

**Ministry of Environment of Denmark** Environmental Protection Agency

# Udvikling af 3. generations vandbehandlingskoncept til decentral rensning og genbrug af regnvand

MUDP report

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Miljøstyrelsen offentliggør rapporter og indlæg vedrørende forsknings-og udviklingsprojekter inden for miljø sektoren,som er finansieret af Miljøstyrelsen.Det skal bemærkes, at en sådan offentliggørelse ikke nødvendigvis betyder, at det pågældende indlæg giver udtryk for Miljøstyrelsens synspunkter.Offentliggørelsen betyder imidlertid, at Miljøstyrelsen finder, at indholdet udgør et væsentligt indlæg i debatten omkring den danske miljøpolitik. Må citeres med kildeangivelse

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# 1. Background

Worldwide, agricultural and industrial activities account for around of 90% of the total water consumption, compared to the only 10% for the domestic use [1]. However, the majority of the water used for agricultural and industrial purposes do not require high quality water (e.g. irrigation), allowing then the use of non-potable water.

Within this context, the use of collected rainwater is emerging as a sustainable and feasible approach, which allows both saving on water costs and reducing the environmental impact caused by the discharge and the consumption of natural water resources [2]. However, an upgrading of the collected rainwater is required to satisfy specific demands on the chemical composition and physical properties for specific industrial applications. These specifications depend on the intended use, and can vary greatly form process to process, just like the chemical com- position of collected water dramatically vary depending on the collecting location.

Main aim of the current MUDP-2014 project ("Udvikling af 3. generations vandbehandlings koncept til decentral rensning og genbrug af regnvand"), was to develop a flexible treatment technology efficiently coping with the mentioned variability of the collected rain both in terms of quantity and quality. The project brought together the competencies in the field of water purification from Provital and DHI. Specifically, the two players collaborated on developing an efficient membrane filtration to enable the optimization of the membrane filtration process and of the following UV polishing process of particularly degradable substances in rainwater.

The initial phase of the project consisted of a literature search with the purpose of mapping the components found in collected rainwater to identify the optimal pore size for efficiency of purification. The possible uses of treated rainwater in industrial processes was also addressed to development of design/sales tool on area and precipitation.

In the second phase of the project, the capability of selected SiC ceramic membranes to treat two different rainwater samples was tested. The ultimate aim of the test was to screen different membrane types for their effectiveness in terms of retention of selected components and to investigate the hydraulic capacity under different operational modes.

# 2. Purpose

The purpose of this project is to develop an innovative cost-efficient water treatment-concept for recovery of rainwater. Where the focus is to industrially reuse water and hereby reduce the consumption of water produced from conventional methods. This will contribute to a reduction of the industries water footprint. Furthermore, the reuse of rainwater from industrial production areas can minimize the load from local recipients, with special pollutant waste and hereby contribute to a better environmental status. The developed technology can also be used in relation with urban areas.

# 3. Literature search

The literature search for the typical composition of the collected water and the quality requirements on water for few relevant industrial applications is herein summarized.

### 3.1 Chemical and biochemical composition of collected rainwater

The composition of collected rainwater is mostly dependents on the location (local traffic and pattern) and on the surface properties and conditions. The most typical compounds that characterize the rainwater are listed in Table 1.

Chemical component groups such as heavy metals, PAHs, BTEX, phthalates and nonylphenols are present in concentrations ranging from non-critical to critical. The discharge of notreated rainwater is considered as the main source of the river pollution.

