalent ions, it is different from demi water and the mixed permeate from both direct treatment and IEX pretreatment. This experiment was carried out at 42 l/h.m^2 constant flux.

Divalent ion free water is the only feed in the second round long-term experiment (14 days), because it is incorporated with the whole process, and the divalent ion concentration must be low to prevent the scaling in NF. This experiment was done constantly at 65 l/h.m^2 flux with the same settings of UF as the first round long-term experiment.

3.2.2 Experiment 2 Target substances removal of whole process
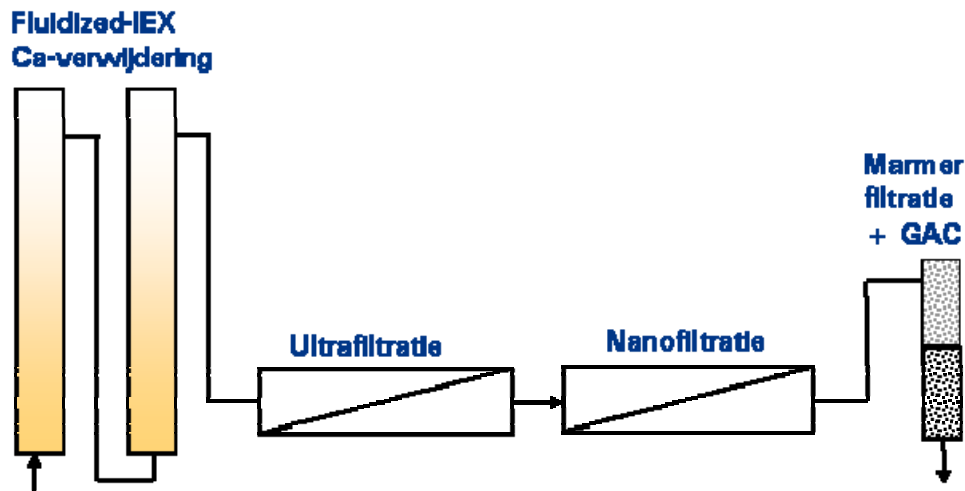
In this stage, we emphasize the prevention of scaling in nanofiltration and effectiveness of the whole process on the removal of micro pollutants, particles, assimilable organic carbon, and microorganisms.

The whole process is: Fluidized IEX system---UF---NF---Marble+GAC adsorption, but in this experiment, marble layer was not incorporated.

For the first two steps, the settings were those used in long-term experiment (14 days) in stage 1. Besides that, 97% recovery was used for the nanofiltration, and the EBCT of GAC adsorption was 3 minutes. The first round complete process experiment, we focus on the operation at high recovery of NF with stable MTC (mass transfer coefficient), and the removal of particles & inorganic substances. In the nanofiltration step, the feed temperature was maintained at 20 degrees by a cooler. In order to prevent the concentration polarization on the membrane, cross flow velocity through membrane was kept at 0.12m/s (400l/h flow rate), combining real feed flow and recycle flow from concentrate. The pressure difference between feed and concentrate, conductivity and pressure for feed, permeate and concentrate could be read from the on-line measurement device. And then the flow rate of permeate and concentrate were determined by measuring the discharged volume in 2 minutes. So far, the MTC of nanofiltration could be calculated by the equation mentioned in the chapter 2. What's more, the turbidity of canal water, feed of UF, feed of NF, and permeate of NF, effluent of GAC adsorption were measured to demonstrate the effectiveness of this process on the removal of particles.

Concerning the removal of microorganisms and pollutants, a series spiking experiment was done. The first 5 times spiking experiment, we used some herbicides, for example atrazine and diuron, as pollutant. The difference among these

5 experiments is the recovery of the NF. In order to check the different rejection of this kind of pollutant at different NF recovery, we adapted recovery from low to high: 10%, 50%, 75%, 87% and 97%.

For the 10% recovery experiment, instead of recycling the concentrate, we recycle both permeate and concentrate so that we can produce certain amount of permeate. Because if we recycle concentrate, the feed would be low, which lead to a lower permeate flow rate and probably lower than the minimum flow that feed pump can maintain. Therefore, both permeate and concentrate were recycled and the feed was kept at 400l/h to prevent the concentration polarization. For another four recoveries experiment, we still recycled the concentrate and maintained the combined feed flow rate (real feed and recycled concentrate) at 400l/h.

Besides the herbicides, some other micro pollutants were spiked in front of the NF-GAC adsorption, such as MTBE, ETBE, TAME, TBA, and pharmaceuticals. Two round experiments were done to check the effectiveness of combined treatment process on these parameters at 80% NF recovery. The first round, we spiked MTBE, ETBE, TAME, TBA. Like the experiment on herbicide at high recovery, we also recycle the concentrate to maintain high velocity in the membrane module, and the combined flow rate was 400l/h too. Other settings were the same as the experiment on herbicide, 20 degree centigrade temperature, 3 minutes EBCT in GAC adsorption column. After this round spiking, pharmaceuticals were spiked and then we did the experiment under the same condition again.

3.2.3 Experiment 3 Modeling of fluidized IEX system

1. Simulation of exchange speed

Measure the calcium concentration, pH value in the canal water first, and then put 2gram, 1 gram, and 0.5 gram resin in the three beakers. After this, we put one liter raw canal water in each beaker, which respectively represent three loading 63g/kg, 126g/kg, and 252g/kg, based on the measured calcium concentration 2.95 mmol/l of canal water. Because the pH value of canal water is around 8, the round experiment can be viewed as start at pH 8.

In order to make the resin contact perfectly with the water, we use jar test equipment to keep stirring. And then the samples were taken after half an hour, 1 hour, 2 hours, 4 hours and 20 hours reaction, so that we can check the change of calcium concentration and pH value.

The same method was used to determine the exchange speed at pH 6, 10, and 12.

2. Equilibrium isotherm

In this experiment, we want to know the equilibrium concentration of exchanged ion

at more or less constant PH value. In that case we can eliminate the influence of pH on the exchange reaction.

Like the experiment on determining exchange speed, we took 4.2g, 3.15g, 2g, 1g, 0.5g, 0.1g resin and put them the beakers, and then added one liter raw canal water in each beaker. That means 6 different loading capacities: 30g/kg, 40g/kg, 63g/kg, 126g/kg, 252g/kg, and 1.26kg/kg.

Keep stirring the samples in the jar test equipment, and maintain the pH value at 8 by adding NaOH solution. We measured the calcium concentration of samples and stop the experiment until there was no change in the concentration any more

4. Results and discussions

4.1 Results

4.1.1 UF pretreatment comparison (effect of divalent ion on fouling)

4.1.1.1 Comparison at 50l/h.m^2 flux

For the dead-end ultrafiltration experiment, two pretreatments (ion exchange or Fe coagulation) were compared with direct Ultrafiltration of Schie water. The characteristics of three feed waters are shown in the Table 4.1. From this table, we can find compared with other two kind of feed water, the divalent ion free water has the lowest pH value and calcium concentration. Low calcium concentration is reasonable, because the resin exchanged the divalent ions in the canal water with attached hydrogen ions. That is also why the pH value of divalent ion free water was lower than the other two kind of feed water. Dosing FeCl$_3$ cannot remove the calcium from the canal water, so the calcium concentration of feed water using Fe coagulation as pretreatment was the same as the raw Schie water. Although concentrated FeCl$_3$ is acidic, because of the small amount of dosing, it decreased the pH value a bit.

	Schie water treated with IEX	Schie water	Schie water treated with FeCl$_3$
pH value	6.22	8.1	7.65
Calcium concentration	0.72mg/l	126mg/l	126mgl/l
DOC*(pre-filtered 0.45μm)*	15 mg/l	16 mg/l	N/A

Table 4.1. water quality for three kind of UF feed water at 50l/h.m^2 flux short-term experiment
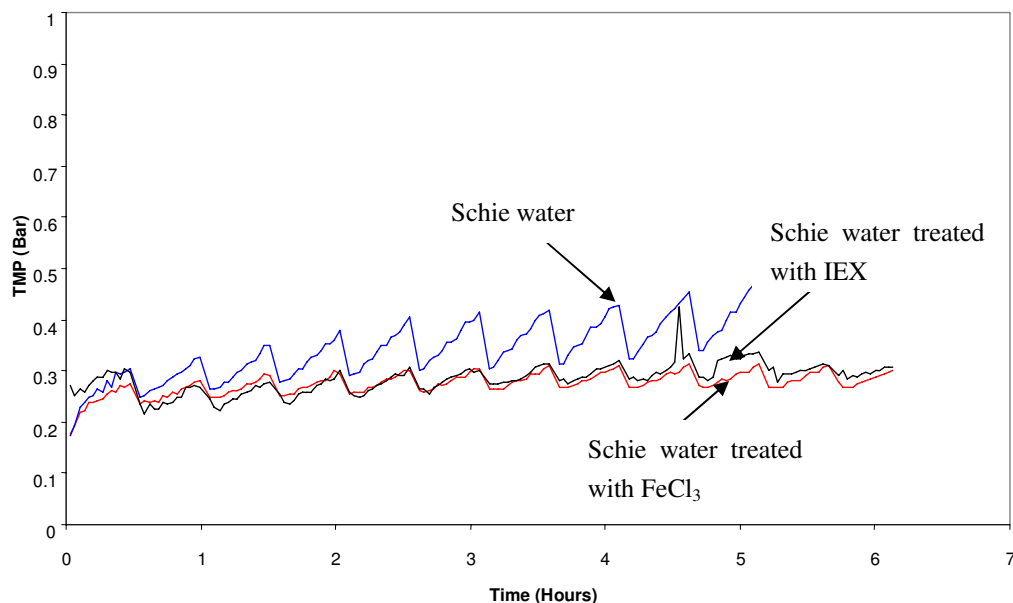

Figure 4.1 Short-term comparison of direct treatment, IEX and Fe coagulation, at 50 l flux, 30 minutes per filtration cycle, backwash 30 seconds, forward flush 30 seconds

Figure 4.1 shows the TMP trend of UF with different pretreatment: direct treatment, iron coagulation and ion exchange. Fe coagulation (red line) exhibited the same TMP trend as ion exchange (black line), increasing slightly from 0.22 bar at the beginning to 0.3 bar in 6 hours, while the direct ultrafiltration (blue line) showed more than three times increase compared with the other two pretreatments, ranging from 0.18 bar to 0.47 bar in 5 hours. This figure indicates both iron coagulation and ion exchange are good pretreatments for ultrafiltration in short-term at 50l/h.m^2 flux. For the iron coagulation natural organic matter adsorbs as the iron flocks, it made the fouling layer on the membrane surface less compact and decrease adsorption in the membrane pores. Those are very good conditions for the backwash restoring the membrane permeability, as have been shown in the previous studies. As what we have found in the laboratory scale experiments [4, 5], calcium removal has a large effect on the UF membrane fouling. That can be explained by the Ca-bridge effect of calcium as glue connecting the natural organic matter with the similar charged membrane material. Breaking this bridge effect also made the fouling layer on the membrane surface less compact, so that the fouling layer can be easily removed during backwash. According to previous research [4], high pH results in less fouling, so the performances of IEX can be improved by raising the pH to 8.1 as Schie water. From the figure 4.1, we can find a peak on the UF TMP trend line using ion exchange as pretreatment, and that is because of the maximum feed pump pressure adjustment. Since during the experiment there is flux decrease, the setting of maximum pump pressure was increased at that time to maintain the stable flux. Therefore the system needs certain time to get used to the new environment.
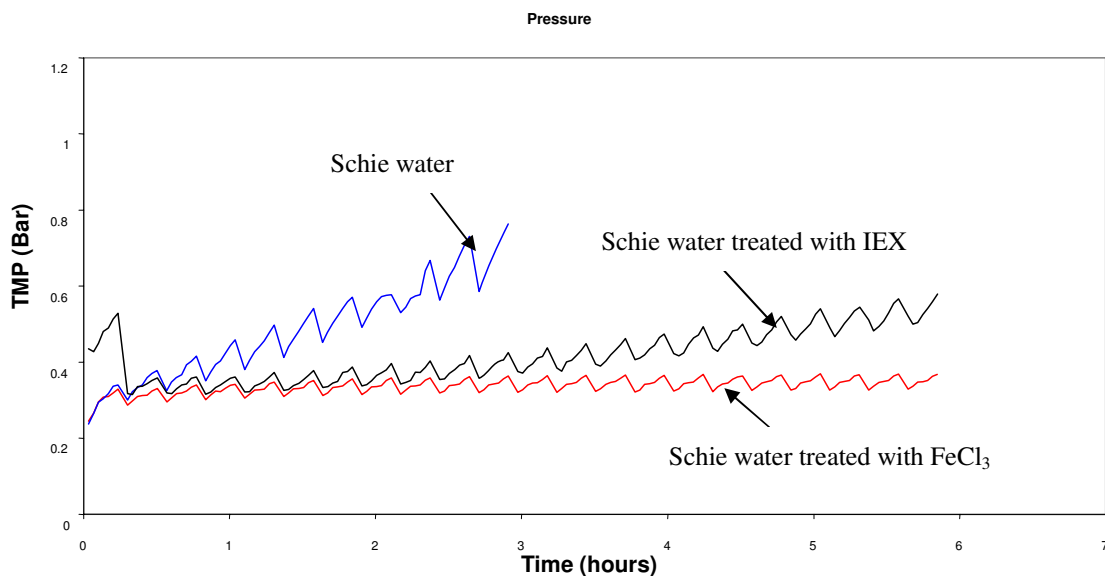
4.1.1.2 Comparison at 65l/h.m2 flux

Figure 4.2 Short-term comparison of direct treatment, IEX and Fe coagulation, at 65 l flux, 15 minutes per filtraion cycle, backwash 1 minute

Another round of short-term experiment at 65l/h.m^2 flux was done with the same feed water, as shown in the Table 4.1. The TMP trends of UF for three types feed water are compared in Figure 4.2. The difference of three type feed water is much clear in this figure: raw canal water still exhibited the highest TMP increase, from 0.25 bar to 0.75 bar in 3 hours, while the feed water treated with FeCl$_3$ remaining stable at 0.3 bar in almost 6 hours. In contrast with figure 4.1, instead of the same trend as Fe coagulation, feed water without divalent ion showed a gradual TMP increase ranging from 0.35 bar to 0.55 bar in 6 hours. There was a big membrane permeability recovery after the first backwash for Schie water treated with IEX, which could be possibly due to the insufficient cleaning after last round short-term experiment, leading to some particle blockages in front of the membrane pores or some air in the membrane. From this figure, we can found that at high flux ultrafiltration, iron coagulation is still a good pretreatment, maintaining the stable TMP under constant flux. However, the ion exchange at 65 l/h.m^2 flux didn't behave as well as 50 l/h.m^2 flux. That is possibly because, compared with the low pressure, high pressure could lead to more particles adsorption in the middle of membrane pores. With the help of FeCl$_3$, NOM formed big particles, so the main fouling mechanism was still blocking in front of pores. This kind of fouling was still easy to remove by backwash. We should also pay attention on time dependence of adsorption in pores. Figure 4.2 shows the TMP trends for Schie water treated by IEX or FeCl$_3$ are more or less the same until 2.5 hours. Probably at that moment, adsorption reached a critical level, the influence of adsorption became more obvious after that. The TMP trends for both cases in Figure 4.1 are the same until 6 hours, and that is possibly because the TMP at 50 l/h.m^2 was lower than 65 l/h.m^2 so that it took more time to reach the critical level. If we continued the experiment at 50 l/h.m^2, perhaps we can also see the same trend at 65 l/h.m^2. Therefore, both calcium concentration and the flux itself are significant fouling factors, just like other publications mentioned [1, 3]. For the same reason, the TMP of direct UF at 65 l/h.m^2 flux increased much faster (almost twice) than that at 50 l/h.m^2 flux.

