

# Effective treatment of the wastewater from ceramic industry using ceramic membranes

Maxim Shurygin, Christiane Guenther, Stephan Fuchs and Volker Prehn

## ABSTRACT

Emissions of organic compounds, heavy metals and chemicals used in the ceramic industry cause significant organic and inorganic pollution of water. The effluent must be treated before it is discharged into a water body. International and EU laws control the chemical oxygen demand (COD) of the wastewater. Conventional technologies, such as sedimentation, flocculation and biological treatment, have lots of drawbacks, whereas membrane technologies give many benefits, as they are chemical-free and allow a reduction of the treatment steps. One-step wastewater nanofiltration with ceramic membranes of 450 Da cut-off is able to reduce the COD of ceramic wastewater to a sufficient level. However, the working time without cleaning is limited and the rejection of membranes can be significantly reduced due to fouling. Multistage filtration can be the solution. Filtration experiments with various combinations (MF, UF and NF) of ceramic membranes were performed at a laboratory scale with single-channel membranes and at pilot scale with 7-, 19- and 151-channel membranes in order to permanently reach the limit value of a COD below 80 mg/L and to increase the operating time. Four types of membranes were sequentially tested in the cross-flow mode: MF (200 nm pore size), UF (2,000 Da), NF (450 Da) and NF (200 Da). 5-day Biological Oxygen Demand (BOD) tests were performed in order to examine the wastewater biodegradability. The test results with single-channel membranes showed that in terms of the highest COD rejection and the highest permeability, the best combination was that of MF and UF membranes. Here, UF membranes were sufficient to reach the limit values. As for the multi-channel membranes, the combination of MF and NF (450 Da) was the best and the final COD concentration ranged from 11 to 48 mg/L. 5-day BOD bottle tests showed a COD/BOD ratio of 3.8, which opened up possibilities for combined treatment.

**Key words** | ceramic membranes, ceramic wastewater, microfiltration, multistep filtration, nanofiltration, ultrafiltration

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## HIGHLIGHTS

- Ceramic industry emissions can cause significant pollution of water bodies.
- Filtration with ceramic membranes is able to reduce the COD of the ceramic wastewater.
- Two-step micro-, ultra- or nanofiltration has advantages over one-step filtration.
- Highest COD rejection and flux showed for the pair of single-channel MF and UF membranes.
- MF and NF combination was the best when multichannel membranes were used.

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## INTRODUCTION

The aim of the research was to determine the best combination of different ceramic membranes in terms of the chemical oxygen demand (COD) rejection and average permeability during the filtration of ceramic wastewater. The limit of 80 mg/L is set by AbwV ('Verordnung über Anforderungen an das Einleiten von Abwasser in Gewässer (Abwasserverordnung – AbwV)' 1997, Anhang 17 Herstellung keramischer Erzeugnisse).

The benefits of ceramic membranes' applications during the filtration of different problematic wastewaters can be found in a lot of publications (Almecija *et al.* 2009; Barredo-Damas *et al.* 2010; Ciara 2003; Cui *et al.* 2013; Dafinov *et al.* 2005; Ebrahimi *et al.* 2010; Ebrahimi *et al.* 2015a, 2015b; Gaulinger 2007; Hua *et al.* 2007; Kramer *et al.* 2015; Mustafa *et al.* 2016; Weber *et al.* 2003). However, in modern scientific literature there are almost no examples of wastewater treatment from the ceramic industry using ceramic membranes.

The wastewater discharges from the ceramic industry mainly contain insoluble mineral components (silt, clay). Different organic compounds, heavy metals and chemicals used are in the minority; however, they cause significant organic and inorganic pollution of surface and groundwater. For the investigation and all tests during the PAKMem project inopor<sup>®</sup>-membranes, delivered by a project partner, were used. The wastewater produced by one of the ceramic industries in Germany was used in filtration experiments. The limit values of COD have to be achieved, so that the wastewater can subsequently be introduced into the water body. Ceramic nanofiltration has already been used in individual experiments with one-step filtration, which allowed the threshold values to be overcome and to the COD to be reduced below 80 mg/L. However, the timeframe of these first tests was quite short. Moreover, the fluctuations in production at the manufacturer affect the quality of the filtrate. In order to permanently reach the limit values and increase the filtration time without cleaning, multistage treatment is necessary. Therefore, different micro-, ultra- and nanofiltration membranes with single-channel and multi-channel tubes were tested sequentially in the cross-flow mode. The two-stage membrane filtration is advantageous, because it allows working in a wider range of input concentrations, reduces the chance of a particle slipping through and potentially keeps the second stage running longer.

Four types of single-channel ceramic membranes were used at the laboratory scale and afterwards the same types

of multi-channel membranes were applied at pilot scale. COD-, TOC-, EC-rejection and average permeability were evaluated during the filtration experiments and the best membrane combination was identified.