Parameter	Unit	Total	Particulate	Colloidal	Dissolved	Refs.
рН	-	4.7-8.2				4, 5, 7
Conductivity	mS/m	2.5-300				4, 5, 7
Alkalinity	mmol/L	0.82-5.98				5
Tubidity	FTU	87				5
TSS	mg/L	0.006-6143				4, 8
COD	mg/L	0.5-3000	-	<6	-	3, 6
BOD5	mg/L	0.15-136	-	-	-	4,6
Total-N	mg/L	0.008-53	-	-	-	5, 6
Total-P	mg/L	0.005-5.6	-	-	5*10 <sup>-4</sup> -2.01	2,4
Iron	mg/L	0.1-29	-	<0.15	0.01-0.24	3, 5, 9
Calcium	mg/L	1-1900	-	-	-	4, 5
Magnesium	mg/L	1-21	-	-	-	4, 5
Silicon	mg/L	5-13	-	<8	4.6-13	3, 5
Lead	µg/L	0.025-1200	15-120	-	0.025-100	4, 7, 9, 12
Copper	µg/L	0.5-3416	14-103	-	0.2-3540	4, 7, 9, 12
Zinc	µg/L	1-4880	-	<15	0.5-493	4, 7, 9, 12
Aluminium	µg/L	200-750	-	<700	5.7-571	3, 6
Cadmium	µg/L	0.015-200	0.23-8.9	-	0.04-150	4, 6, 9
Chrome	µg/L	0.2-250	11.2-138	<2	0.07-150	3, 4, 6, 9
Nickel	µg/L	0.2-230	-	-	0.2-140	4, 6, 9
Mercury	ng/L	2.6-37.2	0.6-30.9	-	1.4-9.67	10, 11
Oil & grease, total	mg/L	0.025-2760	-	-	-	5, 6
Bisphenol A	µg/L	0.21-0.36	-	-	-	5
Benzene	µg/L	0.1	-	-	-	6
Toluene	µg/L	0.1	-	-	-	6
Ethylbenzene	µg/L	0.025	-	-	-	6
Xylene	µg/L	0.025	-	-	-	6
Naphthalene	ng/L	46-130	-	-	-	13
Anthracene	ng/L	5-15	350	-	150	6, 8

TABLE 1. Compounds and parameters found in collected rainwater (From literature).

Benz(a)anthrascene	ng/L	5	250	-	20	6, 8
Chrysene	ng/L	5	450	-	30	6, 8
Acenaphthene	ng/L	5-5	-	-	-	5, 6, 8
Acenaphtthylene	ng/L	1-69	-	-	-	13
Flourene	ng/L	5-5	-	-	-	5, 6 ,8
Phenanthrene	ng/L	5-200	300	-	50	5, 6 ,8
Flouranthene	ng/L	5-1200	1050	-	95	5, 6 ,8
Pyrene	ng/L	5-900	650	-	55	5, 6 ,8
Benzo(b,j,k)flouranthene	ng/L	5-840	700	-	28	5, 6 ,8
Benzo(a)pyrene	ng/L	5-320	380	-	25	5, 6 ,8
Indeno(1,2,3-cd)pyrene	ng/L	5-300	450	-	20	5, 6 ,8
Benzo(g,h,j)perylene	ng/L	5-370	420	-	20	5, 6 ,8
Di-n-butyl phthalate	µg/L	<0.5	-	-	-	5
Benzyl butyl phthalate	µg/L	<0.1	-	-	-	5
Diethylhexyl phthalate	µg/L	3.4	-	-	-	5
Di-2(ethylhexyl)adipate	µg/L	<0.1	-	-	-	5
Di-n-octyl phthalate	µg/L	<0.1	-	-	-	5
Diethyl phthalate	µg/L	0.2	-	-	-	5
Diisonoyl phthalate	µg/L	<0.3	-	-	-	5
Nonylphenol (NPE)	µg/L	0.16	-	-	-	5
NPE monoethoxylate	µg/L	0.11	-	-	-	5
NPE diethoxylate	µg/L	0.36	-	-	-	5
Sum of the 3 NPE's	µg/L	0.63	-	-	-	5

In addition to the chemical compounds, collected rainwater also contains bacteria of various kinds, such as faecal and soil bacteria. As an example, in Table 2 the microbiological analysis of rainwater collected in two different collecting sites in Copenhagen are indicated [5]

**TABLE 2.** The bacteria analyzed are total coliform bacteria, E. coli and enterococci bacteria. Measured as CFU/100 mL. Adapted from Reference 5.

	Sundkrogsgade	Oceanvej
Coliform	24196	6488
E. coli	[Tekst]	291
Enterococci	[Tekst]	579

Besides the natural background contamination, a source for fecal bacteria are from e.g. bird droppings on rooftops [5]. High bacterial counts in the rainwater can poses both health concerns, but also handling problems associated with the growth of bacteria (e.g. biofouling).

