Report AquaSPICE

Case study at Dow Terneuzen
Part II: Dilution Steam Blowdown treatment

The IMPROVED containers on site at Dow Terneuzen

Case study at Dow Terneuzen: test period October - November 2022

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1. Abstract

In the second phase of the Dow Terneuzen trials within the AquaSPICE project, the IMPROVED mobile research infrastructure was deployed to treat dilution steam blowdown from crackers, aiming for reuse as boiler feed water. A key challenge was the removal of small, uncharged organics, as identified in the 'Condensate and Steam quality' project and preliminary AquaSPICE lab tests. Technologies like Membrane Aerated Bioreactor (MABR), Granular Activated Carbon (GAC), Ultrafiltration (UF), Ion Exchange Resins (IEX), Macro-Porous Polymer Extraction (MPPE), and Reverse Osmosis (RO) were evaluated in various configurations.

However, no treatment combination successfully reduced Total Organic Carbon (TOC) to the desired level (<1 ppm). Mini-boiler experiments, conducted to assess organic acid formation – a known cause of corrosion in boilers – indicated that the treated water generated more organic acids than Dow's current boiler feed water, deeming it unsuitable for reuse.

Introduction

Fresh water is of major importance for the chemical industry, as it is used in many chemical processes as an ingredient, for cooling and for steam production. However, the continuous supply becomes more uncertain nowadays, as ground and surface water are depleting or getting less usable due to lower quality (i.e. becoming too saline). The reuse and production of industrial process water as well as turning to alternative sources of water delivers a sustainable solution to this problem. In this research the potential of new technologies for reuse of dilution steam blowdown is investigated within the AquaSPICE project. The dilution steam blowdown is a stream coming from the cracker of Dow where steam has been in direct contact with the product.

1.1 Problem Statement of the Dow Terneuzen Case

The Dow Terneuzen I-Parc is under severe water stress as it is located in a coastal area with very limited availability of fresh water. With the AquaSPICE project, the Dow Terneuzen I-Parc strives to reduce its freshwater intake intensity by (a) enhancing the internal recycle of various process water streams – these comprise (but are not limited to) cooling tower blowdown (CTBD) and dilution steam blowdown (DSBD) streams, and (b) creating a next level of site water management by using smart monitoring, algorithms and control on raw water, discharge and recycle streams.

The Dow Terneuzen I-Parc has already a long history in water reuse and recycling. To reduce the freshwater use per unit of product further actions are needed: close the internal water loop, decrease discharge of water that can be used for other applications and reclaim non-polluted rainwater.

1.2 Goal

Dow Terneuzen has three steam crackers. In its furnaces section dilution steam comes into direct contact with the hydrocarbon product mix. In a series of unit operations hydrocarbons are separated from the water phase and returned into the process, leaving a blow down of water containing certain amounts of hydrocarbons, called dilution steam blowdown (DSBD). Streams from all three crackers are collected and stored in a tank. Currently the collected streams run off to Dow's wastewater treatment plant (total of 1.5 million m^3/y). The objective is to treat this stream closer to its source and reuse it as boiler feed water (BFW) or return it into the return condensate loop (returned condensates are further polished to reach high quality boiler feed water, called polished water), reducing the load on the wastewater treatment plant, while taking advantage of the discharge point temperature (100-130 °C).

The IMPROVED pilots were built within the IMPROVED project funded by Interreg Flanders-Netherlands. The IMPROVED pilots are housed in two 40 ft sea shipping containers and contain 9 water treatment skids that

can be rearranged in different configurations. They can treat up to 2 streams at the same time with nominal flow rate of 250 l/h each. The available water treatment skids are Reverse Osmosis (RO), Ultrafiltration (UF), Ion Exchange (IEX), Granular Activated Carbon (GAC), Membrane distillation (MD), Electrodialysis with reversal possibility (EDR), Advanced Oxidation Processes (AOP), Membrane Aerated Bioreactor (MABR), and coagulation and flocculation including lamella settler. The pilots were placed at the cracker site (LHC1) of Dow where the experiments were conducted in continuous mode taking the water from a tank, in which the streams from the different crackers are collected.

2. Technologies of interest

2.1 Lamella separator

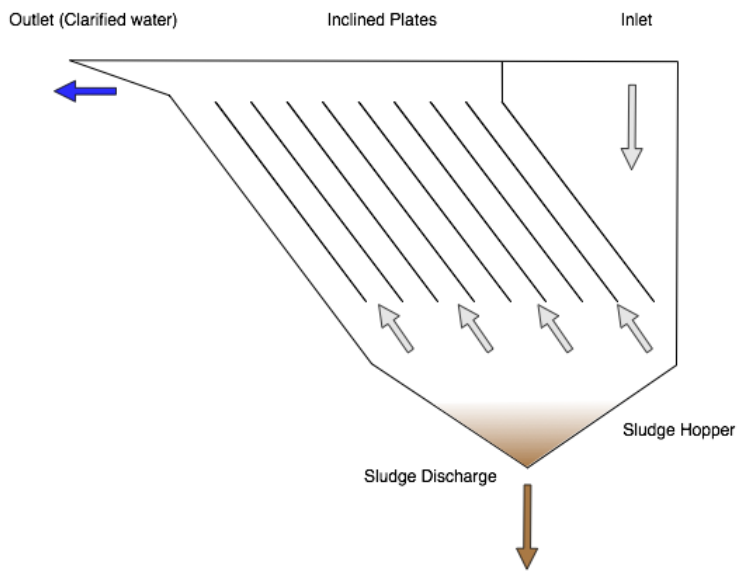

Figure 1 Lamella separator. Image source: Wikipedia

A lamella separator seen in Figure 1 is a technology where inclined plates are installed into a settling tank. The suspended solids are flowing along side the plates and when they touch them, they settle. When a sufficiently thick layer of sludge forms on the plates, the sludge detaches and rolls down into a sludge hopper where it is discharged. Inside the IMPROVED containers, this technology was custom built by the building company IEC. A valve was installed on the sludge hopper that opened for 1 second every 30 minutes discharging about 1 liter of sludge.

2.2 Membrane Aerated Bioreactor

The membrane aerated bioreactor is an attached growth biofilm aeration system which allows for low pressure delivery of oxygen from the carrier side. The system consists of hollow fiber silicone membranes where the biology is attached as a biofilm on the outside of the membranes and is contacted via diffusion through the membrane with air or pure oxygen that flows on the inside of the membrane. Since the air does not need to be bubbled, the required pressures are much lower and blowers can be utilized instead of compressors. The MABR creates an ideal environment to support a very resilient biofilm that can withstand hydraulic shock loads and process upsets. The biofilm absorbs and consumes carbon and nitrogen-based pollutants. It consists of hollow tubes which deliver oxygen directly and continuously to the biofilm growing on the membranes, with little resistance. To control the thickness of biofilm, the membranes can be air scoured regularly [1]. A membrane aerated bioreactor was installed in mixing tank 2, the schematic representation is seen on Figure 2:

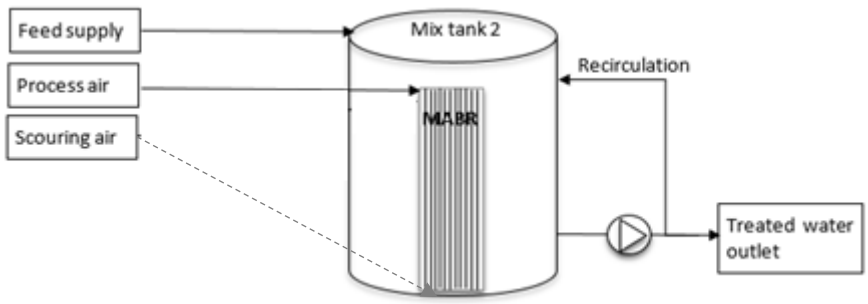

Figure 2 Setup of the MABR reactor placed inside the second of the two mixing tanks

2.3 Granular Activated Carbon (GAC)

In granular activated carbon treatment, large uncharged molecules attach to the surface of the carbon. The granules of the carbon have 3 classes of pores – macropores with diameter larger than 50 nm, mesopores with diameter 2-50 nm and micropores with diameter smaller than 2 nm. Typically, after use, the carbon is replaced and sent to regeneration which can be done using either steam or thermal regeneration typically at 800 °C and a controlled atmosphere.

The activated carbon can also be used as biologically activated carbon, where biofilm is growing on the carbon and (in the presence of sufficient oxygen and nutrients) consuming biodegradable components. In this case, the carbon is not being replaced, but only backwashed with filtrate water to remove the excess biofilm when the pressure drop becomes excessive.

In the IMPROVED containers, there are 3 columns, which are operated in series as GAC1, followed by GAC2 and GAC3 - Figure 3:

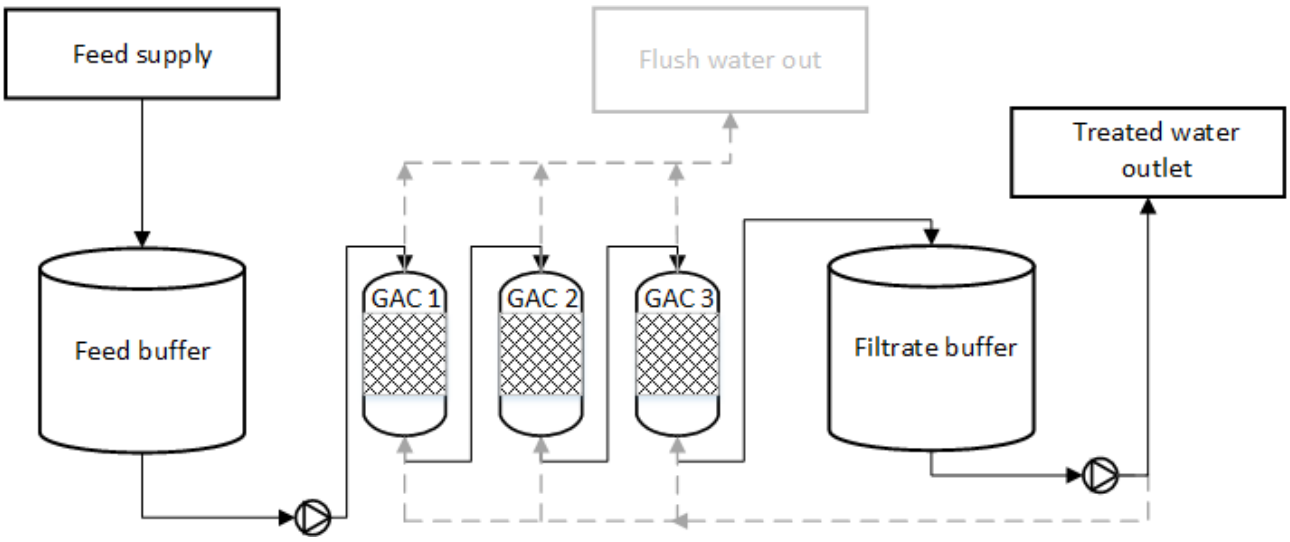

Figure 3 Process diagram of the granular activated carbon in the IMROVED containers

2.4 Ultrafiltration

The ultrafiltration is a process where suspended solids are filtered over a membrane with small pores. This process is commonly used as a pretreatment process for reverse osmosis. The membranes used in UF can be backwashed periodically and are resistant to low levels of free chlorine allowing cleaning in place with bleach - Figure 4:

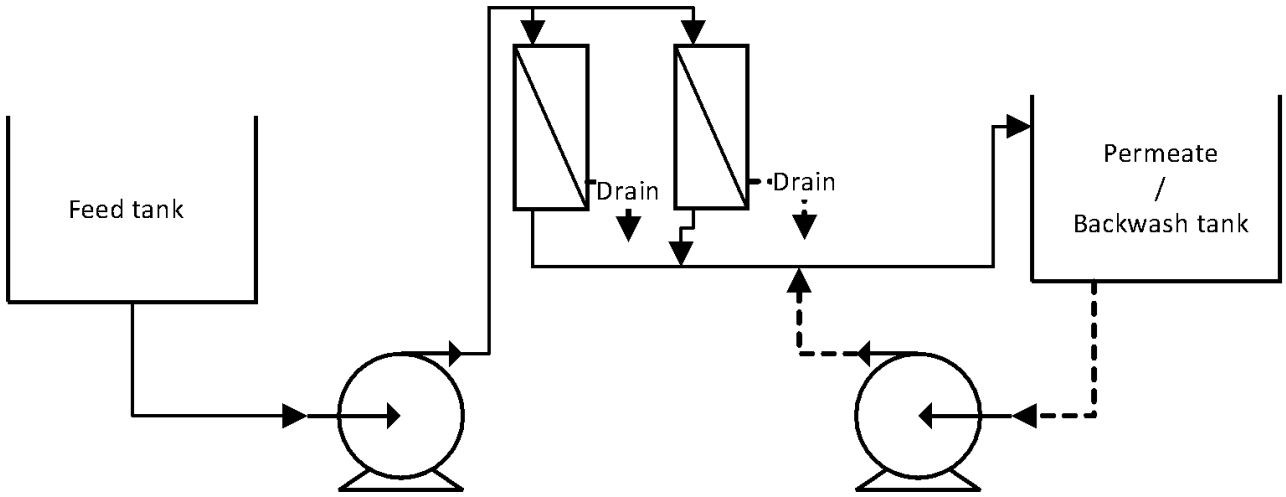

Figure 4 Simplified schematics of the UF skid

The UF is supplied with two hollow fiber 4in modules from Inge with 20 nm nominal pore size. Typically the modules are operated for 30-60 minutes in filtration mode, followed by air drain where the loosely attached fouling can be detached from the fibers. The modules are then backwashed at 2 bar with the filtrate with 10-20 liters followed by a forward flush for 30 seconds at nominal filtration flowrate. Chemically enhanced backwash is also possible where the backwash tank is dosed with chemicals i.e. NaOCl.