## MATERIALS AND METHODS

The experimental part of the research includes two sections:

- Laboratory experiments using the ceramic wastewater with the InoMini filtration test unit, and the single-channel ceramic membranes;
- Pilot experiments of the ceramic wastewater with the Atec-TF111 filtration test unit, using the multi-channel ceramic membranes.

The wastewater of one of the ceramic manufacturers in Germany was used in all the experiments. The wastewater was collected from an outdoor collection basin of 350 m<sup>3</sup> capacity.

The daily wastewater grab samples from the collection basin showed that the COD fluctuated from January 2015 till August 2019 in the range from 58 to 429 mg/L with an average of 180 mg/L. Plant wastewater was characterized with high turbidity, high amount of silt and clay and the other measured parameters varied as follows:

Temperature: 0–25.2 °C;

pH-value: 6.5–8.75;

COD: 3–753 mg/L;

Electrical Conductivity (EC): 364–790 µS/cm;

Total Organic Carbon (TOC): 40–129 mg/L;

Total Suspended Solids (TSS): 0.8–758 mg/L;

Total hardness (as CaCO<sub>3</sub>): 2.8–3.1 mmol/L.

The silt and clay materials are flushed during the ceramic manufacturing and equipment cleaning. The wastewater from the factory enters the collection basin, where the largest particles settle over some time. The particle size distribution analysis was performed in October 2018. Standard percentiles readings from the analysis – D10, D50 and D90 – were obtained. The mass median diameter (median of the volume distribution) D50 showed the size of 11.847 µm. D10 equalled to 1.476 µm; and D90 was 38.495 µm. The minimum size, which was identified by Mastersizer 2000, was 0.244 µm (0.04%); the maximum size of the particles in the wastewater was 137.96 µm (99.88%).

So, most of the particles comprised coarse, fine and medium silt (approximately 84% of volume); the clay particles constitute about 13% by volume.

Four types of inopor ceramic membranes were used in all the experiments: A200, Z3, T0.9 and LC1. The A200-membranes were examined with the mercury porosimetry method in accordance with ISO 15901-1. Z3, T0.9 and LC1-membranes were characterised by the solute rejection measurements ('cut-off' concept) using polyethylene glycol (PEG).

## Wastewater

The wastewater was used in the filtration experiments without any pre-treatment. The laboratory experiments began in January 2019, when the COD fluctuated from 34 to 76 mg/L. So, the concentrate of a polymeric ultrafiltration unit, working with the same wastewater, was also used. Thereby, the COD values of the feed wastewater were increased and ranged from 145 to 7,300 mg/L. The EC varied from 364 to 818  $\mu\text{S}/\text{cm}$ . The COD values in pilot experiments fluctuated from 32 to 1,120 mg/L. The EC varied from 492 to 790  $\mu\text{S}/\text{cm}$  and its pH value changed from 6.85 to 7.87; the TOC ranged from 19 to 161 mg/L.

## Membranes

Four types of new single-channel tube ceramic membranes were used in the filtration experiments: A200, Z3, T0.9 and LC1. Geometry, materials and pore characteristics of the applied membranes are represented in Tables 1–3.

All the membranes exhibit an anisotropic (asymmetric) pore structure. The pore size is determined by the top layer of the membrane. The ceramic support is made of  $\alpha\text{-Al}_2\text{O}_3$  with a pore size from 3 to 5  $\mu\text{m}$ . The number of the layers varied from 2 to 7 in total; the thickness of the layers ranged from 50 nm to 25  $\mu\text{m}$ ; the materials of the layers are  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and/or  $\text{ZrO}_2$ . The LC1-membrane is the latest development of inopor and it is produced only at lab scale.

The membranes were not changed during the laboratory experiments, except the LC1-membrane. Chemical cleaning

was applied only after a membrane blockage, which was indicated by 'nearly zero' permeate flux through the membrane.

Three types of new 7, 19 and 151-channel tube ceramic membranes were used in the pilot experiments with A200-, Z3- and LC1-membranes. All T0.9-membranes have already been used with the same wastewater during 160 days of operation, four alkali-cleaning cycles and average permeability of 1.91  $\text{L}/(\text{m}^2\text{hbar})$ . The geometries of the applied membranes are represented in Table 3. The materials and pore characteristics of the multi-channel membranes are the same as for the single-channel membranes.

## Laboratory experiments with InoMini test unit

### Test unit InoMini

The InoMini filtration test unit was used in the laboratory experiments. The module contains one membrane. The maximum operating pressure (MOP) of the unit is 40 bar. The unit is operated in the cross-flow (tangential) constant pressure mode. The medium circulates through the feed tank. The reciprocating pump supplies a constant pressure and in the process of filtration the flux through the membrane is naturally decreased, while the wastewater is concentrated in the feed tank and the permeate is collected separately. Figure 1 shows the flow diagram of the InoMini unit.