#### 3.2 Reuse of rainwater for industrial purposes

The requirements on the quality of the feed water is of a critical importance in most industrial water consuming processes. If these requirements are not satisfied, issues such as scaling, clogging, biofouling and microbial contamination can occur. A list of the most typical industrial processes consuming water includes:

• INDUSTRIAL PROCESSES WATER. In this category of industrial processes water is direct used in a process line. Examples of this type of water consumption are textile production, tanning, pulp and paper industry, chemical industry, mining, petrochemical and coal, cement

production, pharmaceutical industry, etc. The category is very broad as their respective requirements for water quality are [14, 15]

- COOLING WATER. Water is used in cooling towers to remove the heat from the system. This process is responsible for a large part of the water consumption in many industries and is thus a major contributor to the overall consumption. For instance, an excessive concentration of corrosive compounds (heavy metal, salts) can originate serious issues for a correct operation [16, 17]
- WATER FOR STEAM GENERATION. Steam is used in many industrial applications primarily for heating. In boilers used for steam generation the water is evaporated thereby accumulating the components in the feed water in the boiler. Excessive concentration of anions (e.g. Ca2+ and Mg2+ and CO32-) along with N-based compounds is detrimental for the correct operation [18]
- WASHING AND RISING. Several industrial processes require some sort of washing or rinsing as part of the production. This involves both washing/rinsing of products and of production equipment (washing tanks, piping systems and vehicles and rinsing of textiles and machined metal). Despite the wide variations on the demands on the water quality, a limited TSS is generally recommended along with a low concentration of pathogens and organics
- IRRIGATION. The water consumed for irrigation constitutes a major part of the total withdrawals. The presence of any heavy metals at high con- centration, as well as high concentration of nutrients, and pathogens [14,15] are dangerous for the human health.

### 4. Methods

In this section the methods and experimental conditions used for the characterization of collected water samples are summarized.

#### 4.1 Choosing catchment areas for rainwater collection

With the technical support of Aarhus Vand, two sites for collection of rainwater in an industrial area close to Aarslev were identified. The two sites are

- A carrier station. The catchment area consists mostly of asphalt surface (road and parking) and roofs. There is intensive traffic with heavy vehicles.
- A gas station. The catchment area consists primarily of roads and asphalt surface around the gas station. Only trucks use the gas station.

#### 4.2 Filtration of rainwater samples

The collected samples were stored at 5°C and analyzed/filtered within 24 hours of collection.

The turbidity as function of time was measured and the absence of first-flush effects was verified. The sample was then transferred to a 200 L stirred glass container where was stored for the further analyses.

#### 4.3 Filtration setup

For the filtration tests, three types of LiqTech SiC membranes were selected: 1µm, 2µm and 3µm nominal cut-off. The three selected membranes were tubular in shape with the dimensions of 25/305mm, 31 through-going channels, and a membrane area of 0.09 m2. The feed enters the channels and passes through in crossflow setup.



FIGURE 1. Scheme of laboratory membrane setup

In the membrane setup, feed was taken from the stirred sample container using an adjustable pump with no feedback from pressure or flow. Thus, constant pressure or constant flow operation conditions could not be set. The pressure (and flow) were instead adjusted manually.

#### 4.4 Membrane retention test – dead end

Membrane retention was investigated for the three membrane under dead-end operation. During the tests, TMP was approximately 0.2 bar. 2-4 L of permeate was produced for each membrane and used for further analyses. After each test, the membrane was back flushed extensively with demineralized water.

#### 4.5 Membrane operation test – crossflow

Because of the high membrane flux and limited volume of water available, under lab conditions only one selected membrane was tested. For the membrane operation test, 2  $\mu$ m membrane was selected due to its bet's retention behavior with respect to the other two membranes. Pressure and permeate flow were monitored as a function of time. Both retentate and permeate were continuously returned to the sample container in order to limit the variation in the composition and concentration of the feed. Thus, only minor changes to the composition and concentration of the feed were induced due to the fouling layer build up.

#### 4.6 Turbidity, conductivity and pH

Turbidity, conductivity and pH were measured using a Hach 2100Q Portable Turbidimeter, a WTW Cond 330i conductivity meter, and a Mettler Toledo T70 pH meter, respectively.

#### 4.7 Organic/inorganic total solids and suspended solids

#### 4.7.1 Total solids

The total solids of the collected water were estimated via the gravimetric method. The crucible for the experiment was pre-heated in a 550°C overnight, its weight was noted, and then placed in an exicator. The sample was transferred in the crucible (from a stirred container), weighted, and placed in oven overnight at 105°C. The crucible containing the sample was weighed and transferred to an exicator. Eventually, the crucible-sample unit was treated at 550°C overnight, weighed, and placed in the exicator.