2.5 Ion exchange

IEX is an electrochemically driven process. Ions are removed from the solution, because they are exchanged with ions already present on the IEX resin. In this specific case, regenerated cation resin (weak acid cation (WAC) and strong acid cation (SAC)) has H^+, while regenerated anion resin has OH^- (strong base anion (SBA)) or a free base (weak base anion (WBA)) connected to its functional groups. The degasser (DG) removes CO_2 after cations are exchanged for H+, therefore lowering the bicarbonate load to the anion resin. The mixed bed (MB) contains both SAC and SBA resin and polishes the water to < 1 µS/cm electrical conductivity (EC). The mixed beds can also be operated separately as a condensate polishing unit (CPU). As the IEX module removes ions, the resin slowly gets saturated, creating the need for a regeneration. By measuring pressure, EC, pH, TOC, sodium (Na) and silica (Si) before and after selected columns, the quality of the process can be monitored. A general overview of the IEX layout is provided in Figure 5. For more details about the operation of the IEX module, consult the document 'Functional Description IEX-MB'.

For the case of Dow only SCAV, SAC, WBA and SBA resins and their combinations were interesting, therefore the MB and degasser were hydraulically bypassed or left empty. The scavenger (SCAV) resins were placed in the WAC column, and normally regenerated with the chlorides coming from the regeneration of the SAC, with the SAC being in H^+ form. The scavenger resins are essentially SBA resins in Cl form where organics are exchanged for Cl. The Scavenger resins can also be tuned to have more affinity for certain organics.

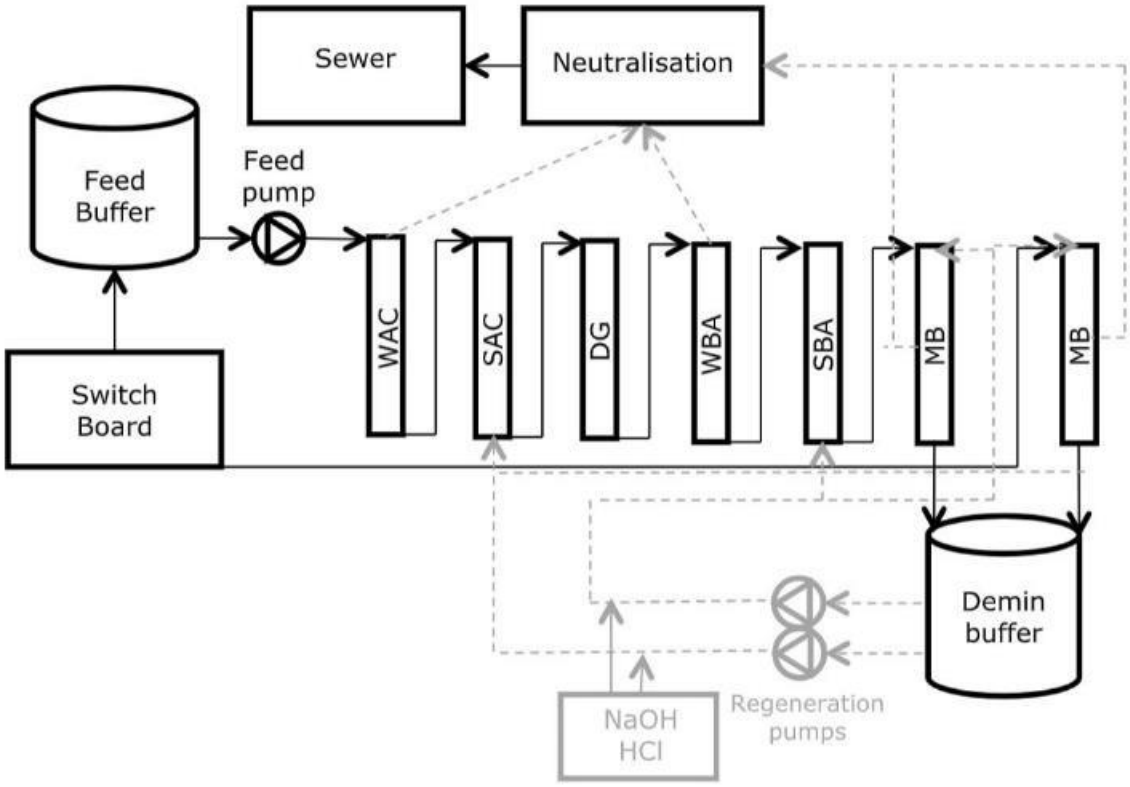

Figure 5 Schematic overview of the IEX module

MPPE

The MPPE or Macroporous polymer extraction are microporous plastic beads with shape and size similar to the regular ion exchange beads. The MPPE resin beds are sized such that they are operated in 1 hour cycles with two beds – one in filtration and one in regeneration. The MPPE is regenerated with steam with up to 170 °C where the steam carries out the volatile components from the MPPE and the steam is later condensed in a condenser, where the water and the volatiles separate by gravity.

Within the IMPROVED containers, steam is not available so the MPPE resins were placed inside one of the IEX columns and operated in once cycle until breakthrough.

2.6 Reverse osmosis

In RO, a pressure gradient leads to separation through a semipermeable membrane. The RO membranes typically do not have visible pores and are considered dense membranes. The suspended solids are mechanically rejected by the membrane, while salts and water are dissolved into the active layer and the rejection is dictated by difference in diffusion coefficients of the water and solutes. Other factors such as membrane and solute charge also have a significant role in the determination of the rejection, but this is out of the scope of this report.

Salts, suspended solids, viruses, and dissolved components are retained in the concentrate, while water and some limited dissolved components move through the membrane in the permeate. RO membranes are typically not cleaned by backwashing but are mostly cleaned-in-place (CIP) with chemicals, or can be flushed with air (AIRO) to remove fouling and prevent clogging of the feed spacer. A general overview of the RO layout is provided in Figure 6.

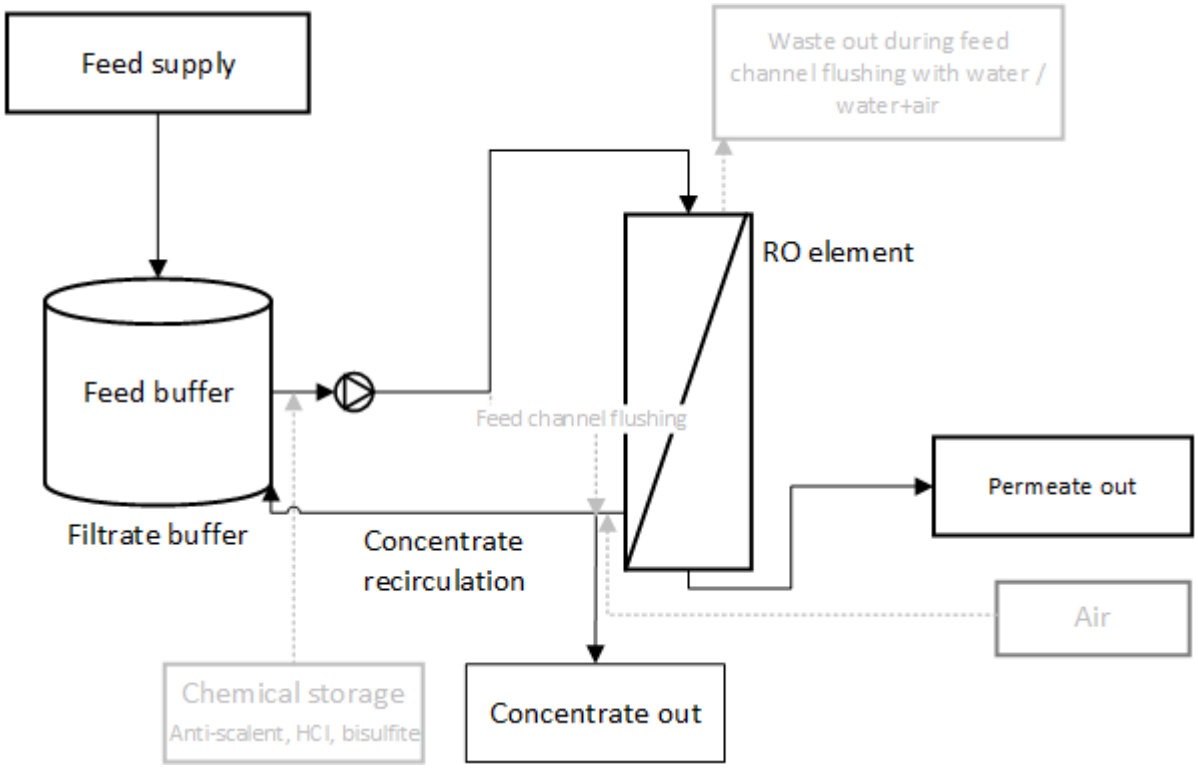

Figure 6. Schematic overview of the RO module.

2.7 Experimental plan

While conductivity can always be removed e.g. by ion exchange or reverse osmosis, the main challenge in polishing this DSBD stream was the removal of organics or TOC. For this purpose several treatment trains were designed.

In the **SCAV-SAC-SBA-RO** both the SCAV and the SBA remove negatively charged organics, as in an essence the SCAV resins are quite similar to SBA but operated in Cl form. The SAC removes cations, but also some of the positively charged TOC such as alkalizing amines that are present in the stream. The RO can remove the larger organic molecules.

The **SCAV-SAC-SBA-GAC-RO** is quite similar in configuration to the previous train with the addition of GAC. The GAC can also remove larger molecules on the basis of adsorption.

The **MABR-Lamella** train was aimed only at developing the biology on the MABR reactor. The MABR bioreactor was very interesting to implement as it is the only technology that can effectively remove small uncharged organics such as methanol, ethanol etc. However it should be noted that the HRT of this reactor in the pilot was only 30 minutes which is quite short compared to the "Steam and Condensate Quality" ISPT project where the DSBD was treated with two MABR pilots in series, each with HRT of 10 hours giving a total HRT of 20 hours. The intention here was to employ the MABR at short HRT in the hope that it would preferentially remove mainly the small uncharged organics that can pass ion exchange and RO as these are known to be very biodegradable.

The **MABR-Lamella-UF-RO** train was aimed at evaluating the TOC removal of RO in combination with the biological treatment of the MABR.

In the **MPPE2-SBA-RO** and **MPPE1-SBA-RO** special microporous polymer extractant (MPPE) was tested. These polymers come in the form of small beads similar to IEX resins but work by absorbing certain pollutants based on chemical affinity into the polymer matrix. The idea was to see if the polymers can remove the small uncharged organics while the RO can polish the effluent to acceptable quality.