The constant wastewater flowrate of 7.5 L/min was maintained through all tests, which corresponded to the cross-flow velocity (CFV) of 3.25 m/s. This is slightly above average (Pinnekamp & Friedrich 2003) but maintains high flow turbulence, which reduces the fouling rate. The transmembrane pressure (TMP) for the A200-membrane was set at 1 bar in all tests and for Z3, T0.9 and LC1-membranes, 20 bar was applied in most cases; 10 and 30 bar was applied in some additional tests. The fluid temperature fluctuated from 15 to 25  $^{\circ}\text{C}$ ; the external cooling was provided when necessary.

## Procedure

The filtration tests were performed with the following membrane combinations: A200 + T0.9, A200 + Z3, A200 + LC1,

**Table 1** | Geometry of 1-channel (A) ceramic membranes used in experiments

Designation	Membrane	Geometry	Diameter [mm]			Membrane length [mm]	Specific membrane area [ $\text{m}^2$ ]	End sealing 13 mm
			Outer	Channel internal	Channel number			
A200	A10	10	7	1	500	0.0110	–	
Z3, T0.9, LC1	A10	10	7	1	500	0.0104	Glass	

**Table 2** | Materials and pore sizes of single-channel ceramic membranes used in experiments

Membrane	Top layer material	Pore size [nm]	Cut-off [Da]	Porosity [%]
A200	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	200	–	40–55
Z3	ZrO <sub>2</sub>	3	2,000	30–55
T0.9	TiO <sub>2</sub>	0.9	450	30–40
LC1	TiO <sub>2</sub>	–	200	30–40

Z3 + T0.9, Z3 + LC1, T0.9 + LC1. Every new membrane was initially tested with deionised water (diH<sub>2</sub>O) during one hour. Approximately 4.5 L of permeate was collected during the first filtration, then it was used as a feed for the next filtration step. The probes for the analysis were taken in 30-mL plastic vials after 10 and 60 minutes of filtration, and sometimes by the end of the filtration. The flowrate was measured manually for 30 seconds every 10 minutes within the first hour of filtration and afterwards, every 30 minutes. The EC and the pH value were measured in some tests.

The temperature compensation was applied for permeability calculation. It is called the ‘adjusted flux for media at 20 °C’ (Gaulinger 2007), ‘temperature-corrected permeability 20 °C’ (Kramer et al. 2019) or ‘temperature compensated specific flux’ (Nitto Hydranautics). The Equation (2) can give an error of about 3–10% if the temperature range is from 0 to 10 and 5% if the temperature is more than 40 °C (Gaulinger 2007).

Considering the above, the membrane filtration efficiency was evaluated based on the following parameters:

$$R_{COD} = \left(1 - \frac{COD_{PERM}}{COD_{FEED}}\right) \cdot 100 \quad (1)$$

$R_{COD}$  – COD-rejection after 60 minutes of filtration [%];  $COD_{PERM}$  – COD of the permeate [mg/L];  $COD_{FEED}$  – COD

of the feed [mg/L]

$$L_{20^\circ} = \frac{J \cdot e^{-0.039 \cdot (T-20)}}{\Delta P} \quad (2)$$

$L_{20^\circ}$  – Permeability at 20 °C [L/(bar·h·m<sup>2</sup>)];  $J$  – Flux [L/(h·m<sup>2</sup>)];  $T$  – Water temperature [°C];  $\Delta P$  – TMP [bar].

In total, fifteen tests were performed. Each combination was tested at least twice, except T0.9 + LC1, which was tested once. In the last two experiments (A200 + LC1 and A200 + T0.9), the same permeate of the A200-membrane was used for the next stage.

### Backwash

The backwash of the membranes was not foreseen. Only the A200 and T0.9-membranes were chemically cleaned when blocked, which was done with 2% P3-ultrasil 115 ECOLAB (alkaline) in 4 L diH<sub>2</sub>O, which lasted 1 hour without cooling. The fluid temperature during the cleaning was increased up to 30 °C due to the heat influx of the pump. After the cleaning, the filtration unit was cleaned with diH<sub>2</sub>O.