Fe coagulation as ultrafiltration pretreatment is the better than Ion Exchange based on short-term performance. However, we must notice that the Fe coagulation will produce a big amount of Fe sludge during backwash. What's more, if we use HCl solution to chemically clean the membrane, dissolved Fe will be adsorbed in the membrane pores, leading to serious blockage in long-term.

4.1.2 Effect of cation on fouling

4.1.2.1 Setting deviations

In the first round long-term experiment, equipment was not running at optimal condition. For example:

➢ Although the setting of UF backwash flow is 2.5 times higher than the filtration flow, which means the backwash flux should be 162.5 $l/h.m^2$, the real BW flow rate as shown in the Figure 4.3 were lower than the settings, especially for the Schie water treated by IEX. That would lead to insufficient backwash, causing negative effect on the long-term Ultrafiltration running. Since one membrane operation normally can be maintained at the set point, this phenomenon is possibly due to the capacity shortage of backwash pump.

➢ Because the maximum pump pressure was set too low, the membrane flux for Schie water treated by IEX was not absolutely fixed at 65 l flux. Therefore, the TMP trend for IEX-UF would increase faster if the flux constant.

However, these problems had been solved after this round experiment, so the results of following experiments are more reliable. Although this round experiment was not running optimal, the result was still good enough to demonstrate the effect of different backwash water.

4.1.2.2 Effect of IEX and different backwash water

For the long-term experiment, Schie water and Schie water treated by IEX were used as feed water. We can check whether ultrafiltration with divalent ion free water is maintained stable by incorporating with Enhanced Chemical BackWash (ECBW). After dosing, the pH value of ECBW water is about 10.5.

Figure 4.4 shows the TMP trend of UF fed with canal water and divalent ion free water. The graph should be considered in two parts, 0 hour---47.5 hours, and 47.5---51.6. For the part 0---47.5, the membrane was backwashed with demi water, while the part 47.5---51.6, backwashed with mixed permeate from both membranes (2 mmol/l Ca^{2+}).

Therefore, for the part from 47.5 hour to 51.6 hour, there are a lot of divalent ions in the backwash water since the UF direct treatment cannot reject the ions. It is really remarkable, the TMP trend for both cases increased much quicker than before. It proved the effect of cation on membrane fouling. What's more, it is more important to remove cation from backwash water than remove divalent ion before membrane filtration. Because schie water and schie water treated with IEX shows more or less the same trend.
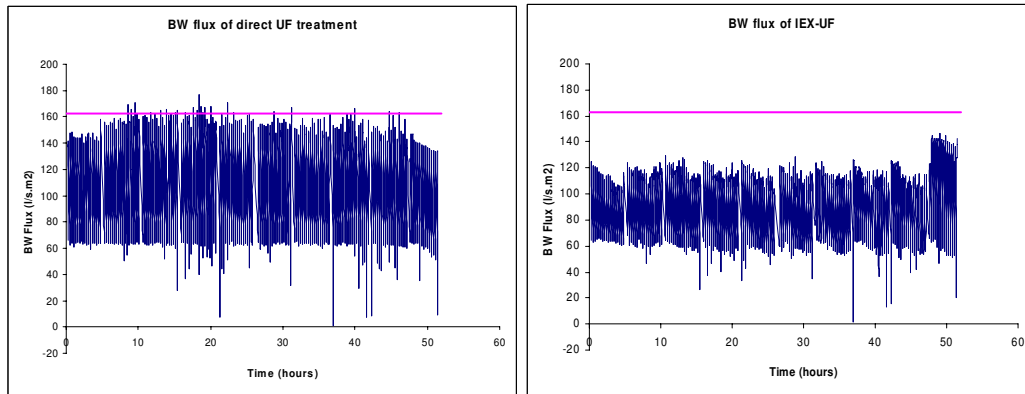
Figure 4.3 backwash flow rate curve at 65 l flux for direct treatment and IEX; (a) backwash flux of direct treatment, (b) backwash flux of IEX-UF
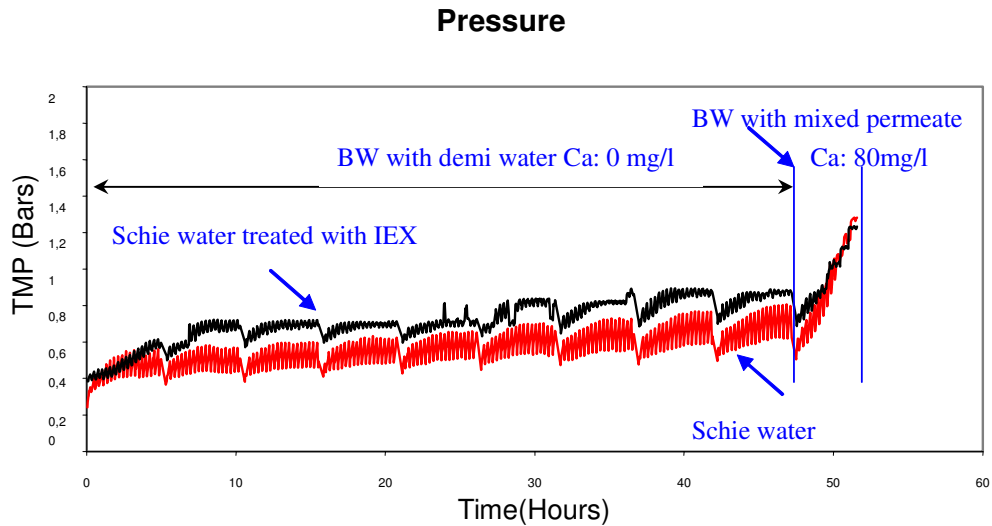
Pressure

Figure 4.4 parallel Long-term UF experiment at 65 l/h.m^2 flux with different feed: Schie water, Schie water treated with IEX

In order to confirm this finding, two short-term experiments were done to repeat the effect of ion free water as backwash water. Figure 4.5 and 4.6 have shown the flux is constant at 65l/h.m^2 during the experiment, and although the backwash flow rate were not at the set point, both cases had around 2 times filtration flow as backwash flow respectively, so the conditions except TMP for both feed waters are more or less the same, and the TMP trend exactly reflect the effect of different feed water and different backwash water on the membrane fouling.
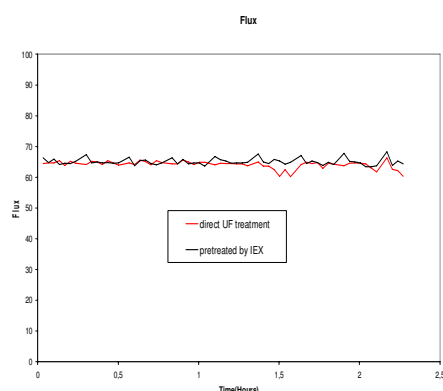
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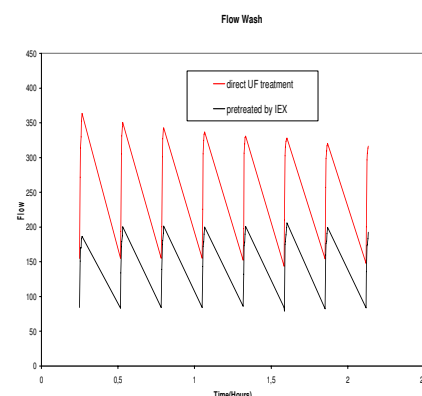Figure 4.5 flux curve for direct treatment and IEX

Figure 4.6 backwash flow curve for direct treatment and IEX
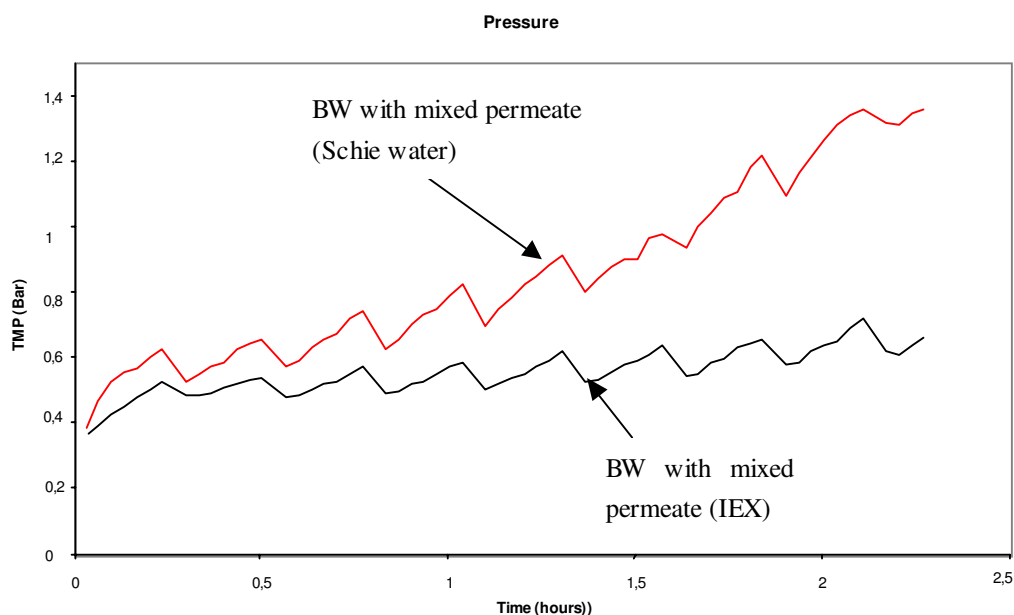
Figure 4.7 TMP tendency curve for direct treatment and IEX, BW with mixed permeate

Direct treatment and Ion Exchange are compared in Figure 4.7. In this comparison, both membranes were backwashed with mixed permeate. This figure perfectly exhibits the benefit of Ion Exchange as pretreatment again, TMP increase ranging from 0.36 bar to 0.66 bar in about 2.3 hours. In opposite, TMP increase for direct treatment rises from 0.4 bar up to 1.4 bar in the same time period. The high TMP start point is due to the long time high-pressure operation, so that the chemical cleaning after the first round long-term experiment could not restore the membrane permeability.

Figure 4.8 compares the TMP trend of direct UF and UF with divalent ion free water, incorporated with demi water as backwash water. It is obvious that the trends for both cases are almost the same. However, considering the small difference on the start

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point, the TMP trend of direct treatment (from 0.4 bar to 0.7 bar) is more stepper than that of divalent ion free water (from 0.5 bar to 0.6 bar). This figure perfectly confirms the finding in the first round long-term experiment (figure 4.4). Divalent ions as bridge connecting factor on the membrane surface cause the primary NOM fouling. Without the divalent ions brought back from the mixed permeate, NOM fouling layer was easily flushed away under high backwash pressure.