In the **SCAV-SBA-MABR-UF-RO** the charge (SCAV, SBA), biological (MABR) and steric hindrance (RO) mechanisms were tested to remove as much TOC as possible. The UF was placed as pretreatment for the RO from the flocs coming from the MABR. The **WBA-SBA-MABR-UF-RO** train is similar, but the scavenger has been replaced with weak base anion exchanger. The WBA resin has larger capacity per liter compared to SBA and hence can be operated longer between regenerations. In these configurations SAC is missing so the cations are removed solely by the RO.

In the **SCAV-SAC-WBA-SBA-MABR-GAC-RO** and the **SAC-WBA-SBA-GAC-RO** configurations besides the charge (SCAV, SBA), biological (MABR) and steric hindrance (RO) mechanisms also adsorption was added with the GAC.

Finally in the last two trains **Lamella-SAC-WBA-SBA-MABR-GAC-RO** and the **Lamella-SAC-WBA-GAC-RO** the best performing and the most promising trains were tested, with the exception of Lamella being added to the beginning of the train due to problem with blockage of the resins from particles contained in the feed.

3. Materials and Methods

3.1 Membrane Aerated Bioreactor

The MABR was placed in one of the mixing tanks, where air was supplied continuous at 0.2 bar. The membranes have active area of 22 m^2, 25 bunches with 540 membranes fibers in each bunch and length of 85 cm. In order to achieve the 0.2 bar before the MABR, a pressure regulator is installed after the fibers to increase the pressure drop of the system. The flowrate of air inside the membrane lumens was 8 l/min. The water inside the reactor was mixed with a circulation pump at more than 1 m^3/h. Once a day the membranes are air scoured for one minute using a course bubble aeration underneath the module. The membranes were always submerged in the water, with continuous recycling of the water in the tank. pH control is possible in the mixing tank. There is a possibility for the pH inside the MABR tank to be controlled.

3.2 Granular activated carbon

The setup in the containers (Figure 3) consists of 3 columns in series with diameter of 26 cm, height of 1 m, filled until 0.81 m, resulting in 43 L volume each. The carbon used in the tests was Norrit GAC 830W. The normal operational flow of the columns is from top to bottom with a flow rate of 250-500 l/h. The backwash is performed in the opposite direction from the bottom to the top with product water.

3.3 Ultrafiltration

The UF in the IMPROVED containers is based on two identical hollow fiber modules from INGE model Dizzer P 4040-6.0 operated in parallel. One of the modules can be isolated from the system by closing down manual valves in case lower production of flowrate is required. The system automatically alternates between filtration, air drain, backwash and forward flush modes. In filtration mode the permeate tank is filled first before outputting water to the next technology. During drain cycle the modules are drained of water and the filtered suspended solids. During backwash the water is rapidly pushed in the opposite direction and the filtered cake material is dislodged from the membrane surface. By dosing chemicals to the permeate tank, chemical enhanced backwash (CEB) is made possible. Finally, the feed space of the modules is flushed before going back into filtration mode.

The flux was set to 25-50 l/m^2/bar and the filtration time was 30 to 60 minutes with backwash duration of 15 seconds at 1.9 bar.

3.4 Ion exchange

The deionization happens from top to bottom in vertical columns with 10 cm internal diameter, while the regeneration happens in the opposite direction. The hydraulic arrangement of the columns is SCAV-SAC-Degasser-WBA-SBA-MB1, where the degasser and MB resins were not used during these trials as the degasser would strip the organics to the ambient air which is unwanted and the mixed beds have little

influence on the removal of the organics. Mixed bed 2 (MB2) is a separate unit that can be connected to another technology.

Table 1 Arrangement and resin type inside the IEX setup

Column	***Bed height, fresh (cm)***	***Resin***	***Column height (cm)***
SCAV	*79 (6.2L)*	*Amberlite SCAV4 Cl*	*85*
SAC	*136 (10.6 L)*	*Dowex 650C (H)*	*145*
WBA	*35 (2.7 L)*	*Amberlite HPR9600*	*145*
SBA	*136 (10.6 L)*	*Amberlite HPR9000 OH*	*145*

3.5 Reverse osmosis

In Figure 6 the scheme of the RO set-up is shown. The RO membrane was a Dupont Filmtec LC HR-4040, with an active membrane area of 8.7 m². The pressure housing was a Codeline 40E100. The pH, flow, pressure, conductivity and temperature were continuously measured online with 2-minute sampling intervals. Antiscalant Genesys LF from Genesys RO (www.genesysro.com) was used in 5 ppm concentration only in configurations where no SAC resin was placed before the RO due to the iron in the water.
The flux was set to 25 l/(m^2.h), with a recovery of 85%.

4. Results and Discussion

4.1 Performance of the pilot

4.1.1 Time schedule

In the available time (October 24th - November 25th) twelve treatment trains have been tested, of which most only for a few days - Figure 7.

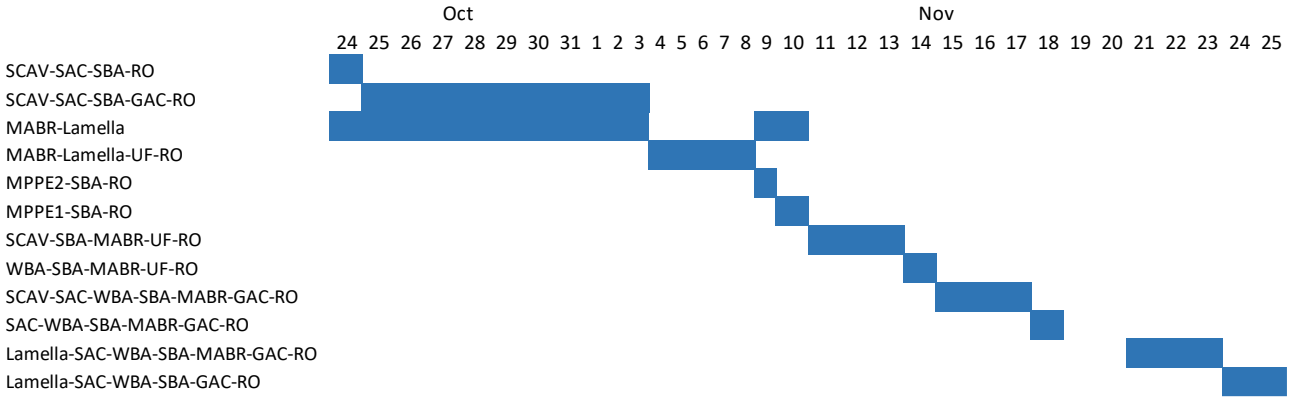

Figure 7 Time schedule of the experiments

5.1.2 Feed water quality

The wastewater streams from the crackers are collected in a tank, from which the water was pumped to the IMPROVED containers.

The feed water quality during the trials at Dow is shown in Figure 8. The dilution steam blowdown contains on average 90 ppm TOC, of which 20 ppm organic acids and 30 ppm phenols and has a conductivity around 140 µs/cm.

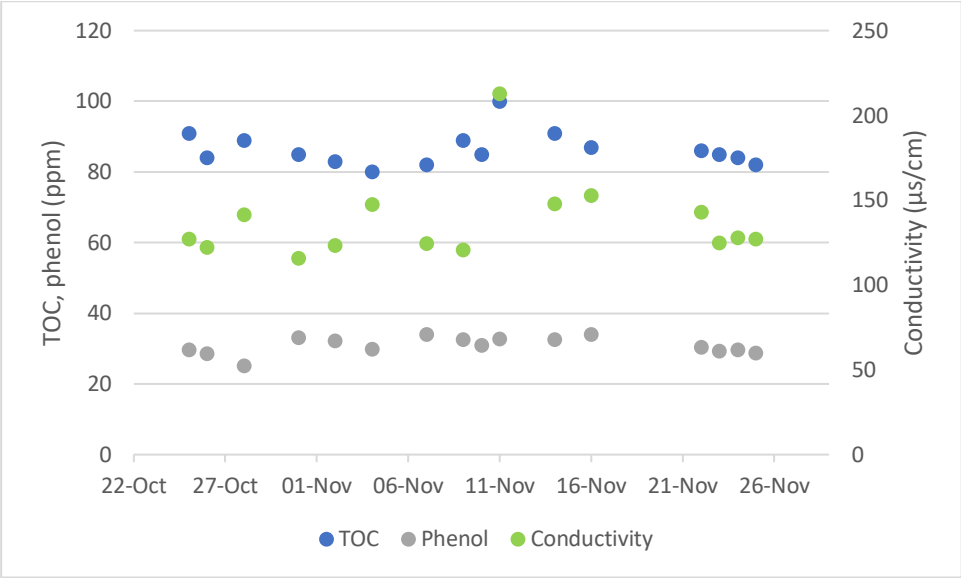

Figure 8 Feed water quality in terms of TOC, conductivity and phenol

The water from the tank (40 °C) cooled down in the pipelines to the container. The feed water temperature measured in the container was around 25 °C at the start (25th October) and decreased to around 15 °C (25th November).

In Table 1Table 2 the feed water quality in terms of cations can be seen:

Table 2 Feed water quality in terms of cations

	Ca mg/l	Mg mg/l	K mg/l	Na mg/l	Zn mg/l	Ba mg/l	Cu mg/l	Mn mg/l	Al mg/l	Fe mg/l
Average	0.22	0.07	0.13	30	<0.05	<0.005	<0.05	<0.05	<0.05	<0.05

In Table 3 the feed water quality in terms of cations can be seen:

Table 3 Feed water quality in terms of anions

	Formate mg/l	Acetate mg/l	Propionate mg/l	Cl mg/l	F mg/l	Br mg/l	NO_2 mg/l	NO_3 mg/l	SO_4 mg/l	PO_4 mg/l
Average	0.06	2.04	0.13	1.15	0.00	0.02	0.00	0.11	4.63	6.08

The major ions are depicted in Figure 9 below:

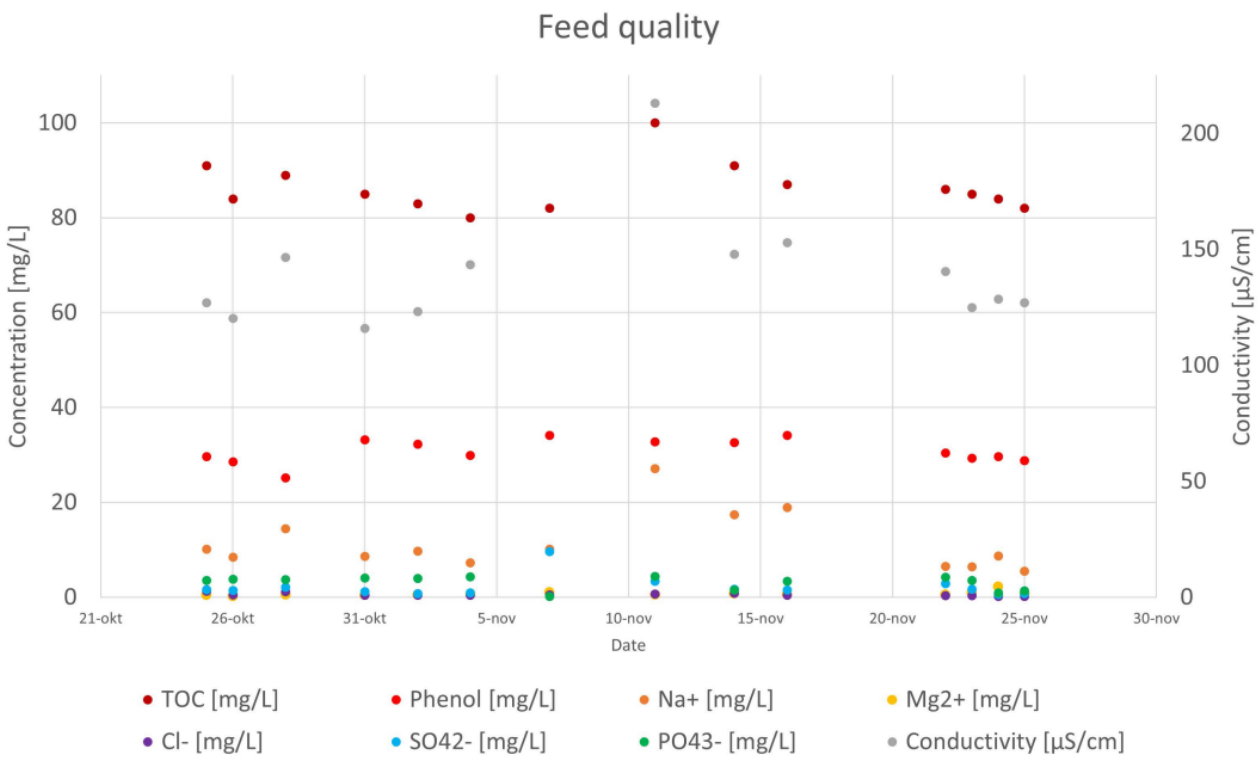

Figure 9 Feed water quality

5.1.3 Performance of MABR

Biomass started to develop on the membranes immediately as noticed visually (Figure 11). The dissolved oxygen was measured, but these values are just an indication of biological activity, and are not valuable itself as air is added continuously through the membranes. The biology on the MABR was disturbed regularly by pH swings, caused by inaccurate pH control (acid dosing was too fast/concentrated) and no proper displacement (washing with demin during regeneration) of IX resins due to insufficient demin water. These pH fluctuations probably killed or at least severely affected the biology at the point where the IEX was placed before the MABR. Due to the short timeframe of the experiments, the practical problems with inaccurate pH dosing could not be resolved in time and the biology could not regrow fast enough. On average the MABR was removing around 3 ppm TOC, and no measurable amount of phenol was removed (Figure 10). It should be noted that there was a difference between the online and grab sample TOC values for the MABR effluent. The online measurement is pre-filtered with 40 µm filter and the value was 2-3 ppm lower than the unfiltered grab sample value, hence maybe some of the TOC was converted to cells which can also measure as TOC in an unfiltered sample. The values displayed below are from grab samples.