#### 4.7.2 Suspended solids

The gravimetric method was also used for the determination of the suspended solids. A GF-C filter (1.2  $\mu$ m) was treated in a 550°C oven overnight, weighed, and placed in exicator. A known amount of sample (from a stirred container) was filtered through the filter using a vacuum filter unit. The filter was then treated in an oven at 105°C oven overnight, weighed, and transferred to an exicator. Finally, the filter was placed in an oven at 550°C oven overnight, weighed, weighed, and transferred to an exicator

#### 4.8 Alkalinity, COD, PAH, zinc, lead, calcium and copper

Alkalinity, COD, PAH, zinc, lead, calcium and copper are measured using analytical kits, as indicated in Table 3-1.

COD, PAH and metal were analyzed both on unfiltered and 0.22  $\mu m$  filtered samples to measure total and dissolved concentrations, respectively.

Metal samples were diluted with concentrated HNO3 and treated in an autoclaved before analysis to ensure complete availability of the metal ions.

#### 4.9 Particle size distribution

Particle size distribution was measured in the interval of 0.8-400  $\mu$ m using a PSS Nicomp Accusizer 780 Optical Particle Sizer with a LE400-0.5 sensor. When necessary samples, were diluted using MiliQ water (0.2  $\mu$ m filtered).

#### 4.10 Bacterial content

The content of Coliform and E. Coli was quantified by MPN using the IDEXX Colilert-18 kits. In details, 100 mL of sample (in some cases diluted) were mixed with substrate. When dissolved, the mixture was placed in a tray that was then sealed and incubated at 35°C for 18-22 h. Fluorescent and non-fluorescent positives are used to determine the MPN.

TABLE 3. Kits used for analyzing

Parameter	Kits supplier	LCK362 (0.5-0.8 mM)
Alkalinity	Hach Lange	LCK414 (5-60 mg/L)

		1.14560.001 (4-40 mg/L)
COD	Hach Lange, Merck	RaPID Assay® PAH (2.66-66.5 µg/L)
PAH	Modern Water	1.00861.0001 (0.025-1 mg/L)
Zinc	Merck	1.14833.0001 (0.1-5 mg/L)
Lead	Merck	1.00858.0001 (10-250 mg/L)
Calcium	Merck	1.14553.0001 (0.05-8 mg/L)
Copper	Merck	LCK362 (0.5-0.8 mM)

#### 4.11 UV transmittance

LiqTech Solutions are designing an UV-reactor which should be used on the filtrated water. The primary goal is disinfection, but also the removal of remaining dissolved organic matter. The light source for the UV-reactor is a three-types of UV-LEDs that emits UV-light at 254nm, 285nm, and 365 nm. The UV transmittance at the three wavelengths were measured with a HP 8543 Photometer.

#### 4.12 Estimation of relevant parameters

In each experiment the TMP and permeate flow (Q) are measured as a function of time. From these data the flux (J), fouling resistance (R\_foul) and specific cake resistance ( $\alpha$ ) are calculated

as follows:

$$J = \frac{Q}{A}$$
$$J = \frac{TMP}{\mu R}$$
$$R = R_{membrane} + R_{foul}$$
$$R_{foul} = \omega \alpha$$
$$\omega(t) = \int Jcp \ dt$$

where

A is the membrane area (0.09 m2)  $\mu$  is the viscosity (10-3 Pa·s) *R* is the total resistance to flow (m-1) *R<sub>membrane</sub>* is the membrane resistance (set to the initial resistance) (m-1)  $\omega$  is the deposited fouling layer (kg/m2) *cp* is the particle concentration in the feed (set to the SS concentration) (mg/mL)

### 5. Results

#### 5.1 Characterization of collected rainwater samples

In Table 4 the results of the biochemical analysis of the two collected water samples are listed.

Parameter	Carrier station	Gas station
pН	7.28	7.22
Conductivity [ <b>†</b> S/cm]	1579	173.3
Turbidity [NTU]	18.2	50.3
Total solids (TS) [mg/g]	0.958	0.145
TS organic [%]	16	26
Suspended solids (SS) [mg/L]	16.5	592
SS organic [%]	84	28
COD total [mg/L]	81.6	32.5
COD dissolved [mg/L]	43.9	8.19
Alkalinity [meq/L]	2.14	1.15
PAH total [オg/L]	11.6	7.7
PAH dissolved [オg/L]	4.4	4.6
Coliform bacteria [#/100mL]	123800	6015
E. coli [#/100mL]	1	216
UVT (254 nm) [%]	44.9	79.2
UVT (285 nm) [%]	62.1	81.6
UVT (365 nm) [%]	88.3	84.9
Zinc total [mg/L]	0.075	0.149
Zinc dissolved [mg/L]	nd	nd
Copper total [mg/L]	0.18	0.28
Copper dissolved [mg/L]	0.20	0.17
Lead total [mg/L]	nd	nd
Lead dissolved [mg/L]	nd	nd
Calcium total	236	217
Calcium dissolved [mg/L]	283	199

TABLE 4. Characteristics of collected rainwater samples.