In figure 4.9, all the above-mentioned four situations are compared, giving us a more comprehensive image. It exhibits combination of using ion exchange as pretreatment and backwashing with ion free water is the best solution to prevent fouling in these four situations, while either using ion exchange as pretreatment or backwashing with ion free water used separately can also prevent membrane fouling in a certain extent. And there is no doubt that if we don't do anything, the fouling problem would be the worst as shown in the figure 4.9.
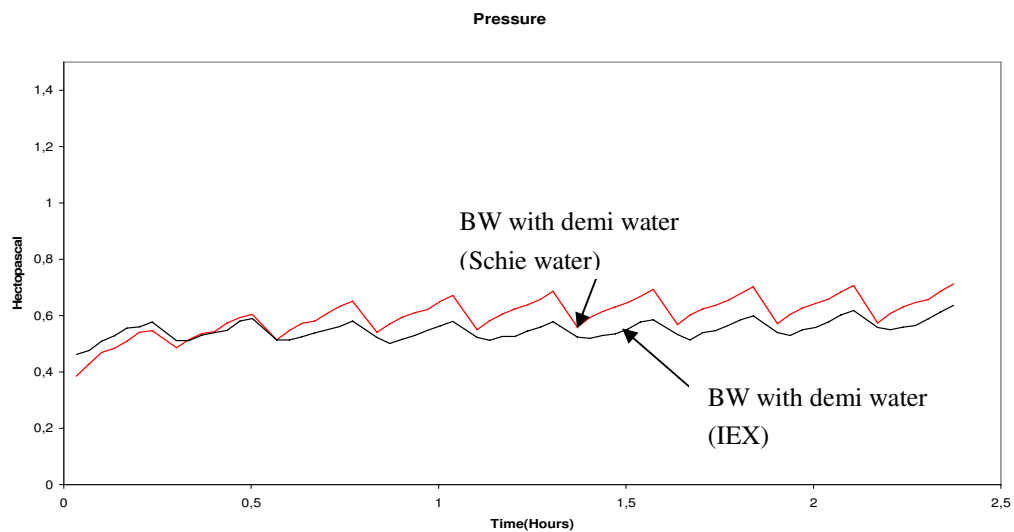
Figure 4.8 TMP trend curve for direct treatment and IEX, BW with demi water
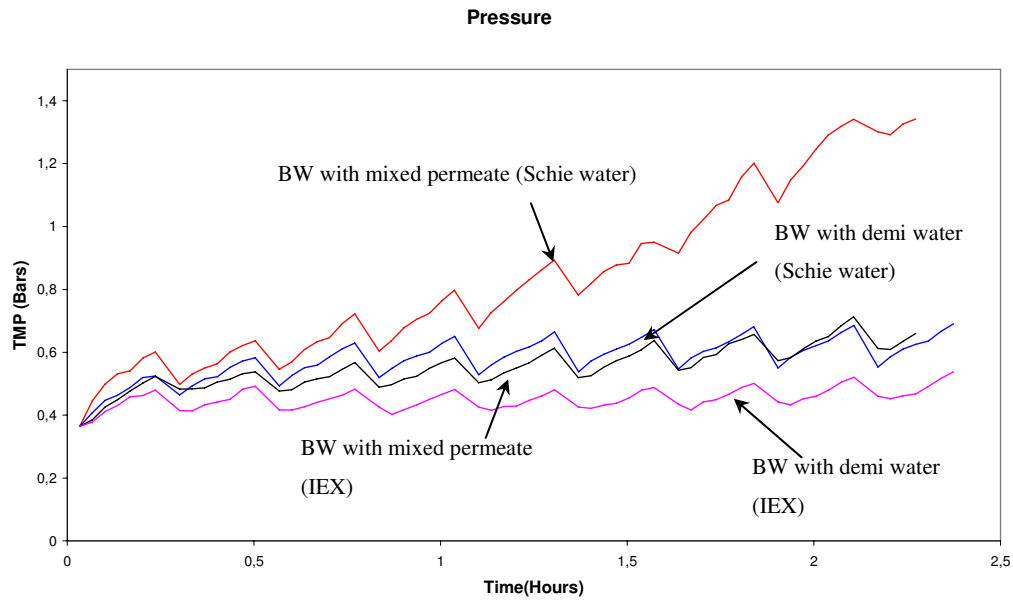
Figure 4.9 comprehensive TMP trend at different conditions
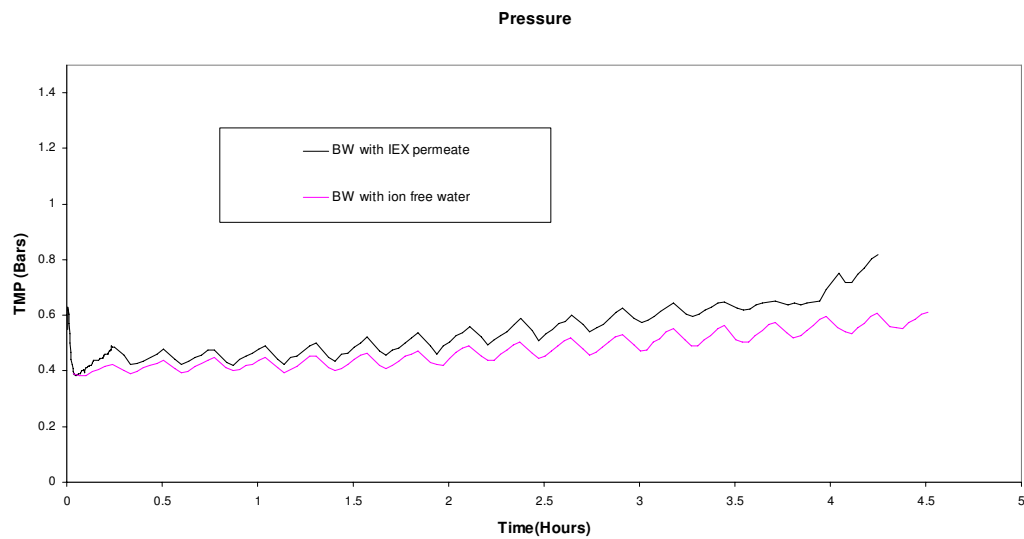
Figure 4.10 TMP trend of UF using IEX as pretreatment for different BW water

4.1.2.3 Effect of divalent ion amount

Since the amount of divalent ion on the membrane surface determine the fouling extent, logically speaking, the more divalent ions are, the more serious fouling. Figure 4.10 shows the effect of different backwash water on the membrane performance with IEX as pretreatment. The first type of backwash was demi water (without any ion), while the second type was permeate after IEX-UF with 0.1 mmol/l calcium. The

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calcium concentration after IEX normally should be 0.01 mmol/l, but the IEX started to breakthrough, so the concentration was 10 times higher. BW with IEX permeate, TMP increased from 0.39 bar to 0.52 bar in 2.3 hours; while BW with mixed permeate with 2 mmol/l calcium increased from 0.36 bar to 0.66 bar. For the complete ion free water, TMP ranged from 0.4 bar to 0.47 bar in 2.3 hours. These results comply with my expectation, less divalent ion on the surface, less compact fouling layer.

Pressure

Figure 4.11 long-term TMP trend at 42l/h.m^2 flux with different backwash water in between, feed pretreated by IEX

4.1.2.4 Optimization of UF

Pressure

Figure 4.12 TMP trend of UF in 13 days at 65 l/h.m2 flux

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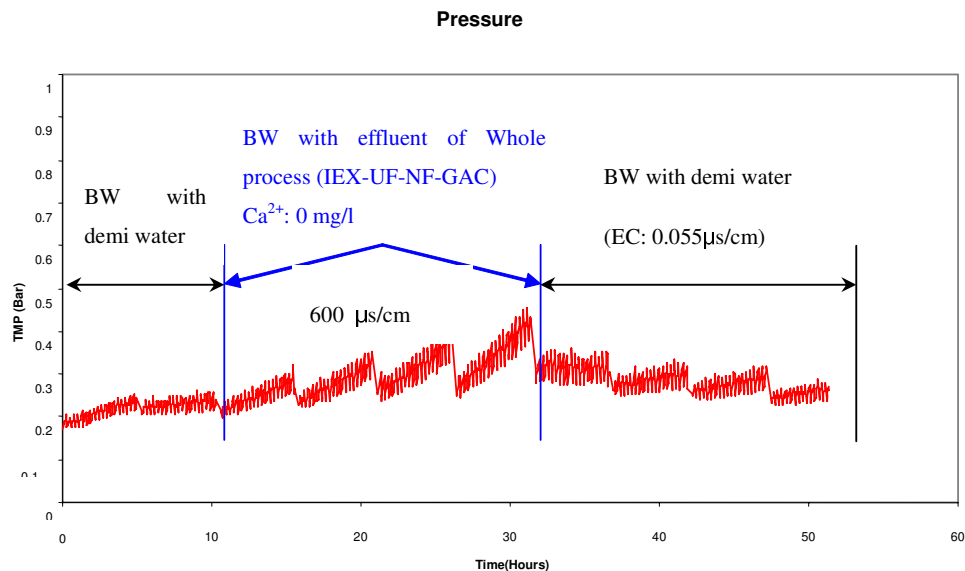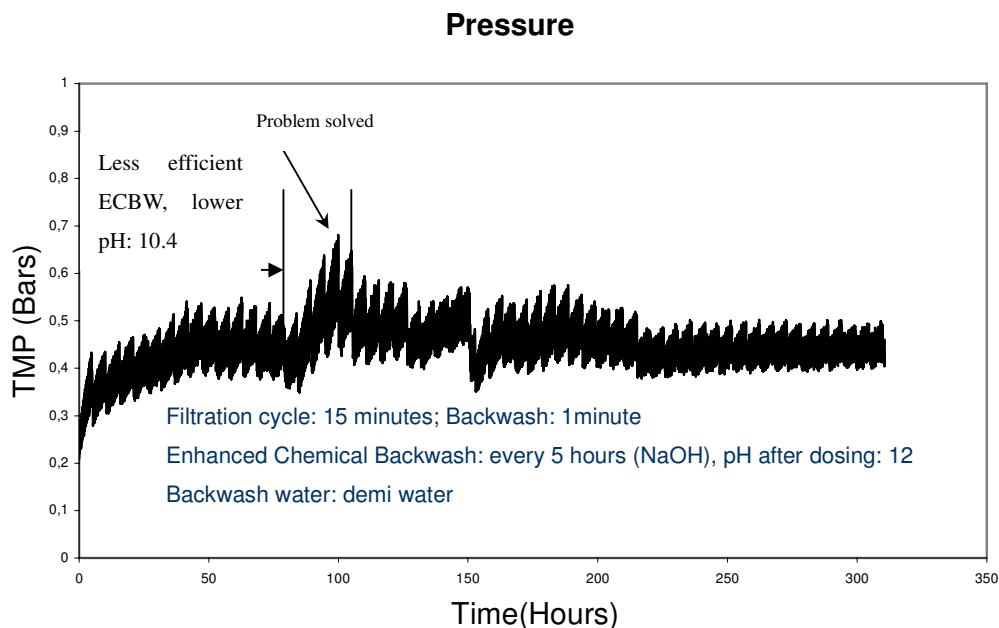TMP trend of second round Long-term experiment at 65 l/h.m2 is presented in figure 4.12. It exhibits that after 50 hours' operation, the TMP trend ran stably around 0.45 bar. The increase from 0.22 bar at the beginning to 0.45 bar at 50 hours is probably because the membrane need some time to get used to the feed water. It happened in many other membrane operations' beginning; include UF, NF and RO. Once the membrane system is used to the characteristics of feed water, it can work properly.

From the short-term experiment, we knew that although we combine the IEX pretreatment and ion free water backwash, we couldn't maintain the TMP as a flat line in 5 hours. Therefore, in order to apply this process in a long time period, we must incorporate the enhanced chemical backwash every 5 hours. However, the result of first round long-term experiment indicated NaOH dosing is not enough, since the pH after dosing is 10.5, far away from the membrane's limit, 12. In this experiment, most of time pH of backwash water was kept at 12, except the period between 80-110 hours.

Basing on the figure, in that period, TMP increased rather quickly, compared with the period before and after that. It means the ECBW was not successful in that period. That is due to the low pH after chemical dosing 10.4, lower than the pH for the rest part of experiment. There is no clear explanation for this decrease, it is possibly because the check valve didn't work properly, leading to the demi water flow back into the chemical storage tank and diluted the dosing solution, and then we couldn't increase the pH of backwash water with the same dosing amount.

After this, I paid more attention on the chemical dosing and made sure the pH after dosing around 12. As a consequence, the TMP run stably. Therefore, the process IEX-UF can run continuously with some optimization measures: backwash with ion free water, keeping pH value after chemical dosing around 12.

4.1.3 Performance of the whole treatment process

4.1.3.1 High recovery application of NF
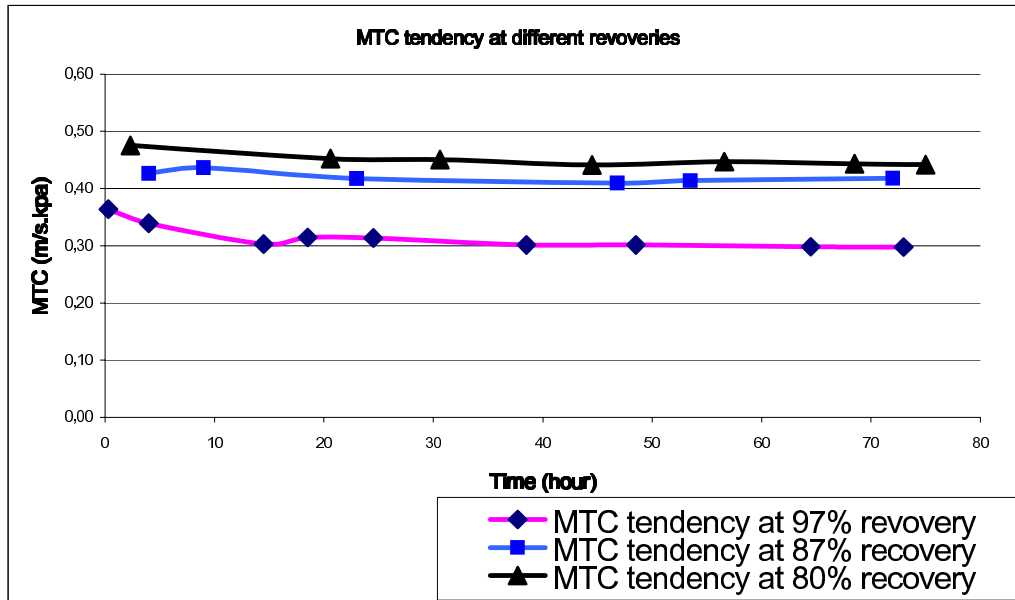
Figure 4.13: Feed treated by Ion exchange-Ultrafiltration at TU Delft

	80% recovery	87% recovery	97%recovery
Ca^{2+} concentration (mg/l)	20	14.4	0.4
pH value (-)	6.7	6.6	6.4
Electronic Conductivity (µs/cm)	980	960	1030

Table 4.2, NF feed water quality for three recoveries

During the whole process experiment, ion exchange and ultrafiltration were used as the first two steps. UF run at optimized condition so that we can do the whole process experiment continuously. From section 4.1, we know that the calcium concentration of UF feed is not really a big problem by using ion free water to backwash, but it is crucial for the whole process. In the previous research [4], calcium concentration has been demonstrated as an important scaling factor in NF. The similar experiment result also has been shown in Katwijk drinking water plant (report is available). Therefore, the Ce/Co ratio of 1st IEX column effluent was controlled below 0.5. Over this value, fluidized IEX system would be regenerated.

The varying calcium concentration is caused by the unstable operation of fluidized IEX system, especially when the $NaHCO_3$ dosing pump was out of order. (Detail information about the operation of Fluidized IEX system can be found in appendix)

Figure 4.13 exhibits the Mass Transfer Coefficient (MTC) of NF as a function of time at three different recoveries: 80%, 87% and 97%. For all cases, MTC trend goes

stably like a flat line except a small decrease at the beginning. The small decrease is probably because the membrane needs some time to get used to the feed water characteristic, like what we have discussed before. After a short time adjustment, all three MTC lines were more or less flat, which means there is no scaling happened in the membrane. This should be attributed to two aspects: divalent ion removal in ion exchange and particle removal in UF. Scaling is due to the high substance concentration, once we remove most of the calcium, the scaling phenomenon can be prevented successfully, and the result has proved this point.