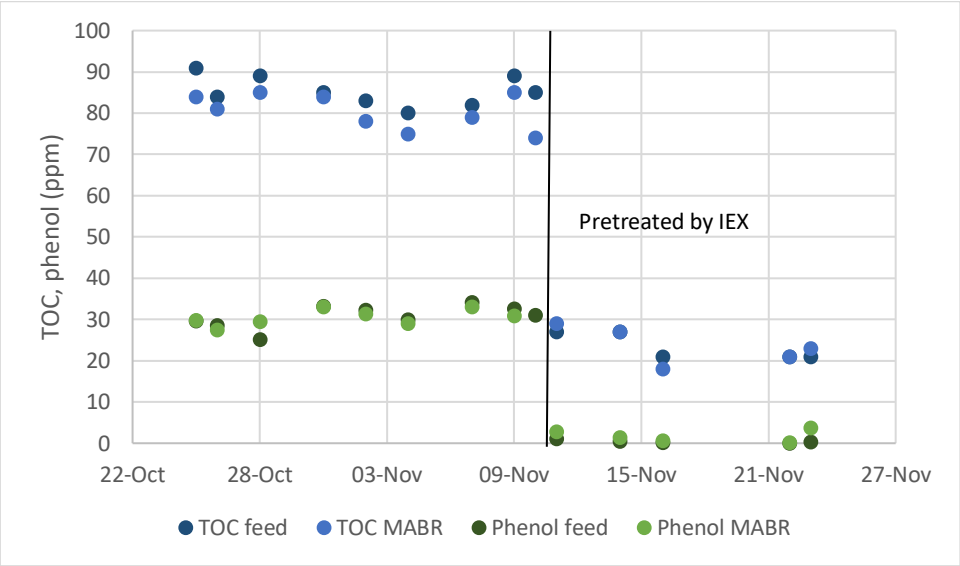

Figure 10 TOC and phenol evolution before and after MABR treatment. In the "Pretreated with IEX" ion exchange was placed before the MABR reactor in the treatment train

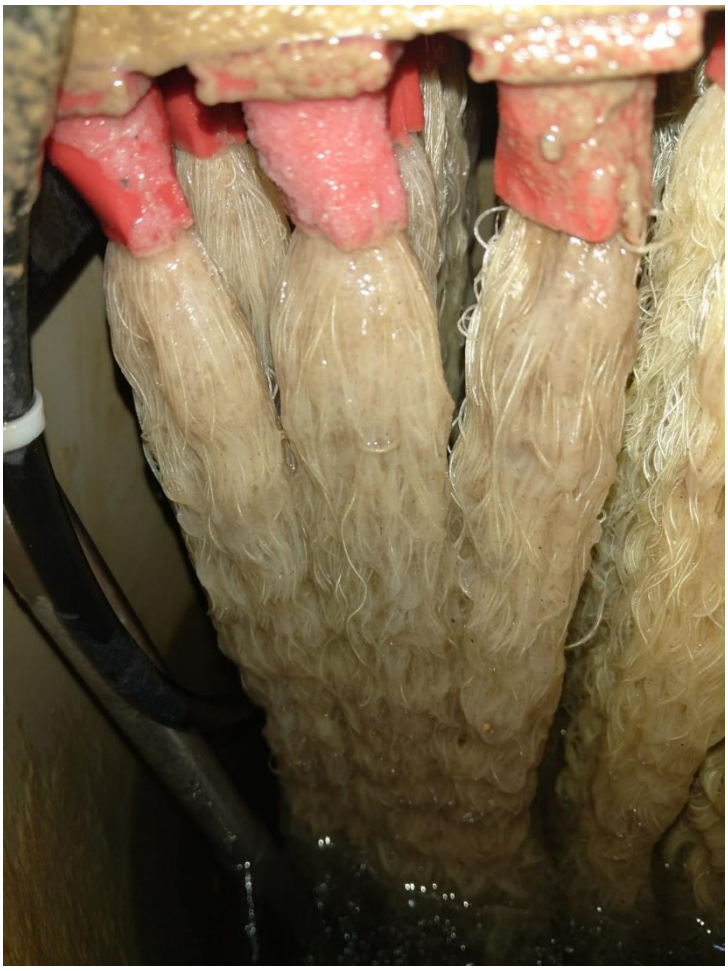

Figure 11 Biology growing on the silicone fibers of the MABR

5.1.4 Performance of GAC

The GAC was operated around 300 l/h in several treatment trains after the IEX, and as pretreatment to RO. No special preservation was done for the periods where the GAC was not used as these periods were less than a week. There was immediately biological activity on the surface of the carbon, indicated by the reduced

dissolved oxygen (DO) as shown in Figure 12. The dissolved oxygen in the feed of the GAC is added by the recirculation loop of the feed pump. In the first weeks around 4 ppm DO was measured after the first column, 1-2 ppm after column 2 and almost no oxygen was left after the last column. At the end of the trials, all the oxygen was used in the first column. The TOC removal might be higher if oxygen is added. There were pH swings, which seems to have limited impact on the biomass based on the consistently low DO after the 3rd column.

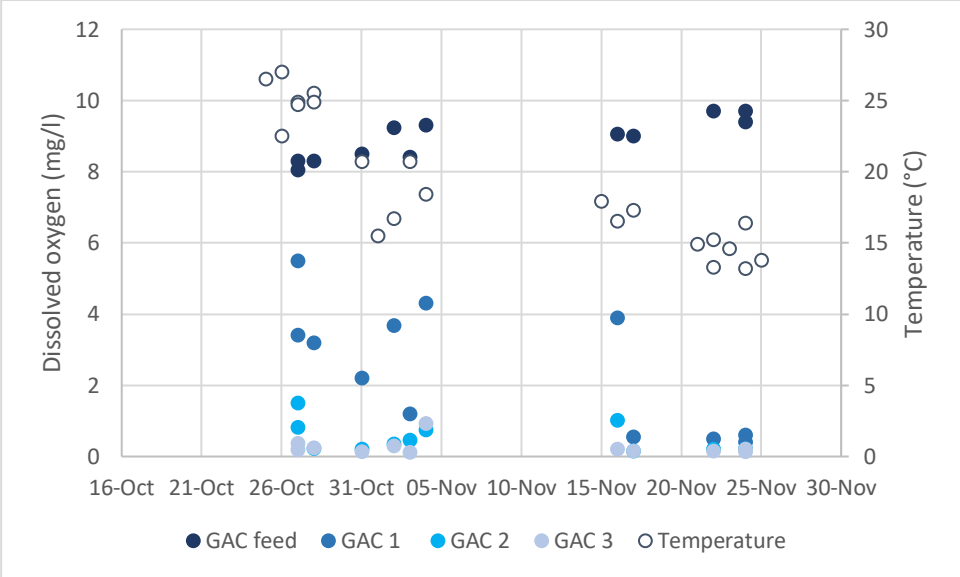

Figure 12 Dissolved oxygen in GAC

A layer of biomass was found on the first column at the end of the experiments, Figure 13. Although biomass was growing on top of the first column, the pressure did not increase to high values (Figure 14) and no backwashes were needed during the trials, resulting in a water efficiency of 100%. Given that the carbon was used for about 3 weeks in total, in the long run the water efficiency could be less as more particles accumulate in the carbon and it needs more frequent backwashes. The system could be potentially optimized by dosing pure oxygen in the feed in a full-scale installation in order to stimulate the biology in the carbon.

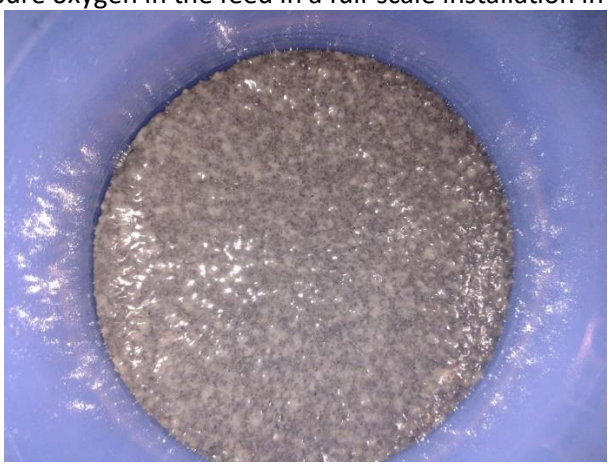

Figure 13 Layer of biomass on top of GAC1

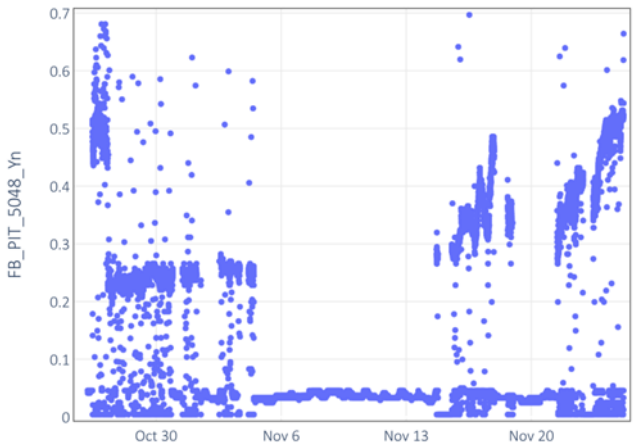

Figure 14 Pressure drop measured over GAC columns

As seen in Figure 15 the first weeks most of the TOC is removed by adsorption in the first column. In the second phase mainly the second and third column are removing TOC. It can be concluded that the adsorption capacity of the carbon for the TOC is depleted for the first column after less than a month.