The following considerations can be made:

Higher content of salts in the sample from the carrier station (e.g. higher conductivity, TS and alkalinity). This could be ascribed to 1) the lower rain intensity (less dilution), or 2) salt leaching from soil.

• Higher content of organics in the sample from the carrier station (e.g. higher organic TS (in absolute terms), COD and PAH, and lower UVT values). This could be due to 1) the lower rain intensity (less dilution), or 2) desorption of organics from the soil.

• Higher particle content in the sample from the gas station (e.g. higher turbidity and SS). This could be due to 1) more intense rain causing increased particle transportation or 2) higher particle concentration in deposits on the catchment surfaces.

• Higher content of coliform bacteria in the sample from the carrier station, whereas the E. Coli level is higher in the sample from the gas station. Coliform bacteria are naturally present in

e.g. soil, whereas E. Coli indicates a fecal contamination. The observed difference could be caused by 1) less dilution of the carrier station sample, 2) leaching from passage through soil to the sample from carrier station sample and 3) animal faecal on catchment surfaces or leakage of sewage into the rain water pipes causing higher E. Coli in sample from gas station.
The concentrations of metals from both sites are similar and within the concentration reported in literature. A slightly higher concentration of Zn is found in the gas station sample. Measurement of the quantitative particle size distribution (Figure 2) indicate a larger sizes and higher content of particles in the sample from the gas station. This is in line with the SS and turbidity results from Table 4.



FIGURE 2. Particle size distribution of the collected rainwater samples

In conclusion, the two collected samples show significant differences as the carrier station sample is dominated by organics, bacteria and salts, whereas the gas station sample is dominated by particles.

#### 5.2 Membrane retention

As mentioned in the Methods (section 3), three different membranes were used for the test. The retention characteristics of the membranes was assessed from the characteristics of the resulting permeates.

#### 5.2.1 Sample from carrier station

In Table 5 the characteristics of the permeate samples are summarized. For all the membranes, few characteristics are almost unchanged by the passage through the filter. This is the case of pH, conductivity, TS, dissolved COD, alkalinity, dissolved PAH and dissolved metals. This can be associated to the dissolved fraction of TS. By contrast, the characteristic associated with particulate matter (e.g. turbidity, SS, total COD, total PAH and bacteria) are reduced in the permeate due to the membrane retention of particles in the low µm range. The best SS removal is observed for the 2µm membrane, while the worst performance is from the 1µm membrane. In- deed, the 2µm membrane is capable of removing 99.2 % of the original SS, while the 1µm membrane only can remove 79.1 % of the original SS. For all the membranes, a slightly higher UV transmittance in the permeate is observed, and ascribable to the removal of either 1) UV absorbing species (e.g. dissolved organics) or 2) UV scattering particulates. As none of the other characteristics suggests a substantial removal of dissolved species, the cause of the observed increase in UVT is likely the removal of scattering particulates. TABLE 5. Permeate characteristics - filtrated water from carrier station