Comparing the experiment result we got at Katwijk treatment plant, result got in this experiment exhibited more stable MTC trend. In Figure 4.14, except 80% recovery, 90% and 98% recovery showed decrease of MTC over time. That is possibly due to the difference of pretreatments. In Katwijk, NF feed was pretreated by aeration with Powder Activated Carbon, softening and ion exchange, while the NF feed in this experiment was treated by Ion Exchange system and Ultrafiltration.
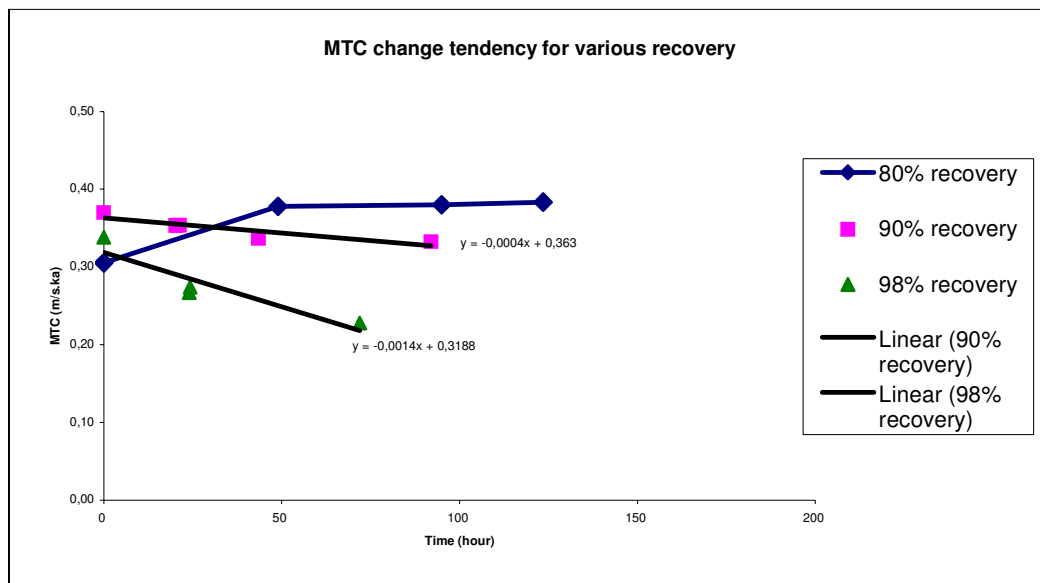
Figure 4.14:   NF Feed treated by aeration-softening-ion exchange at Katwijk treatment plant

Because most of the particles have been removed by ultrafiltration, the Nanofiltration gave better performance than that in Katwijk. It is obvious; the pressure drops between feed and concentrate for this experiment is 156 mbar, less than that in Katwijk 190 mbar. This pressure drop was mainly caused by the particle got stuck in the membrane, so it means more particles accumulated in the membrane used in Katwijk. What' more, a lot of powder activated carbon were found in the membrane used in Katwijk. That is why we could not get a stable line at 97-98% recovery in Katwijk. Therefore particle pre-removal is also an important factor for the stable NF operation.

4.1.3.2 Particle removal

NR	Turbidity (FTU)				
	Canal water	Feed of UF	Feed of NF	Permeate of NF	Effluent of GAC
1st sample	2.2	1.05	0.204	0.17	0.16
2nd sample	3	1	0.203	0.13	0.13
Average	2.6	1.02	0.203	0.15	0.14

Table 4.3 turbidity at different treatment step with 97% recovery at NF

Table 4.3 shows the turbidity of different sampling points. We can see that following the treatment process; the turbidity of water kept decreasing. It means the particles in the canal water were successfully removed. Turbidity decrease from 2.6 to 1.02 after the ion exchange column, and then 80% of the rest turbidity was removed by the Ultrafiltration. Nanofiltration actually behaves like a polish step for the particle removal, bringing the 0.203 of feed to 0.15 of permeate. The particles remained in permeate of NF have very small molecule weight, so as the ending process, GAC adsorption almost has no effect on the particles removal. Therefore, we can see the effectiveness of the double membrane barrier, which leads to almost complete particle removal, at least for the particles has molecule weight higher than 200 Da. This table also indicates the effectiveness of ion exchange column, and that is possibly because of the low upwards flow velocity (3.18 m/h) in the column. Low flow velocity made the particles in canal water accumulated in the resin bed, like somewhat a kind of filter. That is also why I flush the IEX column before regeneration. By passing through the resin bed, the particle loading on Ultrafiltration was also decreased. However, in the real application, when we use high upwards flow velocity, this phenomenon can be avoided.
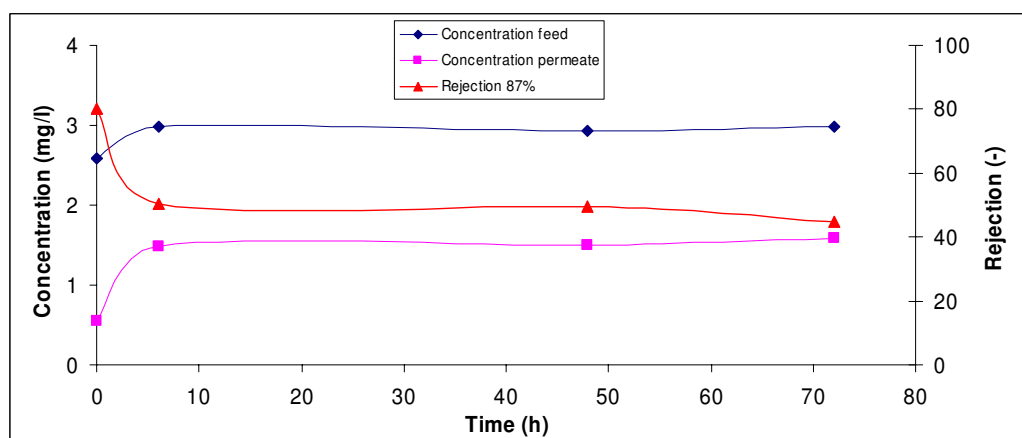
4.1.3.3 Removal of herbicides

Figure 4.15 removal of atrazine in NF over time
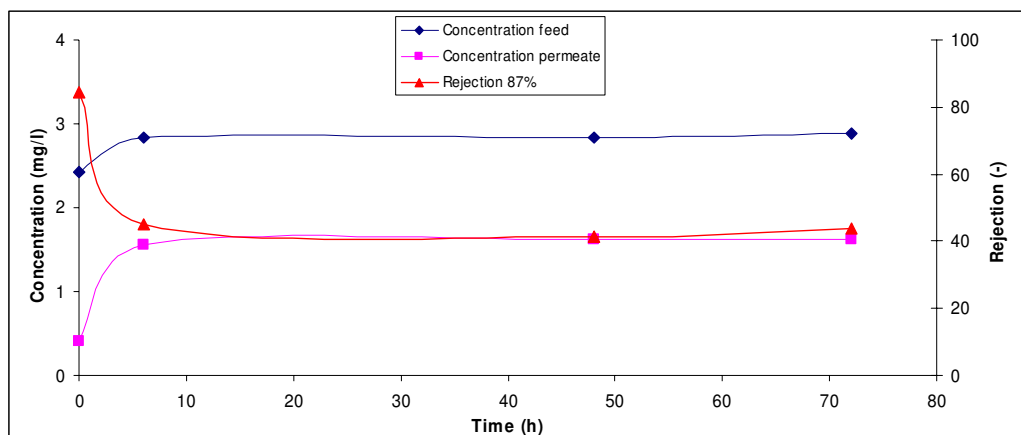
Figure 4.16 removal of diuron in NF over time

As shown in Figure 4.15, rejection of atrazine decreases from 80% to 50% in few hours, and then remains constant at 50%. The huge decrease of rejection at the beginning is probably due to recirculation equilibrium. Because we had internal recirculation in the NF, it took some time for the spiked herbicide to reach an equilibrium on membrane feed side. After few hours, the rejection behaved much more stable over time and that was the real rejection of NF for herbicide. That is possibly due to the adsorption of NF. Some research results [36,37,38,39] also showed that adsorption plays an important role in NF.

For the diuron rejection shown in the Figure 4.16, it exhibits the same trend as atrazine, but the rejection (40%) is a bit lower than atrazine.

4.1.3.4 Removal of pharmaceuticals

Table 4.4 exhibits the pharmaceuticals retention for feed of NF, permeate of NF and the effluent of GAC after three days continuous operation. Most of retentions by the NF were below 40%, except some compounds (Clofibrinezuur 84%, Fenoprofen 72%, Ketoprofen 75%, Diclofenac 100% and Bezafibraat 88%). Although Nanofiltration cannot remove all target substances, combined with the GAC adsorption, all the spiked pharmaceuticals were removed completely (98%-100%). Therefore, the double barriers' effectiveness on pharmaceuticals is promising.

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Compound	Rejection of NF	Rejection of GAC	Cumulative Rejection
Fenazon	44%	56%	100%
Ibuprofen	31%	68%	99%
Clofibrinezuur	84%	16%	100%
Terbutaline	18%	80%	98%
Dimethylaminophenazon	56%	44%	100%
Carbamazepine	36%	64%	100%
Salbutamol	16%	80%	96%
Fenoprofen	72%	28%	100%
Pindolol	11%	89%	100%
Gemfibrozil	34%	66%	100%
Ketoprofen	75%	25%	100%
Propranolol	16%	84%	100%
Cyclofosfamide	35%	64%	99%
Atenolol	12%	87%	99%
Metoprolol	14%	85%	99%
Sotalol	13%	87%	100%
Clenbuterol	20%	80%	100%
Pentoxifylline	23%	77%	100%
Diclofenac	100%	100%	100%
Bezafibraat	88%	12%	100%

Table 4.4 rejection of pharmaceuticals in NF and GAC adsorption, compared with feed of NF
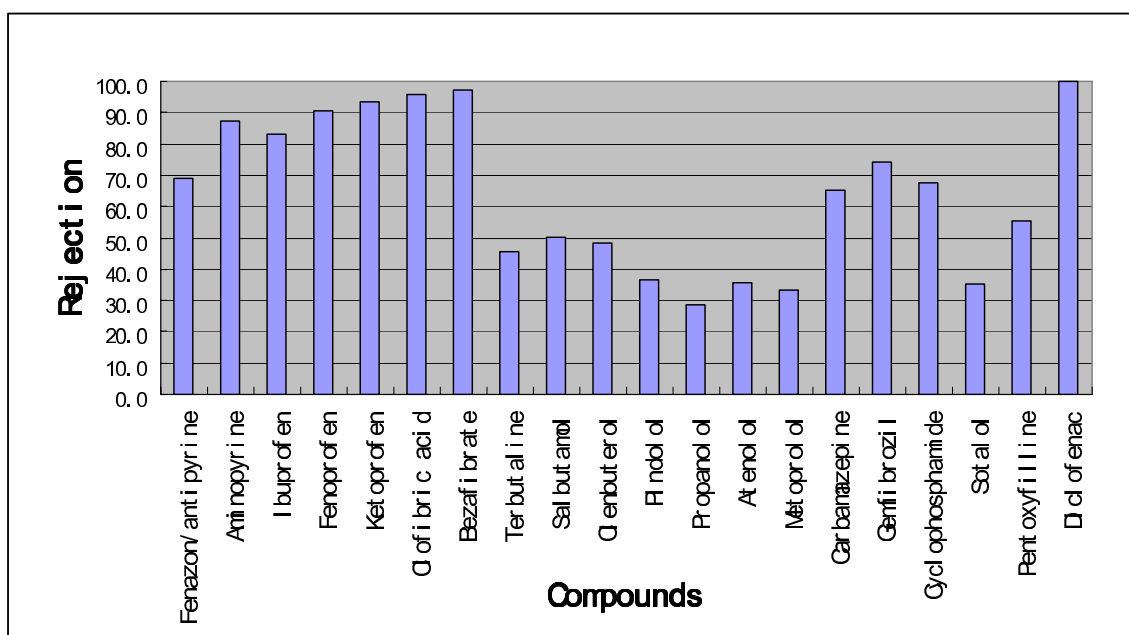

Figure 4.17, rejection of compounds recalculated to low recovery

However, the rejection of NF mentioned in Table 4.4 is the comparison between permeate of NF and the feed of NF installation, instead of the real bulk flow on the membrane feed side. Because concentrate was recycled to maintain the high flow velocity on the membrane feed side, the real bulk flow was more concentrated than the feed of NF. Therefore, this rejection didn't reflect exactly the NF ability. By comparing the feed of NF and the permeate of NF, the integrated NF installation was viewed as a whole, and the recycle flow was viewed as an internal flow. That is also why we can get high recoveries without concentration polarization problem.

In order to understand the real rejection ability of NF membrane on pharmaceuticals, we recalculated the rejection to 15% recovery, basing on the bulk flow (feed of NF and recycle concentrate). Figure 4.17 shows the respective rejections. Compared with the rejection got from Table 4.4, the recalculated rejections are much higher than the original one. 19 compounds have more than 30% rejection, 15 compounds are more than 40%, 9 compounds are more than 70%, and 5 compounds have more than 90% rejection. That is because the real concentration on the membrane feed side is much higher than the feed of NF.

4.1.3.5 Removal of MTBE, ETBE, TAME, TBA

Componenten Meth ID		Feed NF 10-04-2006 C-06 1532		Effluent GAC 10-04-2006 C-06 1533		Permeatie NF 10-04-2006 C-06 1534	
ethyl tert-butyl ether (ETBE)	0	6,7	µg/l	0,10	µg/l	5,6	µg/l
methyl tert-amyl ether (TAME)	0	7,2	µg/l	0,09	µg/l	6,5	µg/l
methyl tert-butylether (MTBE)	0	8,8	µg/l	0,39	µg/l	8,9	µg/l
tert-butanol (TBA)	0	33[*]	µg/l	23[*]	µg/l	35[*]	µg/l

Table 4.5 concentration of *MTBE, ETBE, TAME, TBA* at three sampling points (Feed NF, Permeate NF and Effluent GAC) at the beginning of spiking

Componenten Meth ID		Feed of NF 12-04-2006 C-06 1535		Effluent of GAC 12-04-2006 C-06 1536		Permeate of NF 12-04-2006 C-06 1537	
ethyl tert-butyl ether (ETBE)	0	6,4	µg/l	0,72	µg/l	5,6	µg/l
methyl tert-amyl ether (TAME)	0	7,2	µg/l	0,63	µg/l	6,8	µg/l
methyl tert-butylether (MTBE)	0	9,5	µg/l	4,7	µg/l	9,8	µg/l
tert-butanol (TBA)	0	37[*]	µg/l	43[*]	µg/l	43[*]	µg/l

Table 4.6 concentration of *MTBE, ETBE, TAME, TBA* at three sampling points (Feed NF, Permeate NF and Effluent GAC) after two days spiking

		Feed of NF		Effluent of GAC adsorption		Permeate of NF	
Componenten Meth		13-04-2006		13-04-2006		13-04-2006	
ID		C-06 1538		C-06 1539		C-06 1540	
ethyl tert-butyl ether (ETBE)	0	5,9	µg/l	0,89	µg/l	5,2	µg/l
methyl tert-amyl ether (TAME)	0	6,8	µg/l	0,77	µg/l	6,2	µg/l
methyl tert-butylether (MTBE)	0	9,4	µg/l	3,3	µg/l	9,2	µg/l
tert-butanol (TBA)	0	39[*]	µg/l	32[*]	µg/l	39[*]	µg/l

Table 4.7 concentration of *MTBE, ETBE, TAME, TBA* at three sampling points (Feed NF, Permeate NF and Effluent GAC) after three days spiking

The above three tables show that the Nanofiltration just has a small rejection for the ETBE (12%) and TAME (7%), and almost no effect for the MTBE and TBA. In Table 4.6, the MTBE and TBA concentration of permeate are even slightly more than the feed of permeate, which could be possibly due to the analytical variance. Low rejection for MTBE and TBA is because the size of MTBE and TBA is smaller than the NF limiting molecule weight---100 Da.