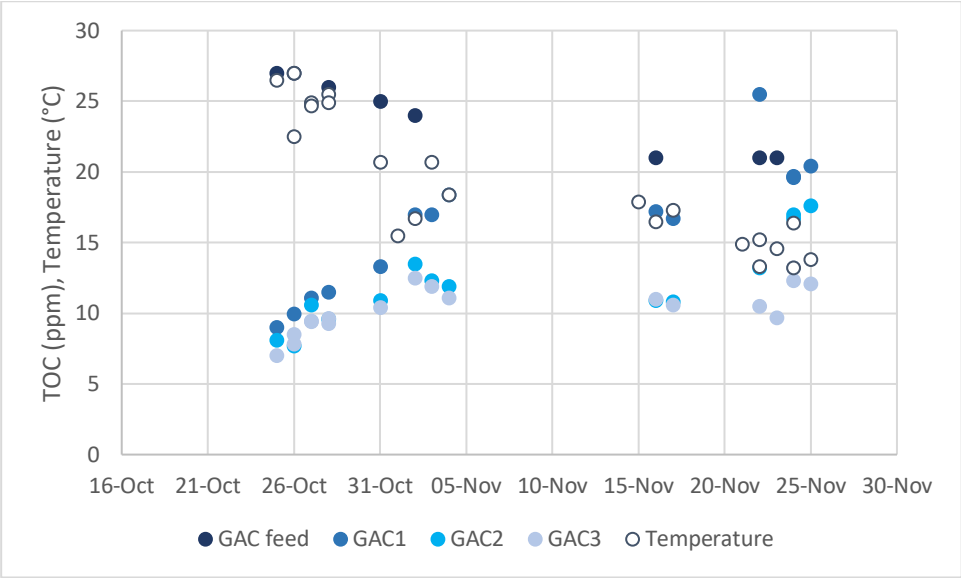

Figure 15 TOC evolution in the GAC columns

5.1.5 Performance of UF

The ultrafiltration was operated during the following treatment trains: MABR-Lamella-UF-RO, SCAV-SBA-MABR-UF-RO and WBA-SBA-MABR-UF-RO. The UF was part of these treatment trains as protection (pre-treatment) for the RO, as biomass was coming from the MABR.

The UF was operated at flux of 50 lmh, 60 min filtration time, followed by module drain, 15 sec backwash and 30 sec forward flush. This resulted in blocking after three days, also seen in Figure 16, as the permeability rapidly decreased over time. The membrane was cleaned in place (CIP) with HCl soak at pH 2, then flushed with demi water, followed by NaOH soak at pH 12 for another hour and finished with another demi rinse.

The filtration time was reduced to 30 minutes after the CIP on November 7th. From November 8th bleach dosing (100 ppm NaOCl) to the filtrate tank was started to explore the effect of Chemically Enhanced Backwash (CEB) on the membrane. The permeability seemed to decrease even faster after the start of sodium hypochlorite dosing, which could be a coincidence with turbidity change in the feed water. The membrane only lasted for two days, and it was concluded that a flux of 50 lmh was too high for this water.

On November 11th, the second UF membrane module was also utilized in order to reduce the flux to 25 lmh and the filtration time was increased from 30 minutes to 45 minutes. After which the permeability remained stable (Figure 17).

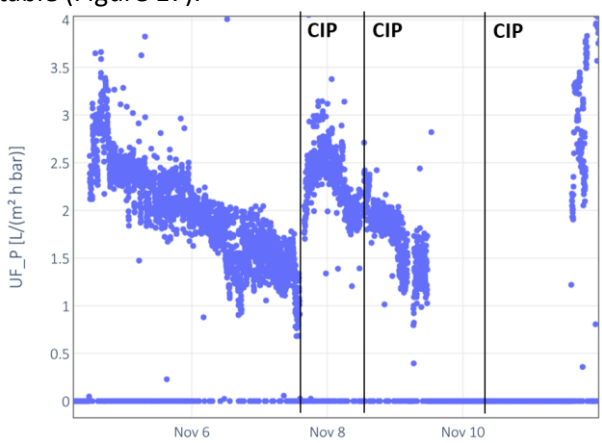

Figure 16 UF permeability with one operational membrane (50 LMH)

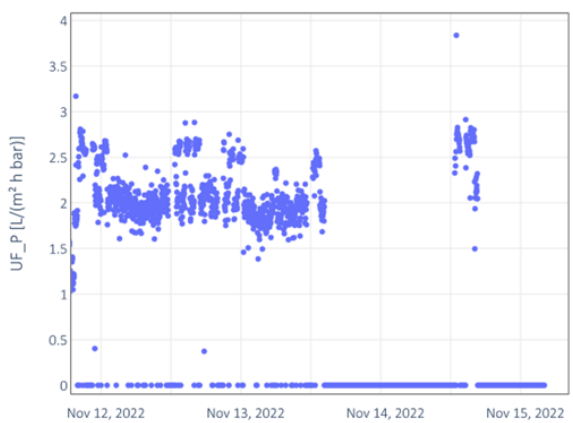

Figure 17 UF permeability with two operational membranes (25 LMH)

5.1.6 Performance of IEX

The feed water was fed directly to the IEX resins, tested in different configurations. The flow rate was set to 290-330 l/h, with a set runtime between 12 and 17 hours. SCAV and SAC are regenerated with 5% HCl, SBA with 5% NaOH, for 30-36 minutes. After which the resins are rinsed with demi water for 20 minutes (180 l/h).

In general, the scavenger was removing 20-25 ppm TOC (removal efficiency of 25%), SAC was removing 3-6 ppm TOC (7%), WBA 2-20 ppm (7%), and SBA removed most of the phenol and 30-40 ppm TOC (60%) (Figure 18 and Figure 19). The water quality after SBA is more or less stable around 20-30 ppm and 2-10 µs/cm, independent on the incoming water quality or resins used. The lowest TOC levels with IEX were reached with the treatment train: Lamella-SAC-WBA-SBA.

During the operation, scaling occurred in the SCAV column and increased pressures over the column. Using the SCAV as first treatment gave problems during the lab trials as well. The SCAV sees the regenerated cations coming from the SAC which caused scaling to occur. Several cleanings with HCl and NaOH were done, but did not remove the scaling on the column. The XRF analysis points out it is sulfur related (35% S) scaling. The feed water consists of 2 ppm sulphate, which would be removed from the scavenger. The sulphate could precipitate with a cation (e.g. calcium coming from the SAC), creating calcium sulfate which is not affected by pH and would explain the scaling and the resilience to chemical cleaning. Therefore, if SCAV is implemented it needs to have a separate chemical for regeneration, e.g. NaCl in order to avoid scaling.

The runtime did not evidently decrease over time, and differed between 12 and 17 hours, dependent on which resins were used and whether the resins were properly regenerated.

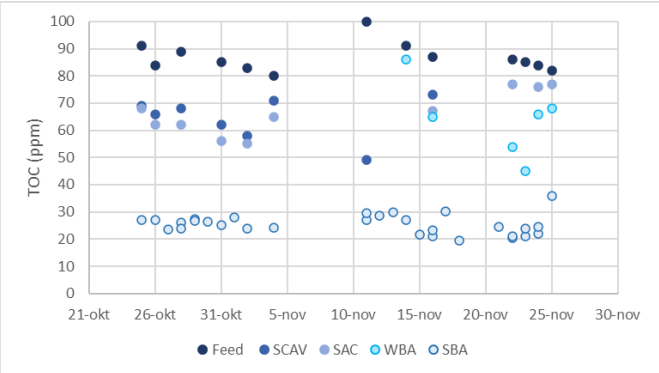

Figure 18 TOC after IEX

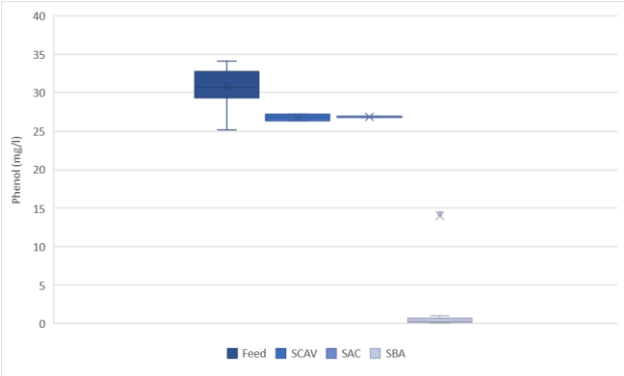

Figure 19 Phenol after IEX

The conductivity obtained after IEX was typically below 5 µS/cm (Figure 21). The sodium was somewhat higher in the beginning of the experiments due to badly controlled demin flowrate during slow rinse and regeneration cause by the blockage on the SCAV column (Figure 20).

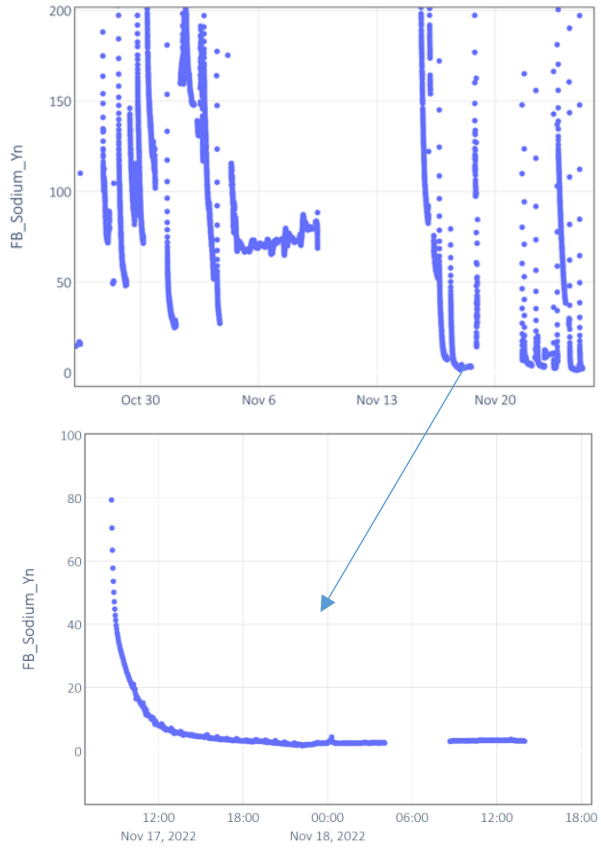

Figure 20 Sodium (ppm) after SBA

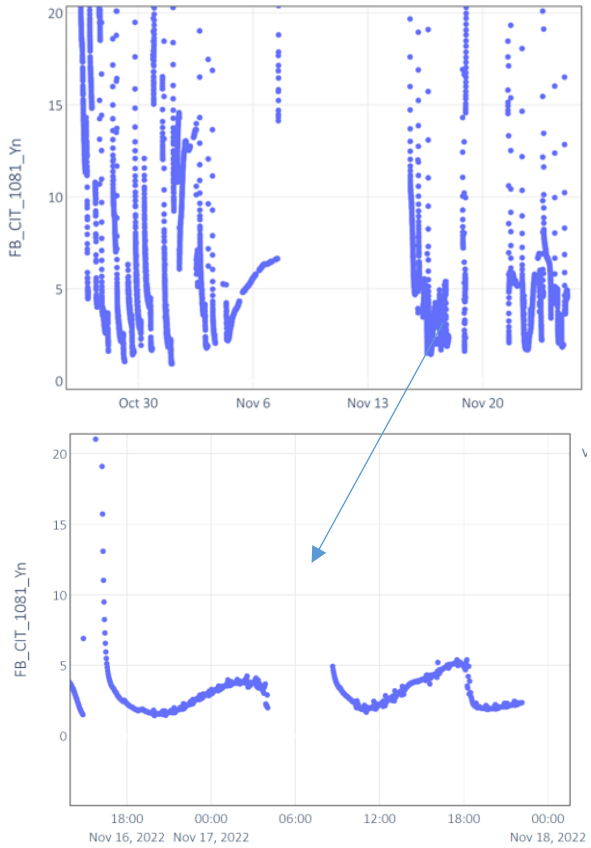

Figure 21 Conductivity (µS/cm) after SBA

5.1.7 Performance of RO

Reverse osmosis has been tested as part of every treatment train during the dilution steam blowdown treatment. Always in combination with ion exchange resins, and other pretreatment, like MABR, GAC and/or UF. The RO experiments were done with a high rejection brackish water membrane: Dupont Filmtech LC HR-4040 membrane.

The membrane was operated at a flux of 25 l/(m^2.h), and a water recovery of 85%. The pH was controlled in the beginning at pH 6.5 when the carbon was new and still washing off from contaminants which may cause scaling. Antiscalant (Genesys LF) was dosed, if no SAC resins were part of the train. SAC removes hardness and iron, negating the use of antiscalants.

The feed water is concentrated by recycling the water through the membrane into the feed buffer tank, hence the conductivity of the feed tank is much higher than the conductivity of the actual feed (see simplified P&ID in Figure 6). The RO in the IMPROVED containers works with recirculation to its feed tank, and the RO feed tank concentration (RO-F) has about 3-4x higher TOC than the feed water itself, therefore the concentration is much higher in the RO-feed. In this way the RO installation of the IMPROVED containers simulates the last module of a full-scale installation that is exposed to the highest concentrations and is most prone to fouling and scaling. This means that in fact the pilot scale results should translate better in a full-scale installation.