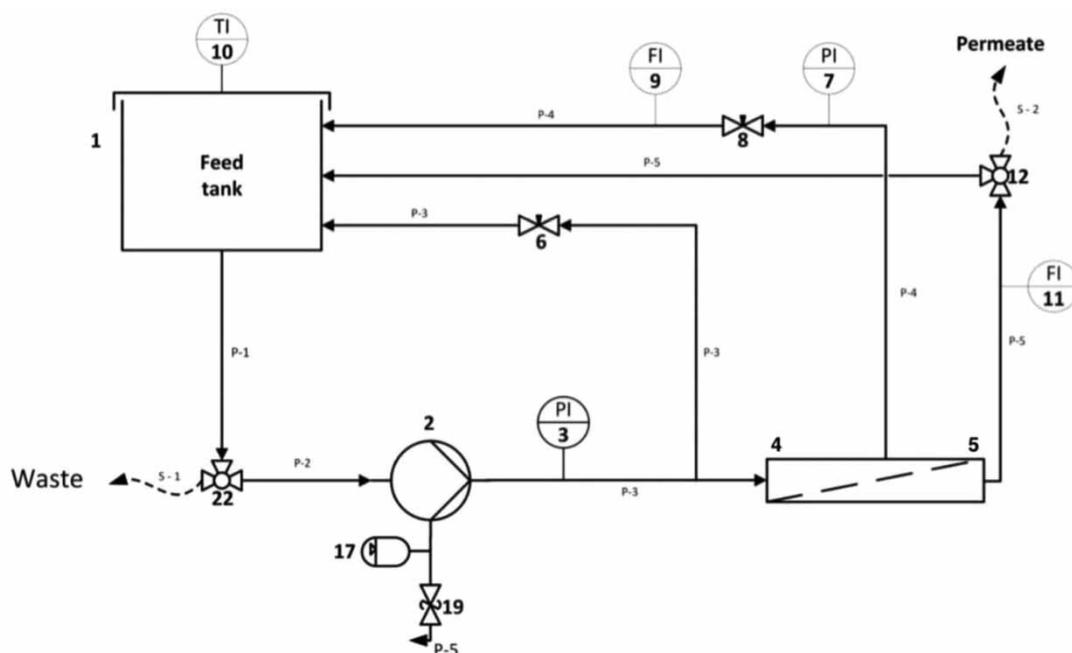
### Measuring methods and devices

The COD of most of the feed and permeate probes was measured immediately after the test. In other cases, the probes were stored in the refrigerator at 4 °C for 48 hours maximum. The COD was determined by means of the UV/VIS spectrophotometer NANOCOLOR UV/VIS II (MACHEREY-NAGEL) according to DIN ISO 15705 after 2 hours of heating at 148 °C.

The EC was measured using the conductivity measuring device GMH 3431 (GREISINGER). The non-linear temperature compensation ‘nLF’ according to EN 27888 (ISO

**Table 3** | Geometry of 7- (B), 19- (C) and 151-channel (N) ceramic membranes used in experiments

Designation	Geometry	Diameter [mm]			Channel number	Membrane length [mm]	Specific membrane area [m <sup>2</sup> ]	End sealing 13 mm
		Outer	Channel internal					
A200	C41	41	6	19	1,200	0.425	Ceramic	
	B25	25	6	7		0.157		
	N41	41	2	151		1.126		Glass
Z3	C41	41	6	19	0.425			
	C25	25	3.5	19	0.248			
T0.9	N41	41	2	151	1.126			
	C25	25	3.5	19	0.248			
LC1	N41	41	2	151	1.126			
	C25	25	3.5	19	0.248			



1 Tank for medium; 2 Plunger pump; 3 Feed manometer PI1; 4-5 Stainless steel module M1; 6 Bypass needle valve V1; 7 Retentate manometer PI2; 8 Retentate needle valve V2; 9 Retentate flow meter FI1; 10 Supply tank manometer TI1; 11 Permeate flow meter FI2; 12 Permeate 3-way stopcock \*H1; 17 Pulse dampener; 19 Pressure relief valve V3 with opening; 22 Discharge stopcock H3

**Figure 1** | InoMini system components.

7888) was applied, which recalculated the wastewater conductivity to a consistent reference temperature (25 °C). The device was calibrated in advance with three standard solutions: 84, 1,413 and 12,880  $\mu\text{S}/\text{cm}$  (25 °C) from CHEM-SOLUTE (Th. Geyer GmbH&Co.).

The pH value was measured using the sensION TM + PH1 Portable Meter from Hach Lange Spain S.L.U. The device was calibrated in advance with three standard solutions: 4, 7 and 9.21 pH (Hach Lange GmbH).

### Pilot experiments with Atec-TF111 filtration test unit

#### Test unit Atec-TF111

The TF111 filtration test unit ('Atec-Testanlage TF111 Nano-tube für Ultra- und Nanofiltration') was applied for the wastewater filtration with the multi-channel ceramic membranes (Figure 2). The unit contains two modules of different sizes with probe samplers. Each module contains 3 membranes of 41 or 25 mm outer diameter. The unit was operated in the cross-flow constant pressure mode. In the process of filtration, the flux through the membranes is