The second barrier for this group micro pollutant, GAC adsorption exhibits good removal for the ETBE and TAME (85%-91%), mediate removal of MTBE (57%), but there was no removal for the TBA. That is due to the structure and characteristic of target substances. We know that non-polar substance and substances with double bounds are respectively better adsorbed than polar substances and substances with single bound. Among these four substances, TBA is the more polar than the other three, so it gave the worst adsorption in GAC bed.

4.1.4 Modeling of IEX system

4.1.4.1 pH influence on exchange speed

calcium removal as a function of time at pH 6

Figure 4.18 calcium removal as a function of time at pH 6

calcium removal as a function of time at pH 8
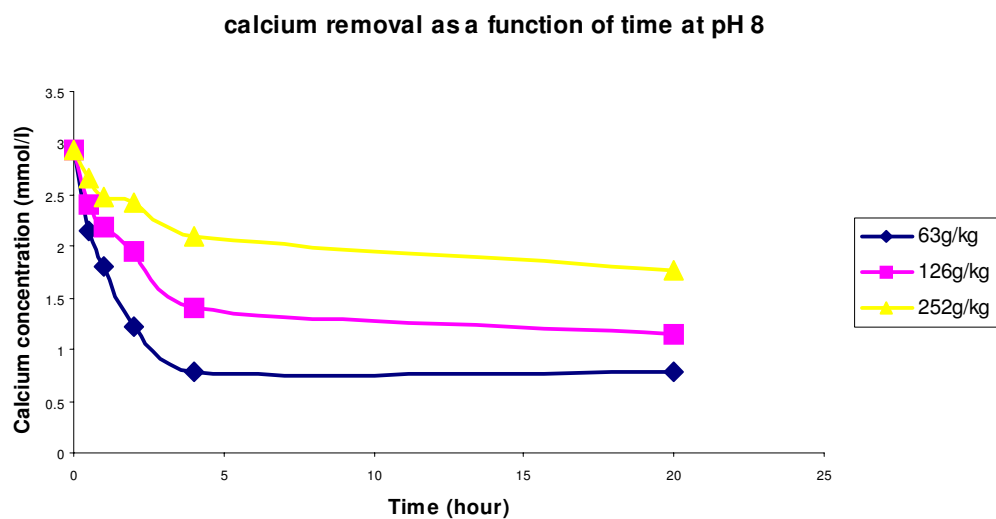
Figure 4.19 calcium removal as a function of time at pH 8

In the Figure 4.18, the calcium removal as a function of time at pH 6 are more or less the same for three loadings: 63g/kg, 125g/kg and 252g/kg. The loading here is the ratio between available calcium in the canal water and weight of resin. The calcium concentration decrease from 3 mmol/l to 2.4 mmol/l in 2.5 hours, and then kept stable. In contrast, for the same three loadings, calcium removal at pH 8 is more complete, as shown in the Figure 4.19. That is possibly because the pH value is higher, so that

exchange process would not be limited by the lack of alkalinity. Some publications [40,41] have demonstrated the effect of pH on the ion exchange process. H+ form Weak Acid Cation (WAC) resin will remove other cations if sufficient alkalinity present, while the Na+ form WAC resin can operate at any pH high enough to prevent formation of free mineral acidity (above a pH about 4.8). Therefore, we could get better removal of calcium at pH 8 than pH 6. It was also the case for the following two pH values: 10 and 12. From Figure 4.19, we can see that the lower loading, the better calcium removal is in 20 hours. That is reasonable, at the low loading; the exchange capacity of resin for calcium is higher, so it can reach the calcium equilibrium concentration much quicker than the high loading. However, even for the high loading in this experiment 252g/kg, it can reach the 0 mmol/l calcium if there is enough time and alkalinity. Because Figure 4.21 shows that calcium concentration for this loading can be 0 after 20 hours when the start pH is 12, which means enough alkalinity in the water.

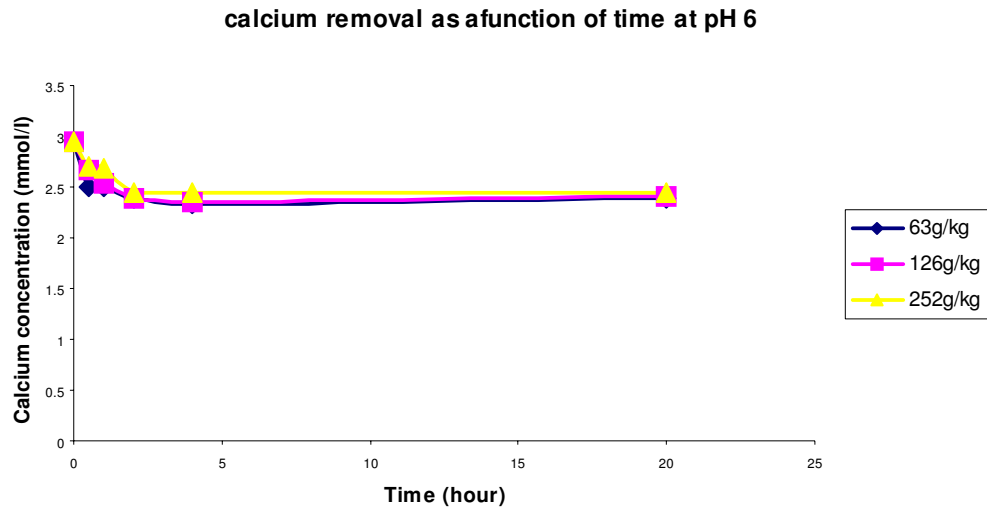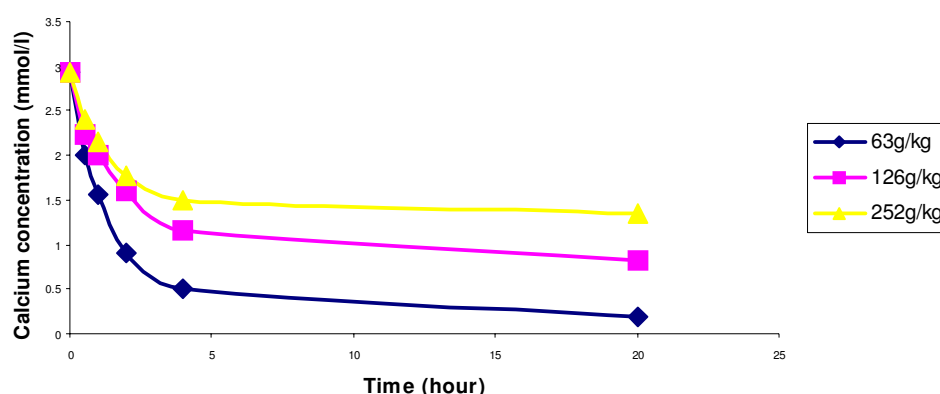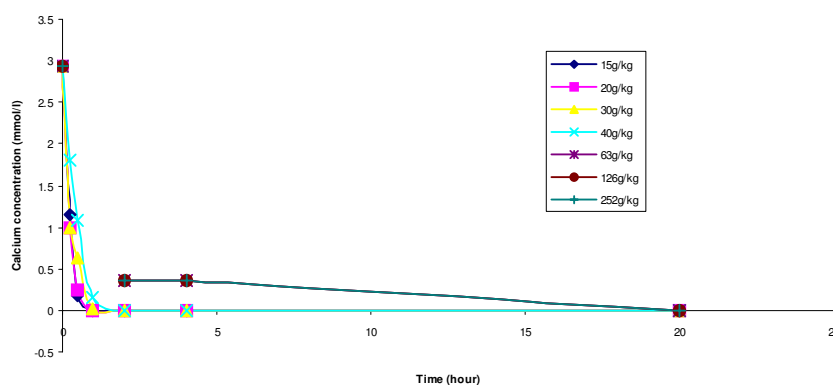Figure 4.20 calcium removal as a function of time at pH 10

Figure 4.21 calcium removal as a function of time at pH 12

Figure 4.20 and 4.21 show more or less the same trend as Figure 4.19. The differences are the equilibrium concentration and the time used to reach this equilibrium. We can find for the same loading, e.g. 63g/kg, the equilibrium concentration (0 mmol/l) can be reached in 20 hours at pH 12, more than pH 10. However, it is partly because the $CaCO_3$ precipitation at high pH value. This equilibrium process was not limited by the pH due to the high start pH. The same loading 63g/kg at pH 8 can reach equilibrium in 4 hours, but that is because the low pH of equilibrium condition, leading to no further exchange. Therefore, the pH influences the ion exchange speed and equilibrium concentration.

Although in this experiment it took few hours to reach equilibrium, the real condition will be much better. Because in such a batch scale experiment, we just used few gram resins to treat one liter canal water, the contact surface would be small. However, in the real application, the same amount water will contact with the whole resin bed, which there are more contact surfaces. Therefore, the exchange speed in the real application can be much faster than that in the batch experiment.

4.1.4.2 Breakthrough of IEX system

Figure 4.24 and 4.25 shows the breakthrough curve and saturated percentage of resin bed as a function of bed volume. The breakthrough curve is different from those of sand filtration and adsorption. Effluent concentration was low at the beginning, and then increased to about 30% of influent concentration and maintained at that level until it reached the sharp breakthrough. Corresponding saturated percentage of bed was 70% when the resin bed reached the sharp breakthrough. The increase of effluent concentration before sharp breakthrough is possibly because of the reduction of pH in the resin bed. We have known that low pH would hinder the further exchange speed, so it leaded to the exchange speed slower than the water upwards flow speed, and then the increase of effluent concentration.
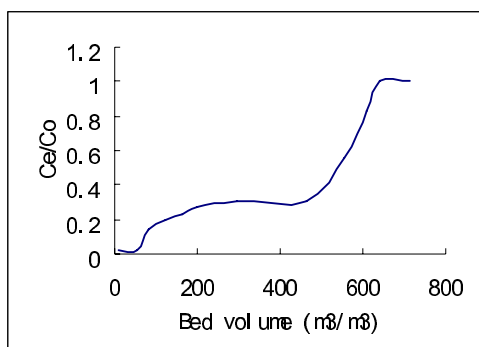
Figure 4.24 breakthrough curve of IEX bed
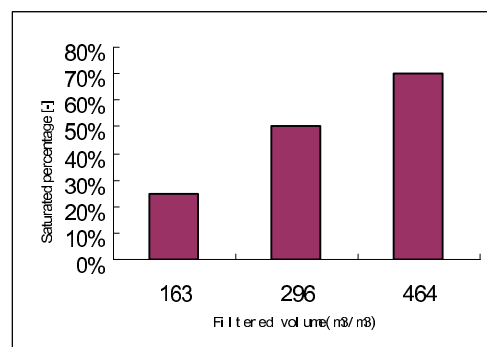
Figure 4.25 saturated bed versus filtered bed volume

4.1.4.3 Adsorption isotherm
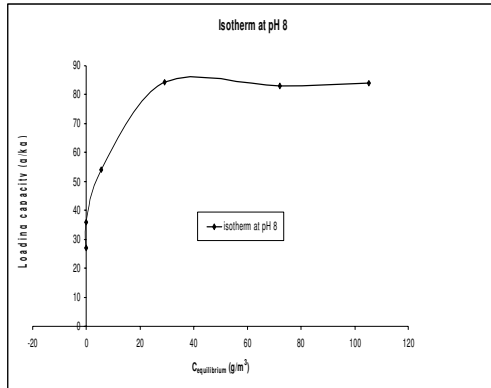
Figure 4.22 isotherm graph at pH 8
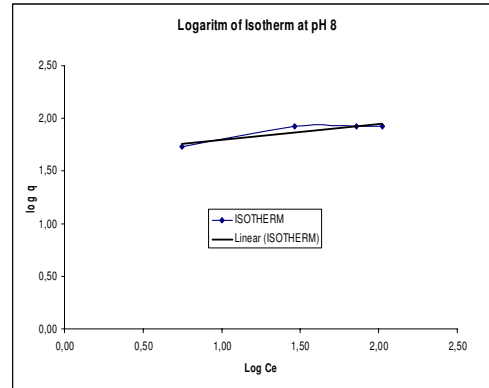
Figure 4.23 logarithm representation of isotherm

According to the isotherm formula in chapter 2, we can get the isotherm constant by doing the experiment. The isotherm graph and logarithm representation of isotherm at pH 8 are presented in Figure 4.22 and 4.23. The logarithm representation is equal to the trend line equation. Therefore, the K and n value are as follow:

$$\log q = \log k + n \cdot \log C_s \longrightarrow \quad y = 1.6425 + 0.1526x$$

So: logk = 1.6425; k = 43.9
    n = 0.1526

This modeling is just a rough simulation, if people want to get a more accurate model; more specific experiments should be done to determine the constants in the modeling equations.

4.2 Discussions

4.2.1 Effect of divalent ion on membrane fouling
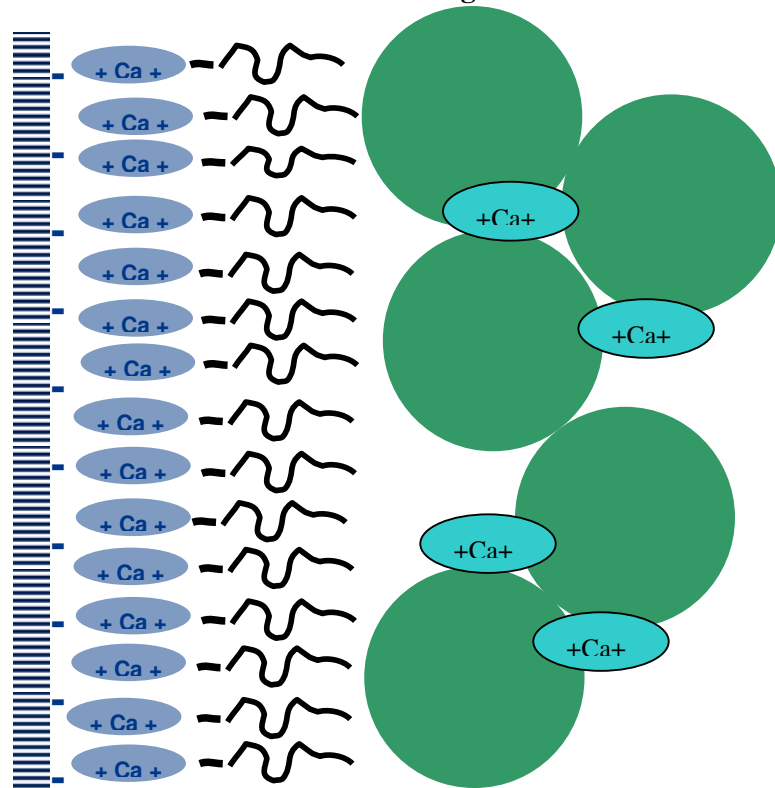
Figure 4.26 hypothetical Ca-bridge effect on membrane surface

Figure 4.4 exhibited the significant effect of ion free water as backwash water on the restoring membrane permeability. This is presumably because the existences of divalent ions on the membrane surface are the most significant factor on the bridge effect. As we mentioned in the chapter 2, several previous studies have shown that calcium ion play an important role on membrane fouling [1,2,3,4]. Because both NOM and membrane material are negatively charged, the existence of divalent ions, such as calcium, can overcome the repulsive force between two similarly charged materials, which I call it "*Glue Theory*". The divalent ions are assumed to work like glue, pasting the natural organic matter on the membrane surface. So what would be the most efficient way to paste something, according to our daily experience? Put the glue on individual staff surface or mix a group of staff with the same amount of glue? We know the first option is better. For the same reason, divalent ions between NOM and membrane are the most crucial factor causing bridge effect, and it is the divalent ions on the membrane surface that make the NOM layer compact. Since part of divalent ions work on connection among NOMs, less "glue" would be used to make the bridge between NOM and membrane if we have the same amount of divalent ions as glue.