The conductivity of feed and concentrate are shown in Figure 22 and the permeate in Figure 23. The conductivities change over time, as several treatment trains were tested. The conductivities are higher when no SAC resins are used in the train.

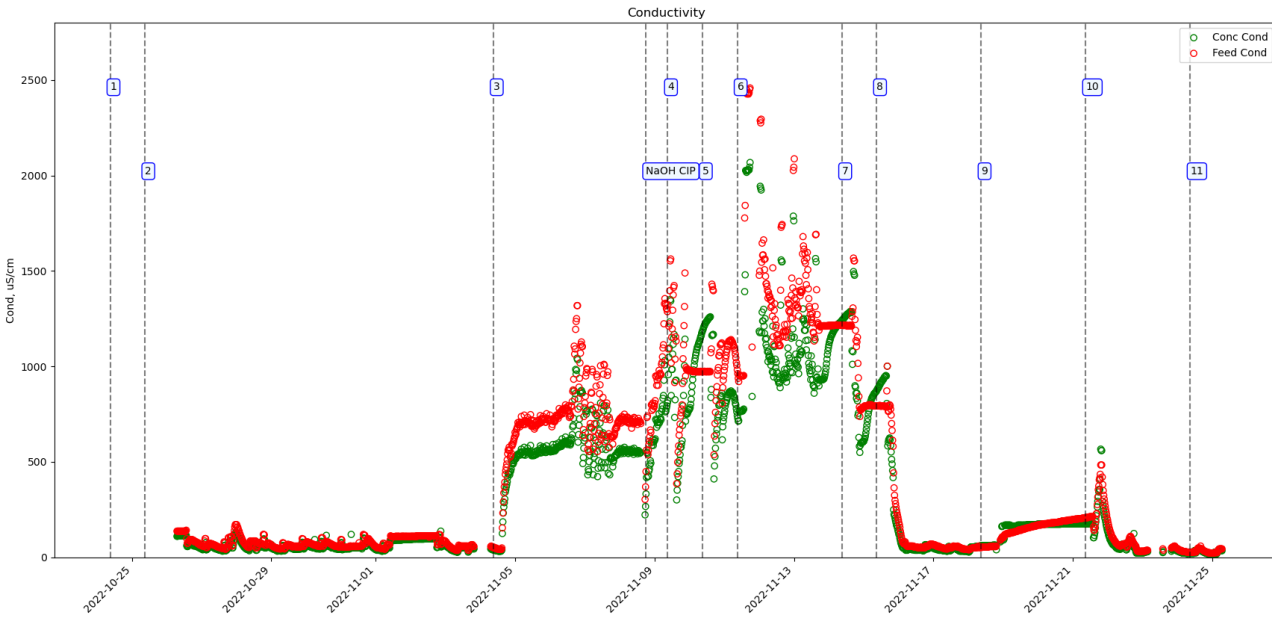

Figure 22 Conductivity of feed and concentrate. 1- SCAV-SAC-SBA-RO, 2 - SCAV-SAC-SBA-GAC-RO, 3 - MABR-Lamella-UF-RO, 4 - MPPE2-SBA-RO, 5 - MPPE1-SBA-RO, 6 - SCAV-SBA-MABR-UF-RO, 7 - WBA-SBA-MABR-UF-RO 8 - SCAV-SAC-WBA-SBA-MABR-GAC-RO, 9 - SAC-WBA-SBA-MABR-GAC-RO, 10 - Lamella-SAC-WBA-SBA-MABR-GAC-RO, 11 - Lamella-SAC-WBA-SBA-GAC-RO

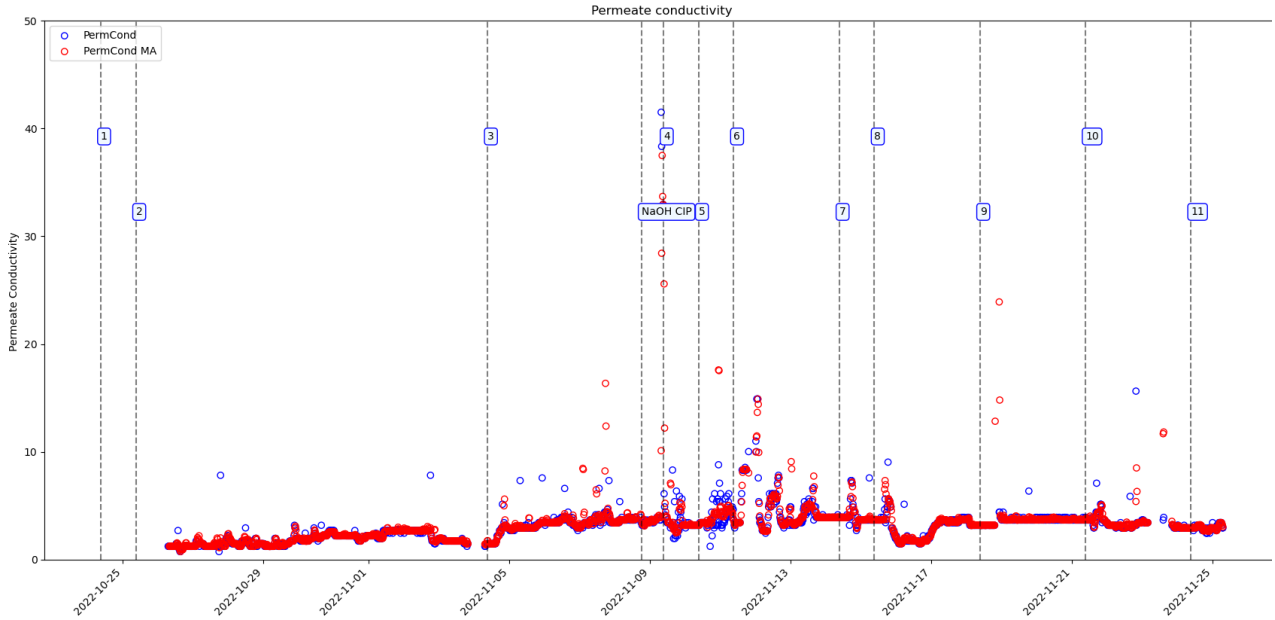

Figure 23 Conductivity of the permeate. 1- SCAV-SAC-SBA-RO, 2 - SCAV-SAC-SBA-GAC-RO, 3 - MABR-Lamella-UF-RO, 4 - MPPE2-SBA-RO, 5 - MPPE1-SBA-RO, 6 - SCAV-SBA-MABR-UF-RO, 7 - WBA-SBA-MABR-UF-RO 8 - SCAV-SAC-WBA-SBA-MABR-GAC-RO, 9 - SAC-WBA-SBA-MABR-GAC-RO, 10 - Lamella-SAC-WBA-SBA-MABR-GAC-RO, 11 - Lamella-SAC-WBA-SBA-GAC-RO

The TOC removal of the RO is very dependent on the treatment steps before RO, but never reached lower than 4.5 ppm TOC (Figure 24). The high amount of TOC in the permeate might be explained by components that have bad rejection in RO (e.g. methanol, ethanol, acetonitrile, formaldehyde, etc.), but this must be further studied.

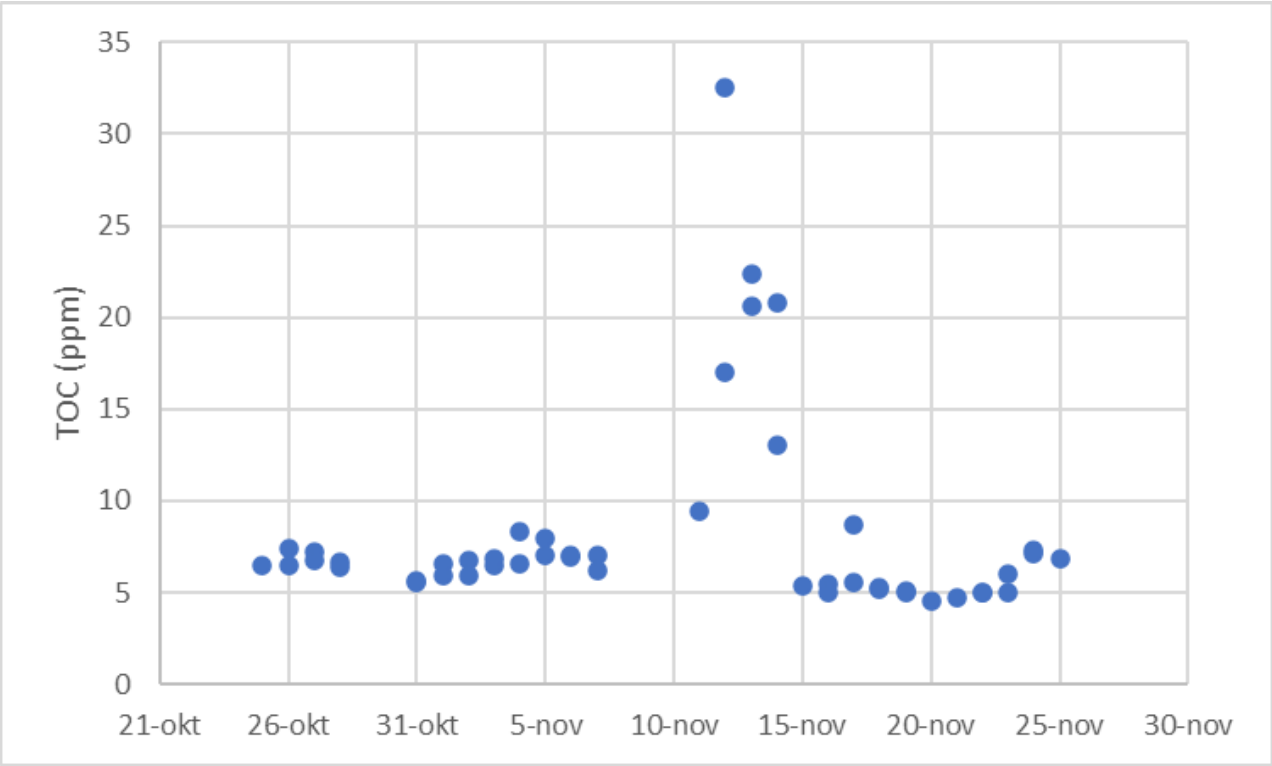

Figure 24 TOC in the RO permeate

The experiments for the trials started with a new membrane. The normalized data for MTC and feed channel pressure drop is shown in Figure 25 and Figure 26. For the first treatment train configuration the data logging was not turned on, hence the online data is missing. One cleaning in place (CIP) was done during the trials (November 8th), by a 1 hour soak using NaOH at pH 12.

The normalized feed channel pressure drop (NPD) which is an indication of feed spacer fouling remained rather stable over time, although an increase is visible after the SCAV-SAC-WBA-SBA-MABR-GAC-RO train indication spacer fouling which is probably caused by biology coming from the GAC. Interestingly the carbon was also placed before the RO in SCAV-SAC-SBA-GAC-RO, but at this stage the biology was probably not very developed in the carbon.

The mass transfer coefficient of the membrane decreased sharply during the trials with MABR-Lamella-UF-RO. Possibly this is due to biopolymers coming from the MABR separator that are passing the relatively large 20nm pores of the Inge UF. A basic CIP was performed, which mostly recovered the membrane, suggesting organic fouling was the cause.

From November 3, the RO was flushed with air bubbles once per day for 5 minutes and to increase the recovery the flush water was recirculated to the feed buffer tank. This caused the cartridge filters after the filtrate tank to block with the dirt coming from the membranes every 3 days. This is an indication of fouling on the membranes, but also that the air flushing is a viable option to control the fouling to some extent.