Paramet	Unfiltered	1 µm	2 µm	3 µm
pН	7.28	7.46	7.67	7.62
Conductivity [ <b>†</b> S/cm]	1579	1568	1565	1568
Turbidity [NTU]	18.2	2.06	2.02	1.97
Total solids (TS) [mg/g]	0.958	0.953	0.947	0.911
Suspended solids (SS) [mg/L]	16.5	3.45	0.13	1.21
COD total [mg/L]	81.6	42.3	42.3	41.5
COD dissolved [mg/L]	43.9	47.8	46.5	46.4
Alkalinity [meq/L]	2.14	2.12	2.23	2.05
PAH total [オg/L]	11.6	5.5	6.8	4.3
PAH dissolved [t/g/L]	4.4	5.3	4.7	5.1
Coliform bacteria [#/100mL]	123800	82300	37450	49550
E. coli [#/100mL]	1	0.5	0.5 0	0
UVT (254 nm) [%]	44.9	45.5	46.6	47.6
UVT (285 nm) [%]	62.1	63.3	64.8	66.0
UVT (365 nm) [%]	88.3	91.1	93.3	99.4
Zinc total [mg/L]	0.075	nd	nd	nd
Zinc dissolved [mg/L]	nd	nd	nd	nd
Coppertotal [mg/L]	0.18	0.18	0.20	0.14
Copper dissolved [mg/L]	0.20	0.22	0.17	0.15
Lead total [mg/L]	nd	0.25	nd	0.25
Lead dissolved [mg/L]	nd	nd	nd	nd
Calcium total [mg/L]	236	273	268	252
Calcium dissolved [mg/L]	283	264	269	271

In Figure 3 the particle size distributions of the carrier station sample and the three permeate samples are shown. Larger particles are efficiently retained, whereas smaller particles are allowed to pass.



FIGURE 3. Particle distribution in raw water and permeate from carrier station

The retention behavior of the membranes has been further explored by estimating the relative retention and plotting it as a function of particle size (Figure 4).

For all membranes the retention is high for large particles but below approx. 2µm it drops significantly.





The discussed results indicate the 2  $\mu$ m membrane as the best performing with respect to the retention of SS and coliform bacteria as well as the particle retention curves.

#### 5.2.2 Sample from gas station

In Table 6 the characteristics of the permeate samples from the gas station are summarized.

TABLE 6. Permeate characteristics - filtrated water from gas station

Parameter	Unfiltered	1 µm	2 µm	2 µm fouling	3 µm
рН	7.27	7.49	7.19	7.28	7.27
Conductivity [ <b>†</b> S/cm]	173.3	162.7	163.2	161.4	162.8
Turbidity [NTU]	50.3	9.39	4.14	0.10	8.01
Total solids (TS) [mg/g]	0.145	0.092	0.073	0.088	0.073
Suspended solids (SS) [mg/L]	592	1.64	1.37	nd	2.04
COD total [mg/L]	32.5	7.15	7.09	7.50	7.36
COD dissolved [mg/L]	8.19	7.31	7.71	7.12	6.90
Alkalinity [meq/L]	1.15	1.08	1.05	1.03	1.07
PAH total [オg/L]	7.7	4.8	6.6	5.9	6.5
PAH dissolved [オg/L]	4.6	5.4	5.6	5.5	5.2
Coliform bacteria [#/100mL]	6015	2165	1414	36.4	970
E. coli [#/100mL]	216	107	28	2	80
UVT (254 nm) [%]	79.2	89.8	92.3	89.4	86.9
UVT (285 nm) [%]	81.6	92.6	95.1	91.9	89.8
UVT (365 nm) [%]	84.9	96.8	99.2	97.2	94.1
Zinc total [mg/L]	0.149	nd	nd	nd	0.113
Zinc dissolved [mg/L]	nd	nd	nd	nd	nd
Copper total [mg/L]	0.28	0.16	0.18	0.18	0.27
Copper dissolved [mg/L]	0.17	0.15	0.22	0.17	0.19
Lead total [mg/L]	nd	nd	nd	nd	0.25
Lead dissolved [mg/L]	nd	nd	nd	nd	nd
Calcium total [mg/L]	217	211	222	219	301
Calcium dissolved [mg/L]	199	217	228	199	206

Similarly to what observed for the carrier station sample, the characteristics related to the dissolved species are almost unchanged by the passage through the membranes (pH, conductivity, alkalinity, dissolved PAH and dissolved metals), whereas the characteristics related to the particulates (turbidity, TS, SS, total COD, total PAH and bacteria) exhibit a reduction of their values due to the particle retention of the membranes.

The dissolved COD in the permeate is observed to decrease slightly, likely due to a high concentration of particulates. When retained, they form a porous fouling layer able to retain part of the dissolved organics.

A large increase in UVT is found in the permeate samples. As the particulate content high, the relative importance of UV scattering from particles is high. Thus, the removal of particulates will effectively increase the UVT.

Calcium is primarily dissolved (<0.22µm) as no difference in total and dissolved concentrations are observed. This allow it to pass the membrane unhindered. The opposite is verified for zinc that is only present in particulate form. Copper is distributed between the dissolved and particulate fractions and thus only part of the total Cu is retained.