Therefore, we can imagine after each backwash, a thin backwash water layer remained on the membrane, which separate the feed water from the membrane. When the membrane was backwashed with demi water, because of absence of divalent ions (glue), the thin demi water layer worked like nonconductor, blocking the connection between NOM and membrane. It is the similar condition like difficult pasting on a wet wall. Because in that case, NOM cake layer is not firmly fixed on the membrane surface, it could be easily removed by backwash. In contrast, the bridge connection was set up due to mixed permeate with 2 mmol/l Ca^{2+}. Since there is only one vessel to collect the permeate, while permeate of direct treatment contained almost the same amount of calcium as canal water, the mixed permeate used for backwash still contained certain amount of calcium. Therefore, when we backwash the membrane with mixed permeate, we actually brought the calcium (glue) back in the membrane. According to the "*Glue Theory*", it means pasting some glue on the membrane surfaces, which lead to the worst fouling situation.

4.2.2 Effect of divalent ions position

From Figure 4.9, we can see only using ion exchange as pretreatment has the same effect as only backwashing with ion free water. Although Schie water of the second option (BW with demi water) had much higher divalent ion concentration than mixed permeate of the first option (IEX pretreatment), it didn't lead to more serious fouling. That is possibly due to the amount of divalent ions really functioning on the membrane surface is equal for both cases. It is true there were more divalent ions in the Schie water; but some of them, instead of connecting the NOM with membrane, just connect similarly charged NOM. Like what we have demonstrated, greatly responding ions on the membrane fouling are those on the membrane surface. What's more, the existence of inserted nonconductor (demi water layer) made the connection less compact than mixed permeate. To be consequence, the negative effect of more divalent ions (glue) in the feed water was compensated by baskwashing with ion free water. The real determinative amount of divalent ion is the amount on the membrane surface.

4.2.3 Effect of monovalent ion on membrane fouling

Figure 4.11 exhibits the different influence of divalent ion free water and complete ion free water on TMP trend. In the first 10 hours, membrane was backwashed with ion free water, and the TMP went smoothly; however, when I changed the backwash water from ion free water to effluent of GAC adsorption, TMP increased much faster than before. Because in the whole process, IEX-UF-NF-GAC adsorption, UF permeates would be treated by NF, which rejects all the divalent ions and let monovalent ions pass through, the effluent of GAC adsorption can be viewed as divalent ion free water. From the 31 hours on, ion free water was used for backwash again, as we can see from the figure, TMP started to decrease. This phenomenon indicates the monovalent ions are also responsible for the NOM fouling. Compared

with the divalent ions, monovalent ions own single valences, so it cannot work as glue to make the bridge connection. Instead of the "Glue Theory", the effect of monovalent ions can be explained by zeta potential, Figure 4.27. We knew that with the increase of salt concentration, zeta potential would decrease and when the zeta potential reach zero, particles start to aggregate. By backwashing with effluent of GAC, the zeta potential of negatively charged membrane was reduced due to the existence of monovalent ions, so the NOMs tend to aggregate on membrane, leading to relatively serious fouling. In contrast, since there was no ion in demi water, the zeta potential of membrane remained the same so that the NOM are dispersed from the membrane. Therefore, the fouling layer could be easily removed by backwash.
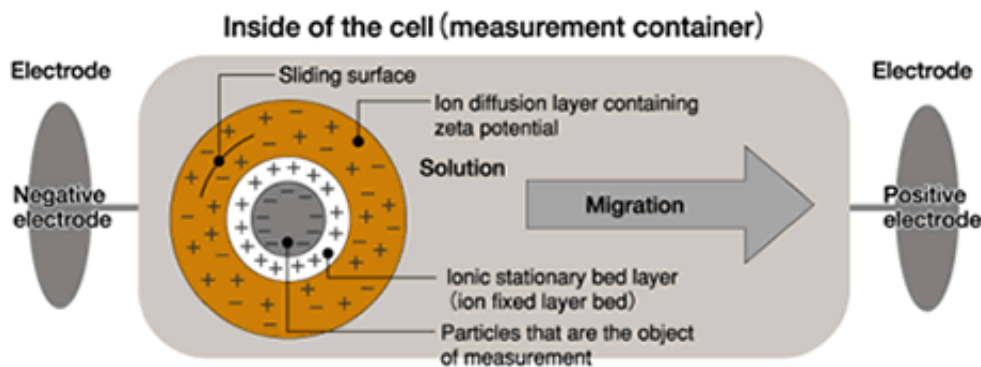
Figure 4.27 zeta potential

Both multivalent ions and monovalent ions play important roles in membrane fouling prevention. For the multivalent ions, it is due to the bridge function as "glue"; for the monovalent ions, zeta potential is responsible for that. However, according to the results, the effect of multivalent ions is more serious than monovalent ions. In another word, the higher ion valence is, the more compact fouling layer is.

4.2.4 Effect of recycle concentrate

We know that concentrate recycle influence the extent of low calcium concentration requirement in the upper section. However, it is not the only impact of recycle concentrate. All of us know that recycling the concentrate can prevent the concentration polarization. Besides that, Figure 4.13 also indicates the different stable MTC for different recoveries. The higher recovery, the lower stable MTC is. Because osmotic pressure difference has been compensated in the MTC formula, it would not be the reason for the MTC difference. The constant MTC also indicated that there was no pore blocking or scaling phenomenon; otherwise the MTC would decrease over time. It is probably due to a somehow constant against pressure, which we didn't take into account; or maybe the formula we used to calculate the MTC is not suitable for this condition. We have to pay attention on this phenomenon, because although we can reduce the membrane investment due to the stable operation at high recovery, we also need to provide much higher feed pressure to get the necessary flux. Considering

the low MTC at high recovery, we need to find the optimized point between energy cost and membrane material cost.

4.2.5 Double barrier for micro pollutants

Although the Molecule Weight Cut Off of NF is 200 Da, the rejection also depends on the logKow of particles. At high logKow, substances with MW smaller than 200 Da would pass through NF; while at low logKow, only substances with MW smaller than 100 Da would pass through. Normally, the substances with high logKow are non-polar, so even though this kind of substances passes through NF, it will be adsorbed by GAC.

To sum up, NF-GAC adsorption double barriers can remove most of the micro pollutants, except those polar substances having Molecule Weight smaller than 100 Da. The amount of these substances is small, such as NDMA, MTBE and TBA.

However, we cannot make the conclusion that this double treatment steps can work continuously. There is no doubt that water quality of GAC effluent was good, because the GAC process was just run for few days. It should be run stably around one year and made sure no breakthrough of any pollutant, otherwise the operation cost will be high if let say regenerating the activated carbon every month.

5. Conclusions and Recommendations

5.1 conclusions

1. Divalent ion removal indeed helps to prevent membrane fouling, so fluidized Ion EXchange system can be an ideal pretreatment for membrane filtration.

2. At relatively low flux (50l/h.m2), as pretreatment for the ultrafiltration, fluidized IEX system is as good as iron coagulation. However, at high flux (65l/h.m2), iron coagulation is better than ion exchange for the short term.

3. The amount of cation on the membrane surface is the most crucial for the membrane fouling, basing on the glue theory. Another feasible theory is based on the repulsion of double layers of the colloids and the membrane surface. The decrease of the double layer at higher salt concentrations or higher calcium concentrations will result in a lower repuilsion and therefor in a higher adhesion energy of the fouling layer to the membrane

4. Backwash with ion free water can improve the UF operations running at this moment in the Netherlands.

5. By incorporating ion free backwash water, fluidized IEX pretreatment and enhanced chemical backwash with NaOH, UF can run stable at 65 $l/h.m^2$ flux and during two weeks of operation.

6. With IEX-UF as pretreatment, NF can run stably at high recovery (97%), and there is the potential to increase up to 99%.

7. IEX-UF-NF-GAC can remove most of the target substances, include: particles, pathogen, microorganisms and micro pollutants, except some polar substances with molecule weight smaller than 100 Da.

8. Divalent ions can be exchanged quickly in the IEX system, but the pH is a limiting factor influencing the exchange capacity in the resin bed. Therefore we should pay more attention on the pH during the modeling of fluidized IEX system.

5.2 Recommendations

1. In order to know more about the effect of cations on membrane fouling, laboratory scale experiment should be done to check the difference of fouling layers with different backwash water or pretreatment.

2. Optimization of UF operation with IEX as pretreatment should be continued, so that the fluidized IEX-UF process can be optimized further.

3. More experimental work on fluidized IEX system modeling is needed in order to know more about the treatment process and make it more regular and convenient.

4. Because permeate of NF is low mineral concentration and pH value, some measures should be taken to increase these parameters. For example, marble filtration can be incorporated with GAC adsorption, forming two layer in the column---Marble + Granular Activated Carbon.

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Appendix

Operation of Fluidized IEX system

- Pre-operation, determination of optimized $NaHCO_3$ dosing amount between two IEX columns: Keep checking the effluent concentration of second IEX column with gradual increase of dosing. 4 mmol/l is good, leading to complete removal of bivalent ions in second column

- Using the Schie water as feed for the first Fluidized IEX column, and control the upward flow at 100l/h by normal valve

- Because the exchange reaction in the column, the pH of first column effluent was low and the resin in second column couldn't work properly in that condition. 4 mmol $NaHCO_3$ was dosed in per liter effluent of first column

- After dosing, the effluent of first column was pumped in the second column

- With the help of dosing, the rest of bivalent ions are removed successfully in second IEX column. For the same reason, pH of second column decreased again, so 72 mg NaOH were dosed in per liter effluent of second IEX column to maintain the pH around 6.5

- After one-week operation, the first column was about 70% saturated, and the ratio of Ce/Co was about 0.5. The first IEX column was regenerated at this moment.

- During regeneration of first column, only second column was in function, with NaOH as pH adjustment solution.

- After regeneration, the order of columns was switched, and the same operation was repeated, except the determination of optimized $NaHCO_3$ dosing amount

During the experiment, the valve sometimes could not control the upward flow very well, and the dosing pump stop function from time to time, so the operation of Fluidized IEX system was not steady.

Experiment graphs automatically plotted by PC

- Parallel experiment for Schie water treated by $FeCl_3$ and IEX at 50 l/h.m2 flux