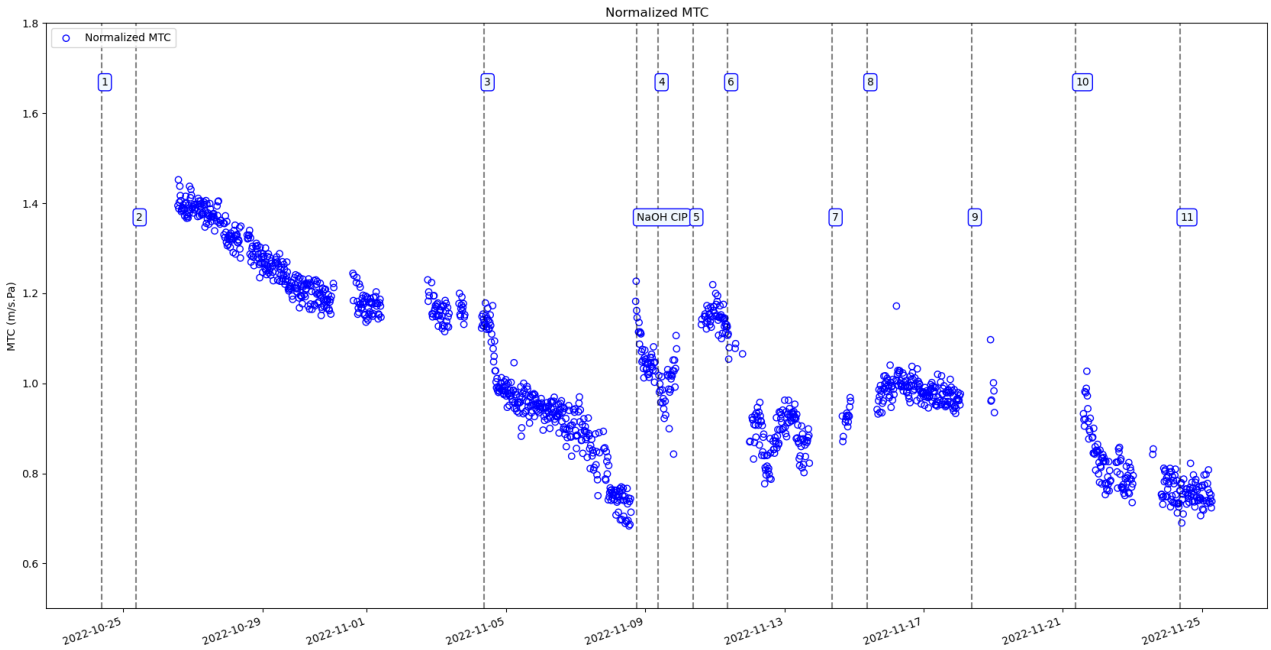

Figure 25 Normalized MTC. 1- SCAV-SAC-SBA-RO, 2 - SCAV-SAC-SBA-GAC-RO, 3 - MABR-Lamella-UF-RO, 4 - MPPE2-SBA-RO, 5 - MPPE1-SBA-RO, 6 - SCAV-SBA-MABR-UF-RO, 7 - WBA-SBA-MABR-UF-RO 8 - SCAV-SAC-WBA-SBA-MABR-GAC-RO, 9 - SAC-WBA-SBA-MABR-GAC-RO, 10 - Lamella-SAC-WBA-SBA-MABR-GAC-RO, 11 - Lamella-SAC-WBA-SBA-GAC-RO

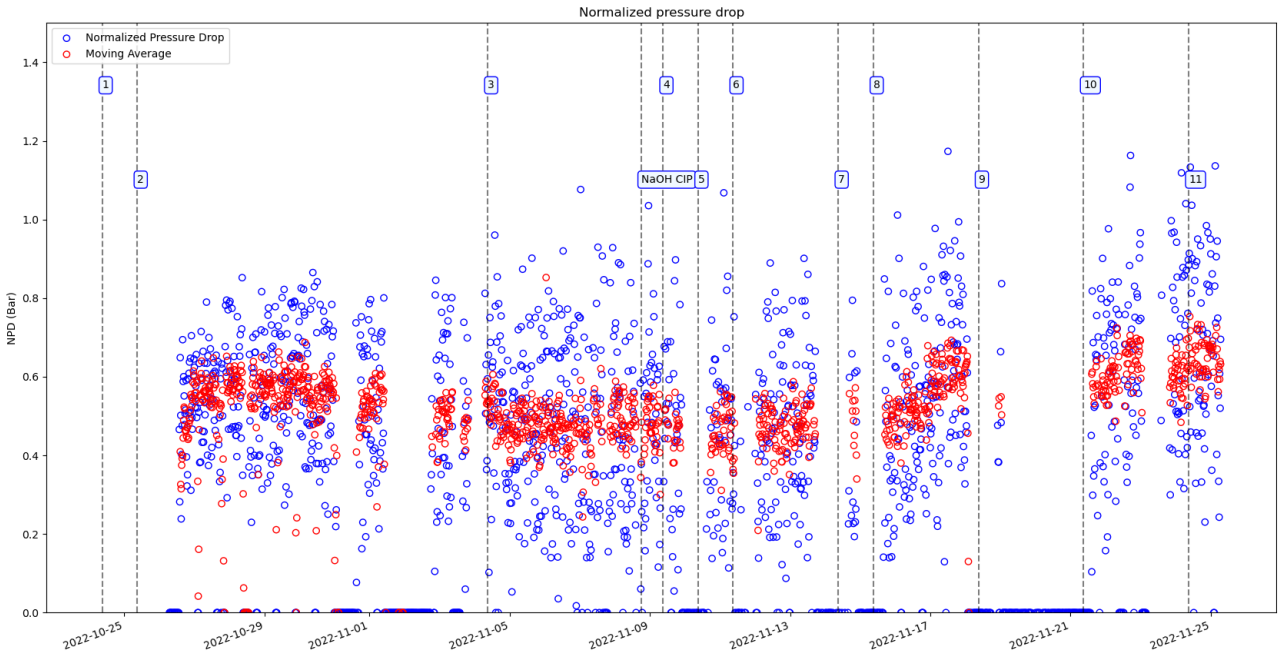

Figure 26 Normalized pressure drop. 1- SCAV-SAC-SBA-RO, 2 - SCAV-SAC-SBA-GAC-RO, 3 - MABR-Lamella-UF-RO, 4 - MPPE2-SBA-RO, 5 - MPPE1-SBA-RO, 6 - SCAV-SBA-MABR-UF-RO, 7 - WBA-SBA-MABR-UF-RO 8 - SCAV-SAC-WBA-SBA-MABR-GAC-RO, 9 - SAC-WBA-SBA-MABR-GAC-RO, 10 - Lamella-SAC-WBA-SBA-MABR-GAC-RO, 11 - Lamella-SAC-WBA-SBA-GAC-RO

Performance of different treatment trains

An overview of the main performance indicators for all tested treatment trains is given in Table 4 and Table 5. It is clear that none of the tested trains could remove the TOC from the dilution steam blowdown to levels used for boiler feed water (<0.2 ppm). The treatment train Lamella-SAC-WBA-SBA-MABR-GAC-RO produced the best quality in terms of TOC (4-5 ppm) and phenol (0.06 ppm).

RO and IEX on its own are insufficient to treat this stream, and a biological step is needed in order to achieve low TOC. The MABR was not working optimally due to the short testing period, the small bioreactor volume (30 min HRT) and the unstable pH control. The GAC removed, mainly by adsorption, on average 10-15 ppm

TOC. For the IEX resins, the scavenger resins got blocked several times due to scaling. When the SCAV was removed due to its scaling issues, the TOC level remained the same, indicating that it is not really needed. The SBA removed most of the phenol and TOC. The RO performed rather stable with air flushes, and a basic CIP remove the organic fouling on the membrane.

Table 4 Key performance indicators of the different technological trains

Train	***TOC (ppm)***	***Conductivity (µs/cm)***	***Phenol (ppm)***
SCAV-SAC-SBA-RO	No data	No data	No data
SCAV-SAC-SBA-GAC-RO	6-8	1-3	<0.05
MABR-Lamella	80-90	120-130	31
MABR-Lamella-UF-RO	18-20	2-4	14
MPPE2-SBA-RO	20	2-6	3.9
MPPE1-SBA-RO	10	2-5	3.3
SCAV-SBA-MABR-UF-RO	10-11	2-30	1.6
WBA-SBA-MABR-UF-RO	14	3-7	2.9
SCAV-SAC-WBA-SBA-MABR-GAC-RO	5-6	1-5	0.1
SAC-WBA-SBA-MABR-GAC-RO	5-7	3	No data
Lamella-SAC-WBA-SBA-MABR-GAC-RO	4-6	1-4	0.06
Lamella-SAC-WBA-SBA-GAC-RO	6-7	1-3	0.09

Table 5 Key operational parameters for the technologies used in the trials

Technology	***Recovery***	***Removes***	***Chemicals***	***Pressure (bar)***
MABR	100%	TOC	HCl	
Lamella	99%	Suspended solids	None	
GAC	100%	Turbidity, organics	None	0.5
UF	90-95%	Turbidity	HCl, NaOH, NaOCl, SBS	0.2-1.3
IEX	96%	Organics, ions	HCl, NaOH	
RO	85%	Organics, ions, turbidity	HCl, NaOH, antiscalant	5-14

SCAV-SAC-SBA-RO

This treatment train was used for one day, after which is what concluded that it was not sufficient to reach the required water quality.

SCAV-SAC-SBA-GAC-RO

After adding the GAC, this treatment train was tested for 10 days. The desired water quality in terms of conductivity was reached, and the permeate contained 6-8 ppm TOC and no phenol. Scaling of the SCAV column was observed making this train unfeasible for implementation unless separate regenerant is used for the SCAV.

MABR-Lamella

This treatment train was used to develop biomass on the MABR at the start of the trials. Almost no TOC was removed with this treatment train due to the short hydraulic residence time of 30 minutes.

MABR-Lamella-UF-RO
Biomass had been developed on the membranes of the MABR, but was only capable of removing 2-3 ppm TOC. The UF was operated with a too high flux (50 lmh), causing blocking of the membrane in 1-2 days. The normalization of the RO (MTC) also indicated fouling during these trials. 18-20 ppm TOC, of which 13.5 ppm phenol, was measured in the effluent water.

MPPE2-SBA-RO
The MPPE042 resins, in combination with SBA and RO, was giving poor results in terms of TOC (20 ppm).

MPPE1-SBA-RO
The MPPE041 resins were more promising in terms of performance, giving 10 ppm TOC in the RO permeate. Since no further information was disclosed from Veolia for the type/specification of resin we cannot make further conclusions.

SCAV-SBA-MABR-UF-RO
The MABR was placed after the IEX, to investigate whether the MABR would remove the TOC that could not be removed with the IEX. It was hard to control the pH in the MABR as when the IEX was regenerated, some of the regeneration base ended up in the MABR causing the pH to spike. This was attempted to be fixed by dosing acid in the MABR, but the control was too slow and the acid concentration was too high causing undershoots in the pH. Due to time constraints, this could not be fixed in time. The RO permeate contained 10-11 ppm TOC, of which 1.6 ppm phenol.

WBA-SBA-MABR-UF-RO
As the SBA exhausted fast with just SCAV resins in front, it was decided to put WBA resins (3L: total volume of column ~11L) in front to expand the runtime of IEX. This improved the quality, in terms of TOC to as low as 14 ppm, of which 2.9 ppm phenol.

SCAV-SAC-WBA-SBA-MABR-GAC-RO
The MABR was added to the second treatment train (best quality in terms of TOC so far). This resulted in a permeate quality of 5-6 ppm TOC and 0.1 ppm phenol. The SCAV resins blocked frequently, causing high pressures. This train is also considered not economically feasible for full-scale implementation.

SAC-WBA-SBA-MABR-GAC-RO
The SCAV resins were removed because of regular blocking due to scaling. The feed water during this trial contained big flocs, causing blockage of the SAC resins. Dow could not explain why the feedwater was different for this period and what was causing the formation of flocks. The product water contained 5-7 ppm TOC, and no data for phenol is available.

Lamella-SAC-WBA-SBA-MABR-GAC-RO
In order to prevent the blockages on the resins, the lamella was added in front. This treatment train reached the lowest levels of TOC (4.5-5.5 ppm). On top of that it was showing stable results during the testing period, without extensive blocking or fouling. There was no significant drawback for not having the scavenger resins upfront, compared to the second treatment train. The removal of the SCAV from the IEX train does not seem to affect the TOC removal in any meaningful way.

Lamella-SAC-WBA-SBA-GAC-RO
This train was tested to conclude what the impact of the MABR in the treatment train was. MABR was removing on average 2-3 ppm TOC. This treatment train, without MABR, produced RO permeate with 6-7 ppm TOC, which is an increase of about 2 ppm TOC in the produced water.