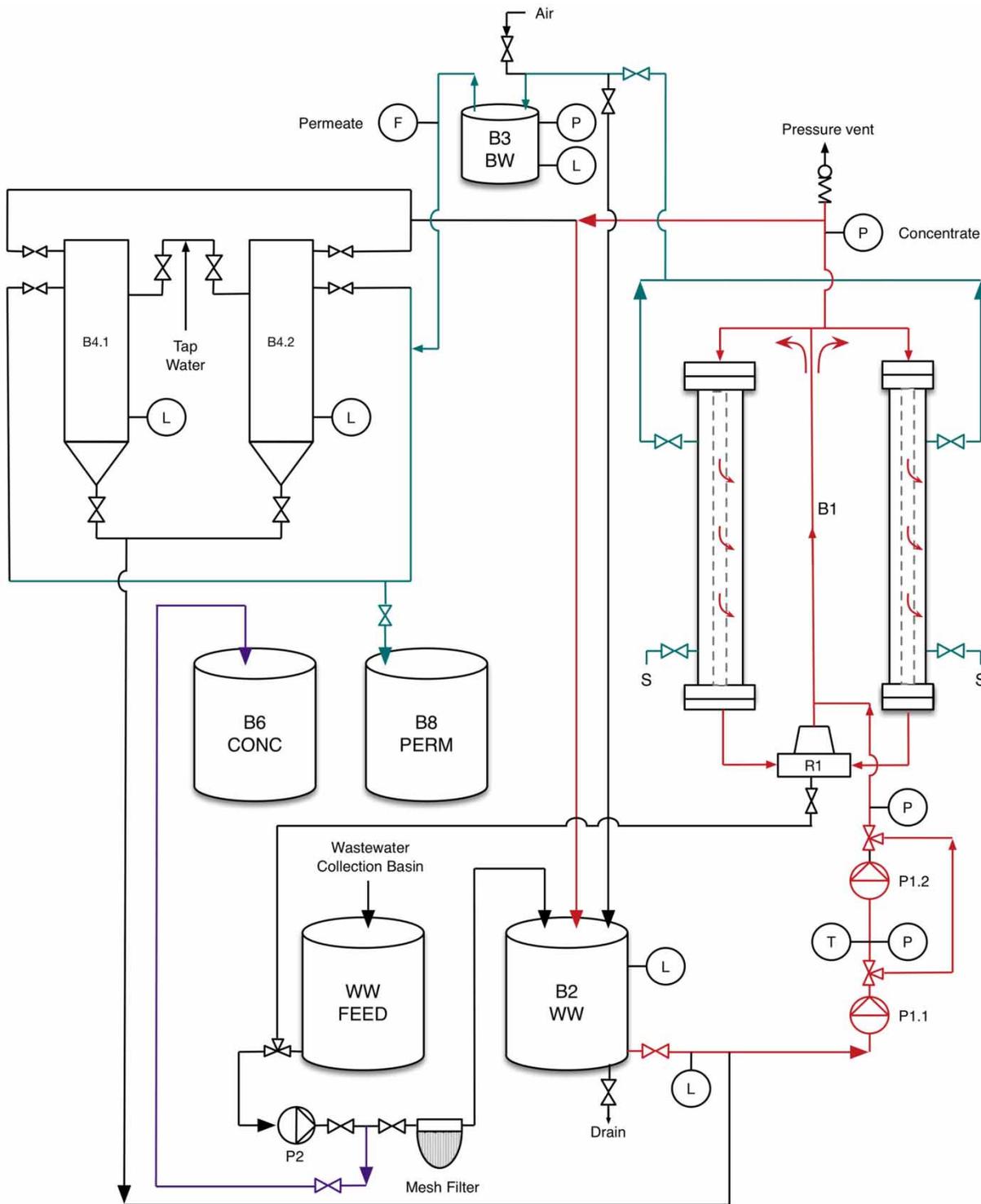
naturally decreased. The MOP of the unit is 25 bar. Two centrifugal pumps, P1.1 and P1.2 of low and high pressure, allow the system to work in Micro- (Ultra-) or Nanofiltration regimes. The pumps work in series during the nanofiltration regime when higher pressure is needed. The permeate flows back into the feed tank. The Agitator R1 ensures cross-flow via the membrane modules.

The TMP for the A200-membrane was set at 1 bar; 20 bar was applied for all other membranes in all tests. The fluid temperature fluctuated from 11 to 37 °C; the cooling was not foreseen. The CFV could not be measured by Atec-TF111.

#### Experimental procedure

Sixteen tests were performed with the Atec-TF111 unit. The first stage in most of the tests was A200- or Z3-membranes accordingly. For the second stage, the Z3-, T0.9- or LC1-membranes were used.