65
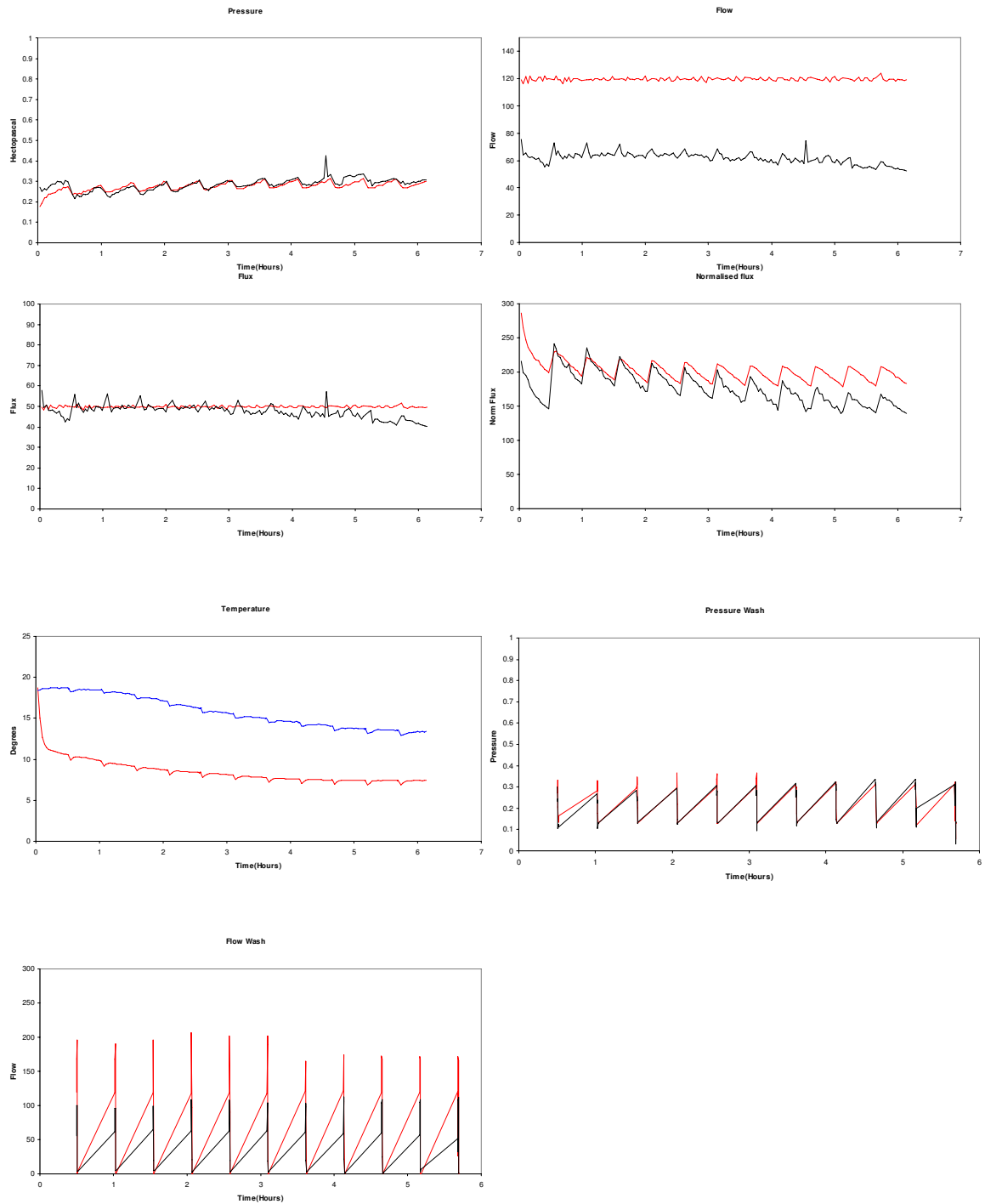
- Schie water at 50 l/h.m2 flux

Pressure

Flow

Flux

Normalised flux

Temperature

Pressure Wash

Flow Wash
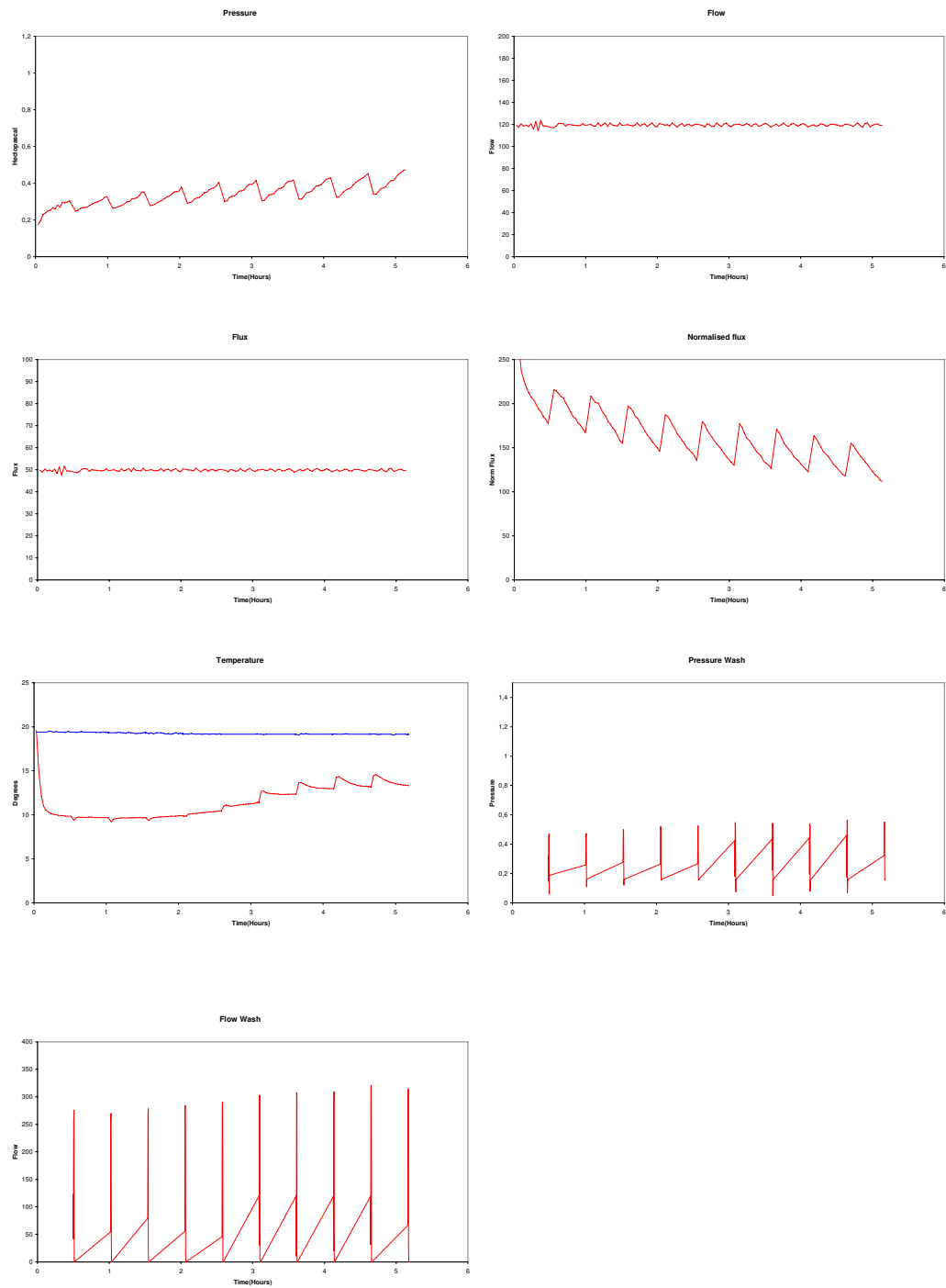
- Parallel experiment for Schie water treated by FeCl3 and IEX at 65 l/h.m2 flux
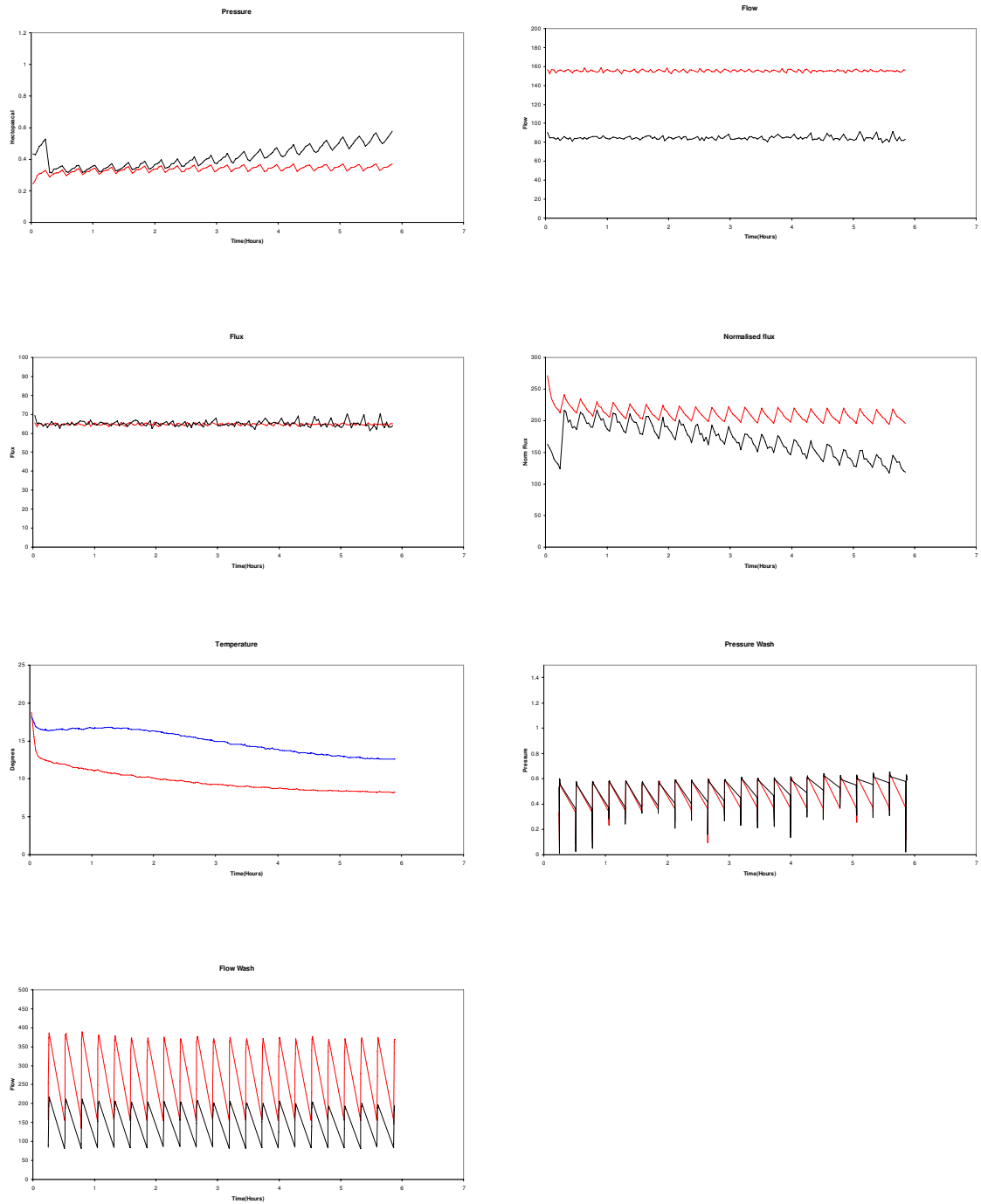
- Schie water at 65 l/h.m2 flux

Pressure

Flow

Flux

Normalised flux

Temperature

Pressure Wash

Flow Wash

68
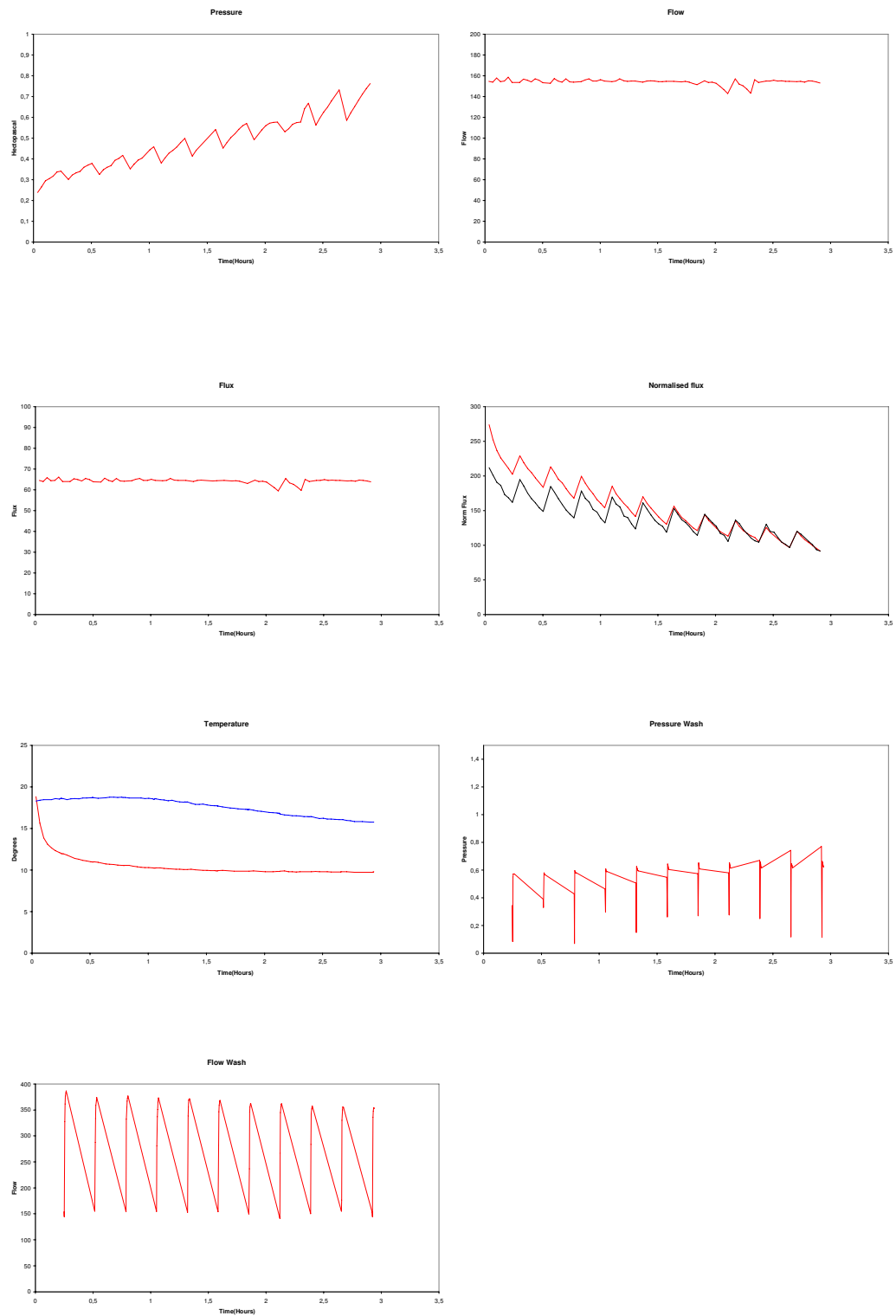
- Long-term Parallel experiment for Schie water and Schie water treated by IEX, 65l/h.m2, using demi water and normal permeate as backwash water
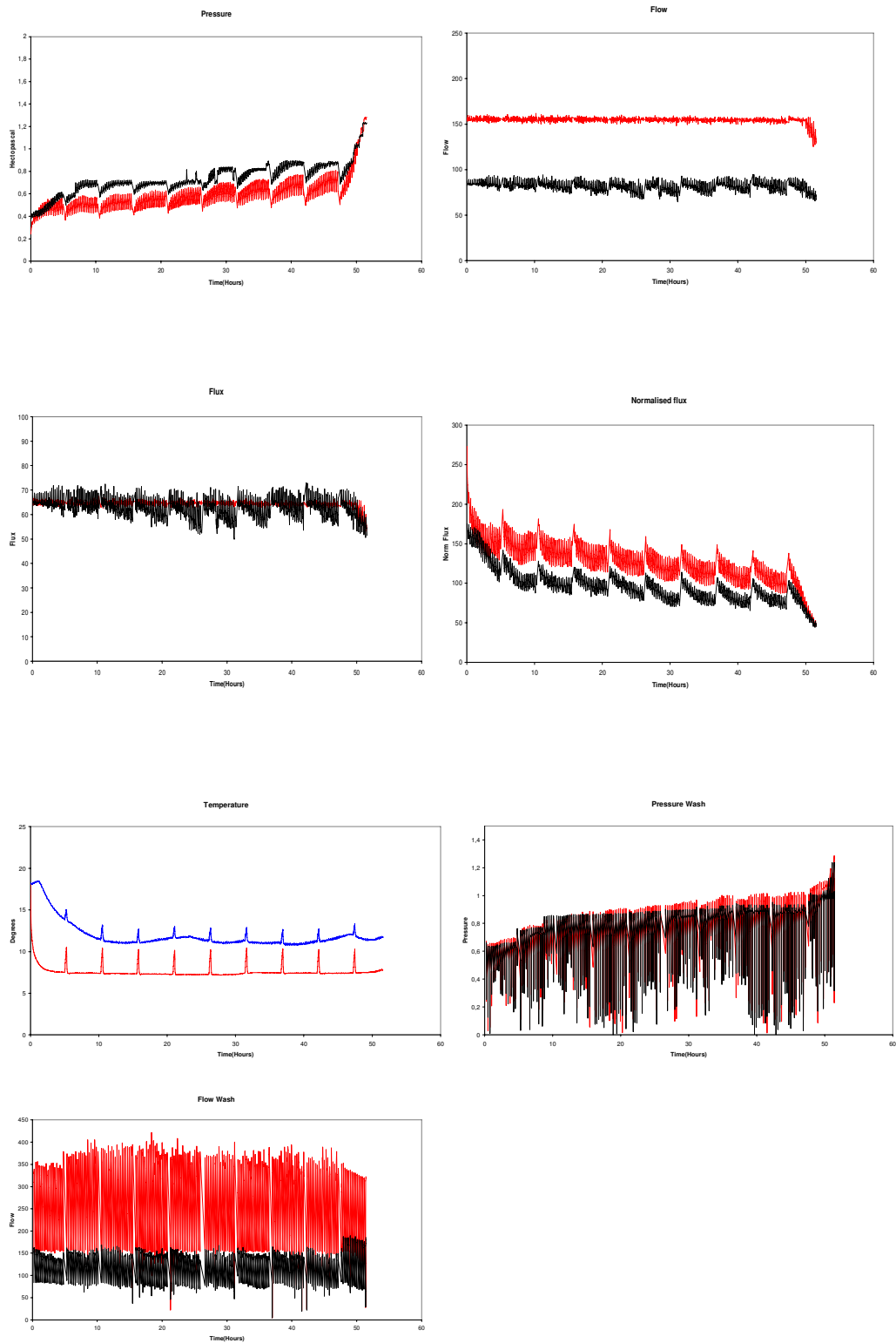
- Long-term Schie water treated by IEX, 42l/h.m2 flux, using demi water and effluent of whole process as backwash water