FIGURE 5. Particle size distribution in raw water and permeate from gas station

In Figure 5 the particle size distribution of the gas station sample and the four permeate sample is shown. In general, the particle retention is high for large particles, and it decreases for lower particle size. Again, 2  $\mu$ m membrane exhibits higher retain behavior with respect to the other membranes. Furthermore, the fouled 2  $\mu$ m membrane shows a significant reduction in particle concentration compared to the non-fouled 2  $\mu$ m membrane. This effect is caused by the lower pore size in the fouling layer.



FIGURE 6. Particle retention of membrane filtration on rainwater samples from gas station

In Figure 6, the relative retention as a function of particle size is shown. The fouled 2  $\mu$ m membrane exhibit a value almost 100% in the measured particle size range, whereas it rapidly decreases at approx. 1.3, 2,1 and 3.1  $\mu$ m for the unfouled 2 $\mu$ m, 3 $\mu$ m and 1 $\mu$ m membranes, respectively.

As observed for the carrier station sample, the 2  $\mu$ m membrane showed the best overall performance in terms of retention. Furthermore, a fouling layer was observed to have a significant positive effect on the retention of particulate.

#### 5.2.3 Remarks

The results of the membrane retention experiment on the samples from the two collecting sites indicate the  $2\mu m$  as the best performing membranes. Accordingly, this membrane has been selected for the following experiments.

#### 5.3 Membrane operation

In the following section, the data from the membrane operation experiments are discussed. Four experiments have been conducted - one dead-end and one crossflow for each of the two samples. The experiments were performed using the 2  $\mu$ m membrane, that results to be the best choice in term of retention properties.

### 5.3.1 Membrane flux, TPM and membrane permeability during operation

In Figure 7 the permeate flux measured during the experiments is shown for the samples from the two collecting sites. A decline in flux during operation is observed for both sites and indeed- end and crossflow conditions.



FIGURE 7. Permeate flux vs. time during dead-end and crossflow operation

A slight decline of the flux over time is observed in all the four plots, likely due to the formation of fouling. Yet, the flux values measured for the gas station sample are considerable smaller than those measured for the carrier station samples. This difference is caused by the higher concentration of particulates in the gas station sample, which accumulates on the membrane surface.

Figure 8 shows the variation of the TMP during the filtration experiments. Because of the formation of fouling, an increase of the pressure during operation is clearly observed. As both flux and TMP change a direct comparison is critical.

A comparison is feasible only comparing the permeability (flux per TMP), estimated and shown in Figure 9.



FIGURE 8. TMP vs. Time during dead-end and crossflow operation

The permeability of the gas station samples results almost an order of magnitude smaller than the one for the carrier station samples. This likely related to the influence of the higher particle concentration.



FIGURE 9. Permeability vs. time during dead-end and crossflow operation

The comparison of the permeability plots at the two operational modes, indicates an initial higher value in the crossflow operation. This is an effect of the continuous fouling removal caused by the cross flow, that thus results in higher productivity. The observed difference between the two operational modes is larger for the gas station sample due to the higher particle concentration that causes a more rapid fouling of the membrane.

### 5.4 Fouling resistance and specific cake resistance during operation

The fouling layer resistance is calculated based on the TMP and flux (section 3.13) and the results are shown in Figure 10. Values of almost an order higher are observed for the samples from the gas station in comparison with the samples from the carrier station.

This difference is caused by the higher particle concentration in the gas station sample, that in turns results in a larger accumulation of particle on the membrane surface.

The resistance contribution to the filtration of the deposited fouling layer can be estimated by quantifying the specific cake resistance ( $\alpha$ ). This parameter is obtained by dividing the fouling resistance (R\_foul) with the accumulated particle mass ( $\omega$ ) as indicated in section 3.13.



FIGURE 10. Fouling resistance vs. time during dead-end and crossflow operation

Figures 11 show the specific cake resistance trend for the samples from the two collecting sites in dead-end and crossflow operation modes. In all the plots the  $\alpha$  value is observed to vary during operation, until a constant value of approximately 5.1012 m/kg is reached. This suggests that the resistance contribution of the cake structure is similar for the two samples regardless the operation conditions and the particle size distribution of the TS.