The filtration tests were performed with the following membrane combinations: A200 + T0.9, A200 + Z3, A200 + LC1, Z3 + T0.9, Z3 + LC1, T0.9 + LC1. The combinations of A200 + Z3, A200 + T0.9 and A200 + LC1 were



P1.1 - Low-pressure feed pump; P1.2 - High-pressure feed pump; R1 - Agitator; P2 - Pneumatic diaphragm drain pump; B1 - Membrane filter (2 modules); B2 - Working tank; B3 - Backwash tank; B4.1, B4.2 - Membrane cleaning tanks; S - Sampling points; P - Pressure indicator; F - Flow indicator; L - Level indicator; T - Temperature indicator

Figure 2 | Atec-TF111 flow diagram.

tested three times. The last tests of these three combinations were performed with the concentrate from the other polymeric ultrafiltration unit as the feed, where around 2 m<sup>3</sup> of permeate was filtrated using A200-membranes and then it was used as the feed for the second stage (Z3-, T0.9- or LC1-membranes). Z3 + T0.9, Z3 + LC1 and T0.9 + LC1 tests were performed once.

In all the tests, 1 m<sup>3</sup> of permeate was collected during the first filtration step, which was stored in the IBC tank indoors at a temperature around 15–20 °C maximum for 24 hours. The membranes were changed and permeate from the first stage was used as a feed for the next filtration step. The probes of permeate and concentrate were taken in 200-mL plastic bottles after 10 and after 60 minutes of filtration for each module. In the long-term tests, the probes were taken after 300 minutes and by the end of the filtration. The flow-rate was measured manually for each module during 30 seconds every 10 minutes within the first hour of filtration and afterwards, every hour. COD, TOC, EC and pH analysis of the probes were performed. All the probes were stored at 4 °C. A two-stage filtration took maximum 5 days.

Similarly to the laboratory experiments with InoMini, the membrane filtration efficiency was evaluated based on the rejection  $R$  [%] of COD, TOC or ions after 60 minutes of filtration and permeability at 20 °C  $L_{20}$  [L/(bar·h·m<sup>2</sup>)] (Equations 1 and 2). The overall rejection of the membrane combination was calculated based on the rejection of each stage of filtration.

From Test 7, the three C25-Z3-membranes were changed and the new C25-Z3-membranes of the same type and geometry were used until the end of experiments. From Test 7, three C25-A200-membranes were changed to N41-A200-membranes. The other membranes were not changed during all the experiments.

### Backwash

Every 10 minutes during the filtration, the membranes were automatically exposed to the air blowing for 30 seconds. The air and permeate from B3 tank was supplied to the outer side of membranes, while Agitator R1 was running it through the inside of the membranes. The pressure during the blowing in the backflush tank B3 was 2 bar in all the tests, whereas the pressure inside the membranes was 1 bar. The Agitator R1 provided the cross-flow permeate circulation inside the membranes. After backwashing, the B3 tank was vented via MV11 valve into the working tank B2.

When the membranes were blocked during the filtration and the flux decreased considerably, the alkaline chemical

cleaning was performed. 2% of P3-ultrasil 115 ECOLAB in 50 L tap water was used for the chemical cleaning, which lasted 1 hour. The fluid temperature increased during the cleaning procedure. After the chemical cleaning, the unit was cleaned with tap water until the pH-value was neutral.

During the short-term experiments, only A200-membranes (3 of 41 mm-151-channel and 3 of 25 mm-7-channel) were chemically cleaned after 13th test.

### Measuring methods and devices

The COD, the EC and the pH value were measured in the same manner and using the same equipment as it was performed during the experiments with the InoMini unit.

The TOC determination was carried out in two steps: 1) disposing of the inorganic carbon (TIC) by means of the air blowing (5 min), using the TIC-Ex. (REF 916993) from NANOCOLOR in opened cuvettes; 2) decomposition of the organic carbon (TOC) during 1 hour at 100 °C and detection of the CO<sub>2</sub> formed by means of an indicator. NANOCOLOR TOC 30 (REF 985075) and TOC 300 (REF 985078) were used in all the tests, depending on the expected TOC concentration. The probes were taken during the mixing with a magnetic stirrer (Heidolph MR Hei-Tec) at 500 rpm for homogenization. The samples were measured in duplicates. In case of the feed wastewater or concentrate, the probes were measured up to eight times.

During the last week of all experiments in July-August 2019, the BOD<sub>5</sub> analysis was performed in the laboratories of the Karlsruhe Institute of Technology (KIT) together with the COD analysis, in order to check the wastewater biodegradability. The evaluation of the wastewater parameters was carried out within 48 hours after the sampling.

The BOD was measured with the OxiTop measuring system (Wissenschaftlich-Technische Werkstätten GmbH). The sample preparation and filling of the measuring bottles was performed according to DIN 38409 H52. Three measuring bottles with the OxiTop were put in an incubator for 5 days at 20 °C. The samples were continuously stirred during the 5 days. The pressure from each of the 3 bottles was recorded every day and finally the average value was taken. The COD, TOC and NH<sub>4</sub>-N of the wastewater were also measured at the start of the BOD test (day 0).