Pressure

Flow

Flux

Normalised flux

Temperature

Pressure Wash

Flow Wash
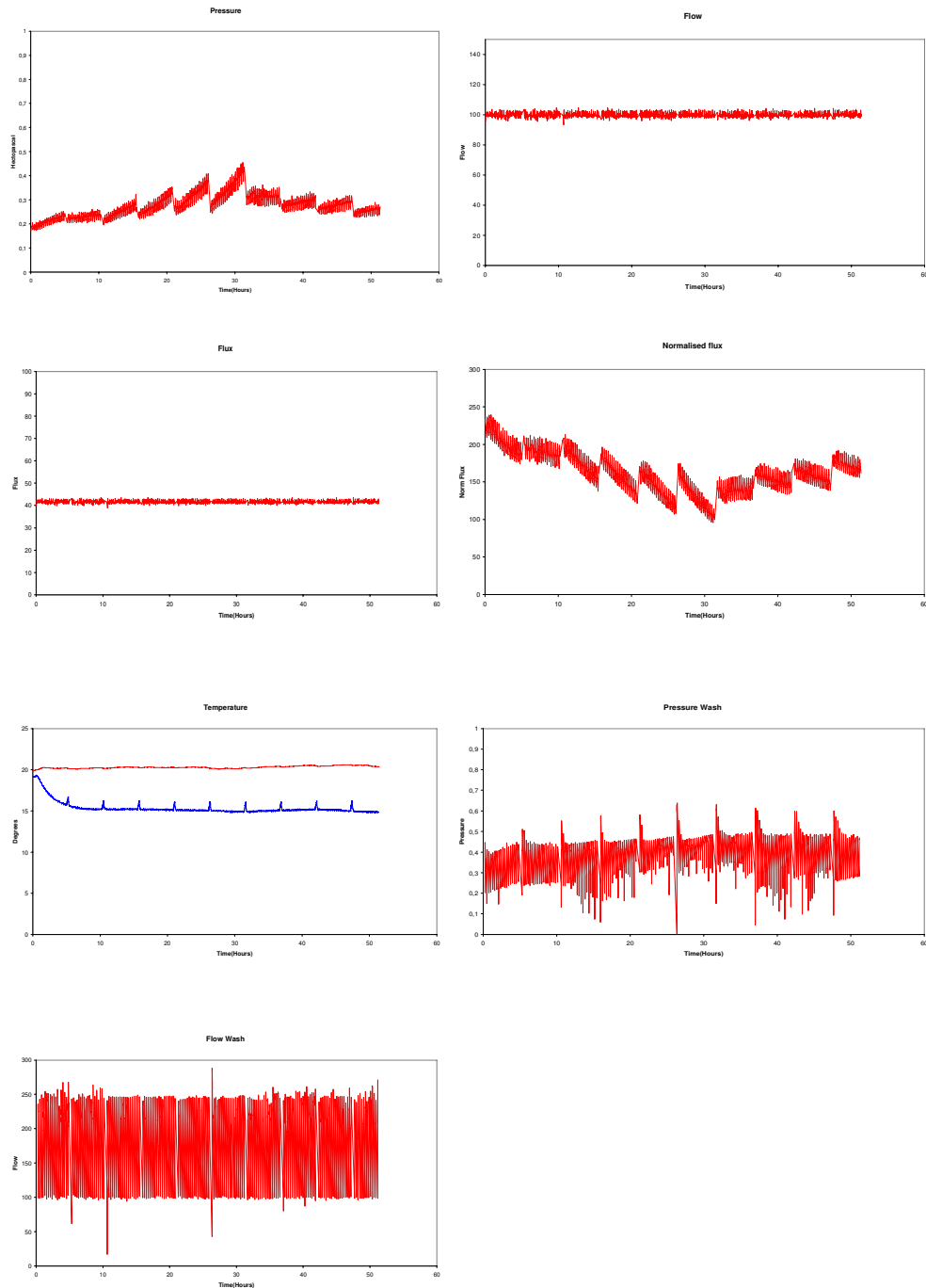
- Long-term Schie water treated by IEX, 65l/h.m2 flux, using demi water as backwash water, ECBW every 5 hours. (14 days)

Pressure

Flow

Flux

Normalised flux

Pressure Wash

Flow Wash

Temperature

71
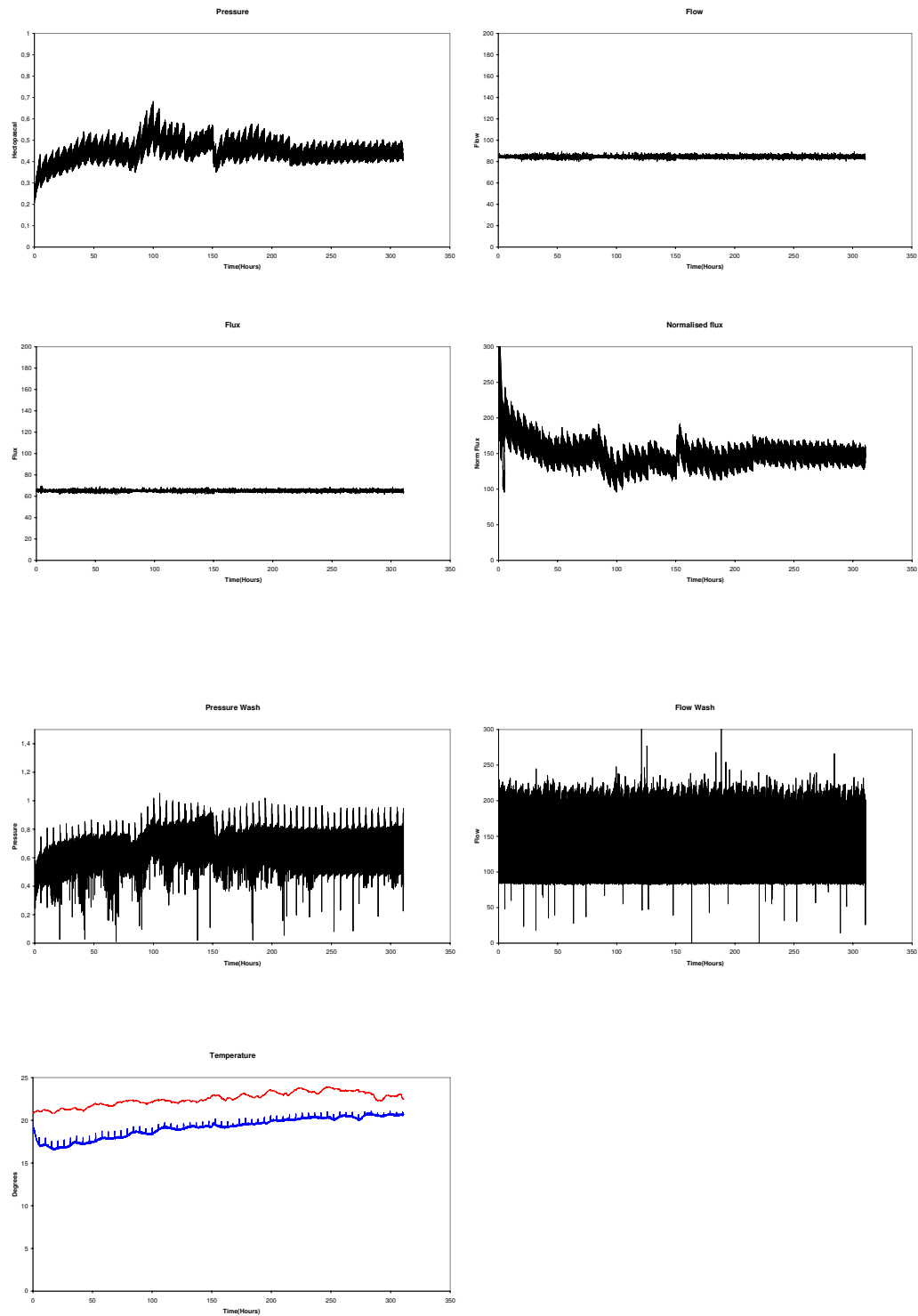
Raw water quality data

Pharmaceuticals, (Measured concentration in µg/l)

Compound	Feed water NF 1	Permeate water NF 1	Effluent GAC 1	Feed water NF 2	Permeate water NF 2	Effluent GAC 2
	10-04-06	10-04-06	10-04-06	10-04-06	10-04-06	10-04-06
Fenazon	110	62	0.49	80	63	0.48
Ibuprofen	26	18	0.28	34	10	0.29
Clofibrinezuur	86	14	0.11	83	13	0.11
Terbutaline	33	27	0.56	28	24	0.55
Naproxen	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Dimethylaminophenazon	94	41	0.20	85	28	0.22
Carbamazepine	25	16	< 0,01	24	18	< 0,01
Salbutamol	2.5	2.1	0.09	2.2	1.7	< 0,01
Fenoprofen	100	28	0.09	75	25	0.09
Pindolol	45	40	0.18	39	34	0.17
Gemfibrozil	96	63	0.05	97	52	0.06
Ketoprofen	29	7.2	< 0,01	29	6.3	< 0,01
Propranolol	94	79	0.18	79	79	0.18
Cyclofosfamide	80	52	0.73	73	51	0.72
Atenolol	50	44	0.47	45	40	0.47
Metoprolol	66	57	0.39	58	54	0.40
Sotalol	2.3	2.0	< 0,01	2.1	1.9	< 0,01
Clenbuterol	2.0	1.6	< 0,01	1.9	1.6	< 0,01
Pentoxifylline	73	56	0.16	73	57	0.16
Diclofenac	3.7	< 0,01	< 0,01	4.9	< 0,01	< 0,01
Bezafibraat	36	4.5	< 0,01	34	3.6	< 0,01

Diuron concentration (mg/l)

	Feed concentration	Permeate concentration	Retention
Beginning	2,430659	0,413592	84,4%
6 hours	2,839123	1,561758	45,0%
Day 2	2,83808	1,626122	41,5%
Day 3	2,891853	1,615277	43,7%

Atrazine concentration (mg/l)

	Feed concentration	Permeate concentration	Retention
Beginning	2,588826	0,548642	80,4%
6 hours	2,981333	1,479573	50,3%
Day 2	2,924342	1,492904	49,4%
Day 3	2,974199	1,579532	44,8%

pH 12, Ca concentration of different loadings over time, mmol/l

Time (hour)	15g/kg		20g/kg		30g/kg		40g/kg	
0	2.94		2.94		2.94		2.94	
0.25	1.15		1		1		1.8	
0.5	0.17	pH:8,3	0.25	pH:8,85	0.63	pH:9,39	1.08	pH:9,71
1	0	pH:7,3	0	pH:7,68	0.03	pH:8,15	0.16	pH:8,65
2	0		0		0		0	
4	0		0		0		0	
20	0		0		0		0	

Time (hour)	63g/kg		126g/kg		252g/kg	
0	2.94		2.94		2.94	
0.25	N/A		N/A		N/A	
0.5	N/A		N/A		N/A	
1	N/A		N/A		N/A	
2	0.35		0.35		0.35	
4	0.35	pH:8,59	0.35	pH:10,23	0.35	pH:11,03
20	0		0		0	

pH 10, Ca concentration of different loadings over time, mmol/l

Time (hour)	63g/kg		126g/kg		252g/kg	
0	2.94		2.94		2.94	
0.25	N/A		N/A		N/A	
0.5	2		2.24		2.4	
1	1.56		2		2.16	
2	0.9		1.6		1.77	
4	0.5	pH:7,2	1.15	pH:8,05	1.5	pH:8,38
20	0.2		0.83		1.34	

pH 8, Ca concentration of different loadings over time, mmol/l

Time (hour)	63g/kg		126g/kg		252g/kg	
0	2.94		2.94		2.94	
0.25	N/A		N/A		N/A	
0.5	2.15		2.4		2.66	
1	1.8		2.18		2.48	
2	1.23		1.95		2.43	
4	0.78	pH:6,42	1.4	pH:7,53	2.09	pH:7,94
20	0.78		1.15		1.77	

pH 6, Ca concentration of different loadings over time, mmol/l

Time (hour)	63g/kg		126g/kg		252g/kg	
0	2.94		2.94		2.94	
0.25	N/A		N/A		N/A	
0.5	2.5		2.66		2.7	
1	2.5		2.54		2.68	
2	2.38		2.39		2.45	
4	2.34	pH:4,1	2.35	pH:4,43	2.45	pH:5,25
20	2.39		2.41		2.45	

Breakthrough curve

Time (hour)	Ce (mmol/l)	Ce/Co	Bed volume (m^3/m^3)
2	0.08	0.02	7
15	0.076	0.02	54
23	0.5	0.14	82
34	0.7	0.19	121
45.5	0.84	0.23	163
55.5	1	0.28	198
83	1.1	0.31	296
130	1.1	0.31	464
155	2	0.56	554
170	3	0.83	607
180	3.6	1.00	643
200	3.6	1.00	714

Co (mmol/l)	Flow rate	Volume of resin bed
3.6	100l/h	0.028 m^3

Isotherm

loading (g/kg)	equilibrium concentration (mmol/l)	exchanged Ca (g)	equilibrium concentration (mg/l)
30	0	113,6	0
40	0	113,6	0
63	0,14	108	5,6
126	0,73	84,4	29,2
252	1,8	41,6	72
1260	2,63	8,4	105,2

Ca concentration of Schie water: 2.84 mmol/l

loading (g/kg)	Log Ce	Log q
30	N/A	1,43
40	N/A	1,56
63	0,75	1,73
126	1,47	1,93
252	1,86	1,92
1260	2,02	1,92