FIGURE 11. Specific cake resistance vs. time

This experimental observation is of significant relevance for practical use of filtering membranes. Indeed, a constant  $\alpha$  value enables for the modelling of the filtration behavior of a sample with known SS concentration by using the equations indicated in section 3.13. An estimation of TMP for a constant flux application (or vice versa) could be also obtained. The definition of the operational criteria in terms of back-flush frequency to maintain a defined productivity (assuming no irreversible fouling of the membrane) is also allowed.

#### 5.5 Summary

### 5.5.1 Comparison of rainwater characteristic with values from literature

The two sample of collected rainwater differ each other mainly for the content of organics, higher for the sample collected at the carrier station, and for the content of total solids load, higher for the sample collected at the gas station.

Compared with the data from literature, the concentration of the identified compounds for the sites is closer to the lower limit, except for total PAHs which are found at almost twice the concentrations reported in the literature. The traffic in both catchments is mainly due to trucks with a lot of breaking and idle running (loading/unloading goods and gas filling), which could likely increase the overall PAHs load.

#### 5.5.2 Evaluation of membrane performance

The three membranes were tested for their retention behavior. Although none of them can be considered an absolute barrier to particulate, all have been proven to retain a large fraction of the particulates present in the water samples. In contrast, very poor retention of the dissolved species has been observed.

The 2 µm membrane exhibit the overall best performance in terms of retention of particulates.

#### 5.5.3 Evaluation of membrane operation

The results from the dead-end and crossflow tests, show that the crossflow mode as the most appropriate. This is due to the faster increase in TMP observed in dead-end vs. crossflow, which is caused by a faster accumulation rate at the membrane surface. When operating in crossflow mode, the accumulation is counteracted by the flow across the membrane surface.

Despite the specific concentrations and the operation mode, a constant value for the cake resistance has been also demonstrated. This experimental evidence is of a great practical relevance as it makes possible to model the filtration behavior. This is an important input needed for the design software.

#### 5.5.4 Evaluation of the need of UV photolysis

While the membranes investigated in this study are demonstrated to efficiently retain a large fraction of the particulates in the rainwater samples, most of the dissolved matter has not retained. Therefore, the treated water likely contains salts, metals, dissolved COD, dissolved PAH and microorganisms along with other dissolved or small particulate components that have not been analyzed for in this study.

However, the results obtained in this study also suggest that the formation of a fouling layer during operation aids the retention and lowers the concentration of the mentioned components in the permeate.

Despite that, a post treatment may be required if the filtered water does not fit the quality requirements of a specific industrial application. The need for post treatment will depend partly on the industrial process in which the water is to be used and partly on the rainwater characteristics.

Within this context, an UV photolysis process as post treatment can be used both as a disinfection and oxidation process removed bacteria and organics. However, UV photolysis is not able to remove inorganics like salts and metals. An additional post treatment step (e.g. ion exchange) would be necessary to reach the required quality.

# 6. Conclusions

The analysis on the collected rainwater sampled from a carrier station and a nearby gas station in Aarslev near Aarhus, show:

- Similar metal composition, except for higher zinc values at the gas station;
- Higher solids and organic loads, including PAHs, at the carrier station;
- The concentration of most of the species is closer to the lower limit found in the literature;
- PAHs found in concentration twice the amount listed in the literature study.

The samples for the two collecting sites have been filtered in dead-end and cross-flow modes, using the three membrane types (1µm, 2µm and 3µm pores)

- The 2 µm membrane exhibits the best retention of particles;
- Better performance when operating in cross-flow mode;
- Poor removal of dissolved species;
- · Post treatment with UV photolysis could remove the remaining dissolved organic content;
- An ion exchanger is needed for the removal of the remaining dissolved metals.

# 7. Work packages

The project was defined by three work packages:

- Characterization of rainwater in relation to determining optimum membrane pore size, reuse in industry and identification of polishing technology
- Development of optimal operating, backflush / back pulse / CIP strategy for membrane filtration and development of UV photolysis concept for polishing,
- Reporting and dissemination

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### Udvikling af 3. generations vandbehandlingskoncept til decentral rensning og genbrug af regnvand

The purpose of this project is to develop an innovative cost-efficient water treatmentconcept for recovery of rainwater. Where the focus is to industrially reuse water and hereby reduce the consumption of water produced from conventional methods. This will contribute to a reduction of the industries water footprint. Furthermore, the reuse of rainwater from industrial production areas can minimize the load from local recipients, with special pollutant waste and hereby contribute to a better environmental status. The developed technology can also be used in relation with urban areas.



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