5.1.9 Chemical usage for technologies

Membrane aerated bioreactor
Hydrochloric acid (HCl) was dosed for a few days (during SCAV-SBA-MABR-UF-RO) as pH control, because the water coming from SBA was alkaline/caustic which would kill the biology growing on the membranes.

Granular activated carbon
No chemicals were used in the operation of the GAC.

Ultrafiltration
In the operation of the UF, HCl (pH 2), sodium hydroxide (NaOH at pH 12) and sodium bisulfite (SBS for free chlorine quenching) were used for two cleanings in place. Sodium hypochlorite (100 ppm) was dosed to the filtrate tank to have chemically enhanced backwash (CEB).

Ion exchange
Regeneration of the resins was needed every 10-12 hours. The SCAV and SAC resins were normally regenerated with HCl, and a few regenerations were done with a salt solution (NaCl). The WBA and SBA resins were regenerated with NaOH.

Reverse osmosis
pH control (HCl) was needed during the start (the new GAC leaking ions, possibly including hardness) and the trials without SAC IEX resins in the treatment train. In cases where no SAC resins were part of the treatment train, Genesys LF antiscalant was dosed at 5 ppm. The RO was also once cleaned in place by soaking it with recirculation in sodium hydroxide for an hour at pH 12.

5.2 Mini boiler experiments

The effluent from the two best-performing treatment trains (*Lamella-SAC-WBA-SBA-GAC-* and *Lamella-SAC-WBA-SBA-MABR-GAC-RO*) of the IMPROVED pilot was further tested at CAPTURE (UGent). In these tests, the water is placed inside of a mini-boiler where temperatures and pressures are kept similar to a full-scale boiler. In these conditions the remaining TOC tends to break down and form organic acids that would cause corrosion in the boiler. While the treated water indeed has much higher TOC, the aim was to check if this TOC would form organic acids, or would be passed through the boiler without conversion. In this report, only the Lamella-*SAC-WBA-SBA-MABR-GAC-RO* configuration is shown, the rest can be seen in the MSc thesis of Reinout Van Dooren. The boiler was operated at various temperatures and flow rates to assess the influence of temperature, residence time, and saturated and superheated steam conditions on the decomposition of TOC to organic acids. The condensate of the boiler was collected and ion chromatography was used to measure the organic acid anions content (formate, acetate, propionate) in the condensate. First, the current boiler feed water was tested to evaluate the formation of organic acids - Figure 27:

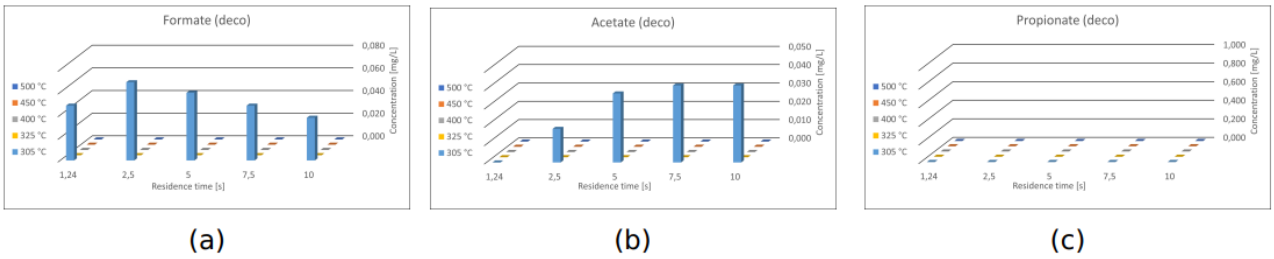

Figure 27 Formation of organic acids with the current boiler feed water of Dow (DECO) was only produced in measurable quantities at 305 °C

To make a comparison, the best performing train Lamella-*SAC-WBA-SBA-MABR-GAC-RO was tested at the same conditions* – Figure 28*:*

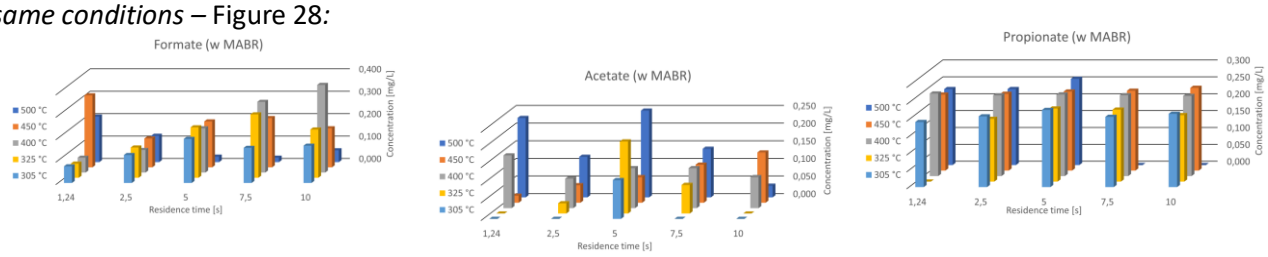

Figure 28 Formation of organic acids with the Lamella-SAC-WBA-SBA-MABR-GAC-RO at different conditions

The separation of formate and acetate in ion chromatography was poor and as a result, data have to be interpreted with caution for these species. No obvious trend of organic acid anion concentration as a function of boiler temperature and residence time could be observed. The same goes for the influence of saturated and superheated steam conditions.

No clear relationship between the magnitude of organic acid formation and the aforementioned parameters was observed. With certainty, it can be concluded that poor peak separation during ion chromatography contributed to this random nature. Despite that no such clear relationships could be observed, the formation of organic acids themselves was observed, confirming the necessity of limiting TOC in boiler feed water. The boiler results seem to indicate that fewer organic acids were formed in the condensate from boiler feed water that was treated by the train that included the biological step (MABR), but there is no hard proof of this observation due to poor peak separation during ion chromatography. It would seem logical that fewer organic acids are formed in the condensate of dilution steam blowdown treated by the MABR train since it contained less TOC to begin with. However, care should be taken when making such claims, as literature shows that there is no linear relationship between the TOC concentration in the boiler feed water and the concentration of organic acids formed in the condensate [2] [3].

These experiments are part of the master thesis of Reinout van Dooren, in which a more detailed description of the results can be found [4].

6 Conclusions

Within the 5 weeks of testing many configurations were tested on the dilution steam blowdown in order to try to find a configuration that can produce water with TOC lower than 0.2 ppm TOC, which would make it suitable for reuse as boiler feed water. Previous knowledge from former projects as well as lab-scale tests showed that removing the TOC is going to be the main challenge from these tests. This is why besides the regular ion exchange and RO, novel technologies such as membrane aerated bioreactor and microporous polymer extraction were also tested. The small molecules that are produced at the cracker can pass the RO and if they are also lacking charge they can also pass the IEX. In that respect none of the tested configuration produced water with TOC lower than 5 ppm and the stream is therefore not reusable as boiler feed water (<0.2 ppm TOC).

The MPPE proved to be a promising technology since it achieved relatively low TOC with small treatment train, although it was not able to achieve the required water quality. Overall this technology is also more applicable in higher-TOC loading where the feed TOC is in the gram-per-l range or higher.

The MABR had a lot of operational challenges due to troublesome pH control and very short hydraulic retention time of 30 minutes. Moreover, the 5 weeks of testing are quite short for a biological step to be operated stable with robust biological community. It should be noted that a biological step is critical to the reuse of this stream as it is the only technology that can remove small uncharged organics. The question is then can a small reactor with short HRT be integrated with physicochemical treatment steps like it was tested in these tests, or a full-scale wastewater treatment plant is needed. Within these tests we were not able to achieve below 5 ppm TOC, hence it seems like a short HRT technology is unlikely to achieve the required quality of <0.2ppm.

The effluent from the two best-performing treatment trains was used for mini-boiler experiments to determine the extent to which organic acids are formed as a function of boiler temperature, residence time, and boiler operation under saturated and superheated steam conditions. The formation of organic acids is an indication of corrosion potential, hence we wanted to test the hypothesis that the TOC while being high may not cause problem in the boiler. The boiler experiments showed significantly more organic acids being formed with the water produced in the AquaSPICE tests compared to the current boiler feed water. Therefore it was confirmed that the water produced in the tests is not possible for reuse.

In general, it can be concluded that, despite thorough treatment of the dilution steam blowdown, the tested treatment trains were not sufficient in terms of removing TOC to reuse it as boiler feed water. The MABR seemed to have a positive effect on the TOC removal and the formation of the two most important organic anions (formate and acetate) but the MABR bioreactor was not working optimally.

7 Acknowledgments

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List of abbreviations

BGAC	Biological granular activated carbon
CapEx	Capital Expenditure
CIP	Cleaning in place
COD	Chemical oxygen demand
DO	Dissolved oxygen
EDR	Electrodialysis reversal
GAC	Granular activated carbon
IC	Inorganic carbon, ion chromatography
IEX	Ion exchange
IMPROVED	Integrale Mobiele PROceswater Voorziening voor een Economische Delta
MABR	Membrane aerated bioreactor
MB	Mixed bed resin
MPPE	Macro porous polymer extraction
MTC	Mass transfer coefficient
NDP	Net driving pressure
NPD	Normalized pressure drop
NSP	Normalized salt passage
OpEx	Operational Expenditure
RO	Reverse osmosis
SAC	Strong Acid Cation
SBA	Strong Basic Anion
SCAV	Scavenger
TC	Total Carbon
TOC	Total organic carbon
WBA	Weak Basic Anion

Appendices

A.1 Equations used in the RO normalization

$$SP = EC_p \times T_{cf\_EC} \times Q_{cf}$$

$$EC_p = 100 \times \frac{EC_{permeate}}{(EC_{feed} \times \left(log \frac{1}{1 - Recovery}\right))/Recovery}$$

$$T_{cf} = exp^{(U_{par} \times \left(\left(\frac{1}{T_{feed}+273.15}\right) - \left(\frac{1}{T_{ref}+273.15}\right)\right))}$$

Where U_{par} is the Dow membrane U-value, equal to 3200, EC_p is the recovery corrected permeate conductivity, T_{ref} is the reference temperature equal to 25 °C and T_{cf} is the conductivity corrected temperature.

$$NPD = dP \times Q_{cf} \times T_{cf}$$

$$dP = P_{feed} - P_{concentrate}$$

$$Q_{cf} = (\frac{Q_{vc}}{\frac{Q_{permeate} + Q_{concentrate}}{2}})^m$$

$$Q_{vc} = \frac{Q_{feedn} + Q_{concentraten}}{2}$$

$$T_{cf} = (\frac{\eta_{ref}}{\eta_{feed}})^n$$

Where NPD is normalized pressure drop [kPa], Q_{feedn} normalized design feed flow of the RO system [$m^3.h^{-1}$], $Q_{concentraten}$ normalized design concentrate flow [$m^3.h^{-1}$], T_{cf} is the viscosity corrected temperature, $Q_{vc}$is the viscosity corrected flow, η_{ref} and η_{feed} are reference and feed viscosity respectively, m and n are Dow membrane values, equal to 1.6 and 0.4, respectively.

$$MTC = \frac{Q_{permeate} \times T_{cf} \times 10^{-5}}{36 \times Q_{pemeate}}$$

$$NDP = ((\frac{P_{feed} + P_{concentrate}}{2} - P_{permeate}) \times 100) - (\frac{OP_{feed} + OP_{concentrate}}{2} - OP_{permeate})$$

$$T_{cf\_OP} = \frac{T_{feed} + 273.15}{T_{ref} + 273.15}$$

$$OP_{feed} = EC_{feed} \times EC_{OP\_feed} \times T_{cf\_OP}$$

$$OP_{concentrate} = EC_{concentrate} \times EC_{OP\_concentrate} \times T_{cf\_OP}$$

$$OP_{permeate} = EC_{permeate} \times EC_{permeate} \times T_{cf\_OP}$$

Where MTC is the mass transfer coefficient [$m.S^{-1}.Pa^{-1}$], NDP net driving pressure [kPa], OP osmotic pressure calculated for feed, permeate and concentrate [kPa] and T_{cf_OP} is the osmotic pressure corrected temperature.