## RESULTS AND DISCUSSION

The test results were evaluated separately for the laboratory and pilot scale. The sequence of the experiments plays a role

for the permeability evaluation, as the permeability through the membranes decreases over time, even if cleaning is applied, due to irreversible fouling. And in the beginning of the experiments the permeability is naturally higher. The membrane rejection could be increased or decreased over time, which is highly dependent on the membrane morphology, the COD concentration in the feed, and the fouling rate.

### Laboratory tests results with the InoMini

Fifteen tests were performed with the inoMini filtration test unit using the different single-channel ceramic membranes. The wastewater from the collection basin (Tests 1–4) or its concentrate (Tests 5–15) was used in the experiments.

### COD-rejection

The rejection of the COD of all the membrane combinations is represented in Figure 3. In Tests 14 and 15, the same wastewater concentrate was used as the feed for the first stage (A200-membrane) and its permeate was subsequently used for the 2nd stage (LC1- or T0.9-membrane). So, the LC1-membrane in Test 14 and T0.9-membrane in Test 15 had the same inlet conditions. Furthermore, the pressure of 20 and 30 bar was consistently applied in these tests for the 2nd stage.

All the combinations demonstrated high COD-rejection, the COD concentration of permeate ranged from 2 to 51 mg/L. The highest COD-rejection was achieved with the T0.9-membrane. A lower rejection of the combinations occurred only if the inlet COD concentration was low

(Tests 1–4) or in some experiments with LC1-membranes (Tests 7 and 8). A200 + T0.9, A200 + Z3 and Z3 + T0.9 provide the best and roughly the same COD-rejections. The A200 + Z3 combination is preferred, as it allows reducing the pressure of both stages.

Figure 4 shows the relation of the COD rejection of each-membrane to the COD concentration in the feed wastewater. The data from all the performed tests with single-channel membranes were taken into account. Both LC1-membrane rejections are represented on the graph and designated as LC1. For an ideal membrane, the COD rejection is independent from the inlet COD concentration. In reality, the COD-rejection is decreasing with the decrease of the inlet COD. The logarithmic trendlines best describe the scattered data of the chart and show how sharp the relations could be. The best characteristics demonstrated the Z3- and T0.9-membrane. The curves of the LC1 and A200-membrane are more blunt and therefore the membranes might not provide the sufficient level of rejection at low inlet COD concentrations.

### Ion rejection

The total ion rejection was analysed using the electrical conductivity (EC at 25 °C). It was measured from Test-8 to 15 and varied in the range of 530–884  $\mu\text{S}/\text{cm}$  for feed.

The Z3 + T0.9 combination showed the best ion rejection (70%). The EC was reduced from 623 to 187  $\mu\text{S}/\text{cm}$ . In general, the Z3-membrane demonstrated the highest ion rejection in all tests (44–55%), which was close to the values of the T0.9-membrane (43–51%). Normally, the UF membranes exhibit lower ion rejections than NF

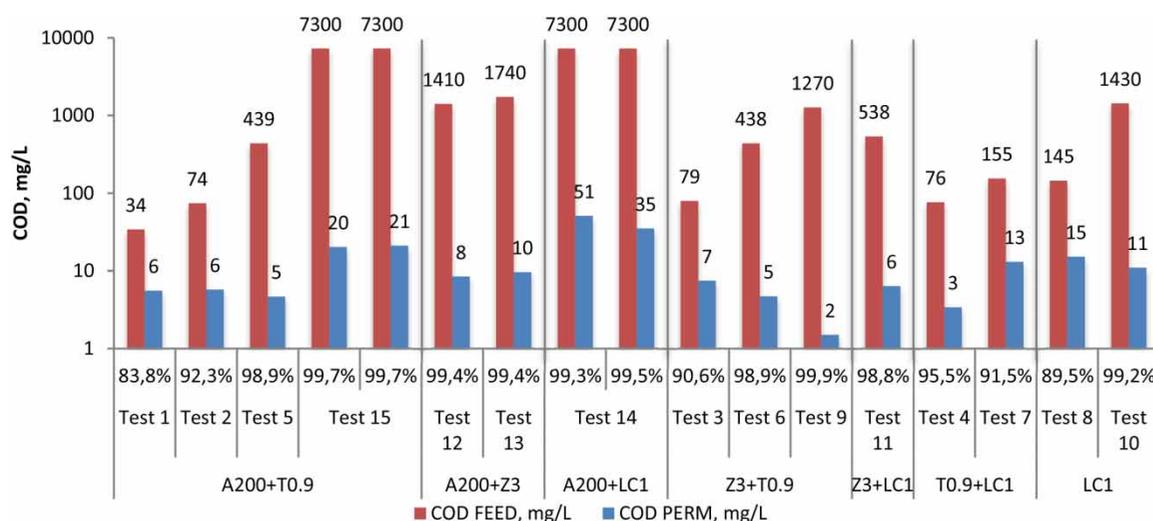
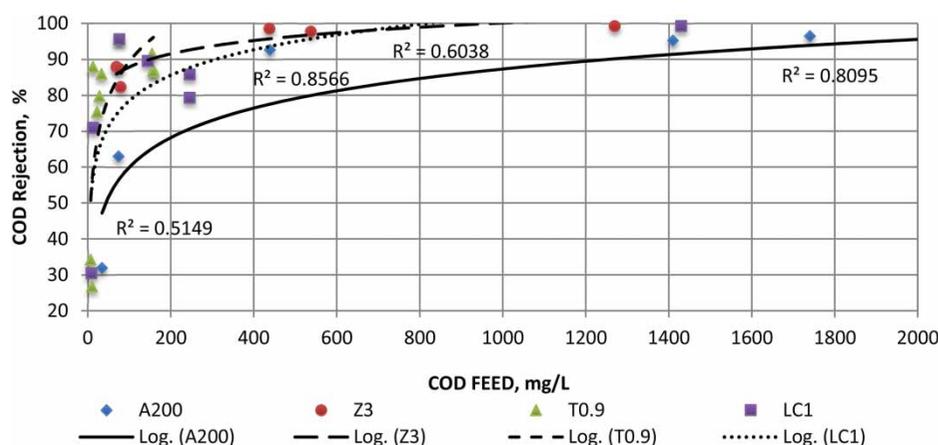


Figure 3 | COD-rejection of all tests with single-channel membranes using the inoMini unit.



**Figure 4** | Membranes' rejections over the COD concentration in the feed wastewater.

membranes. The chemical bonding between the cations and negatively charged organic material can take place (Gaulinger 2007). These bounded ions could be partially retained even by MF, which demonstrated A200-membrane in Tests 12 and 13 (2.3 and 6.5% rejection respectively). LC1-membrane showed lower ion retention than Z3 and T0.9-membranes in almost all the tests and showed greater scattering in the rejections (from 34.5 to 47.7%).

### Permeability

Table 4 shows the permeability at 20 °C of all the single-channel membranes, which were used with the InoMini unit. The tests with diH<sub>2</sub>O are not shown.

The LC1-membrane did not work long, so the data is hardly comparable with the other membranes. The A200-membrane was chemically cleaned once after 1,520 min; the T0.9-membrane was cleaned twice – after 1,470 and 2,430 min.

The average permeability of each membrane was calculated, taking into account only the most stable periods of membrane operation – from 800 to 1,400 min and from 1,900 to 2,400 min (Figure 5).

A200, Z3 and T0.9-membranes provided on average 38.8, 1.76 and 1.08 L/(m<sup>2</sup>h·bar) accordingly. The Z3-membrane

demonstrated the most stable performance. The permeability data are correlated with Mulder (1996); however, the permeability obtained in experiments remained below the minimum reported values in L/(m<sup>2</sup>h·bar): MF: from 50 (0.1–2 bar); UF: 10–50 (1–5 bar); NF: 1.4–12 (5–20 bar); RO: 0.05–1.4 (10–20 bar). Z3 and T0.9-membranes demonstrated a quite high hydraulic (filtration) resistance. However, Mulder (1996) did not specify the type of liquid and other parameters at which such permeability was obtained. Also, the terms of MF, UF and NF differ in the various sources.

The A200-membrane worked for about 3,500 min. The COD of the permeate of the A200-membrane slightly increased with the increasing inlet COD concentration. However, this dependency is weak. In Test 15, the inlet COD concentration in the first day of filtration was 7,300 mg/L. On the second day, the new concentrate, which was added to the feed tank, reached a COD concentration of 13,580 mg/L. Eventually, the average permeate concentration of the COD was 165 mg/L, compared with 101 mg/L after 10 min of filtration. The filtration and pore blockage of A200-membrane were guided by the cake filtration mechanisms (Gaulinger 2007), which could deteriorate the quality of the filtration.

The Z3 and T0.9-membranes worked for 2,860 and 2,970 min. The Z3-membrane was not cleaned during all experiments; the T0.9-membrane was cleaned twice – after 1,710 and after 2,670 min. The permeability curve of the T0.9-membrane has a sharper stabilization period than the curves of the A200 and Z3-membranes, even considering the lower COD concentration in the first tests with T0.9-membrane. The mechanisms of the pore blockage for used MF-, UF- and NF-membranes are different than for fresh membranes, as they retain different particles and colloid material.

**Table 4** | The average hydraulic permeability of single-channel membranes

Membrane	Average permeability, L/(m <sup>2</sup> h·bar) at 20 °C	
	800–1,400 min	1,900–2,400 min
A200	31.23	46.37
Z3	1.77	1.75
T0.9	0.92	1.24

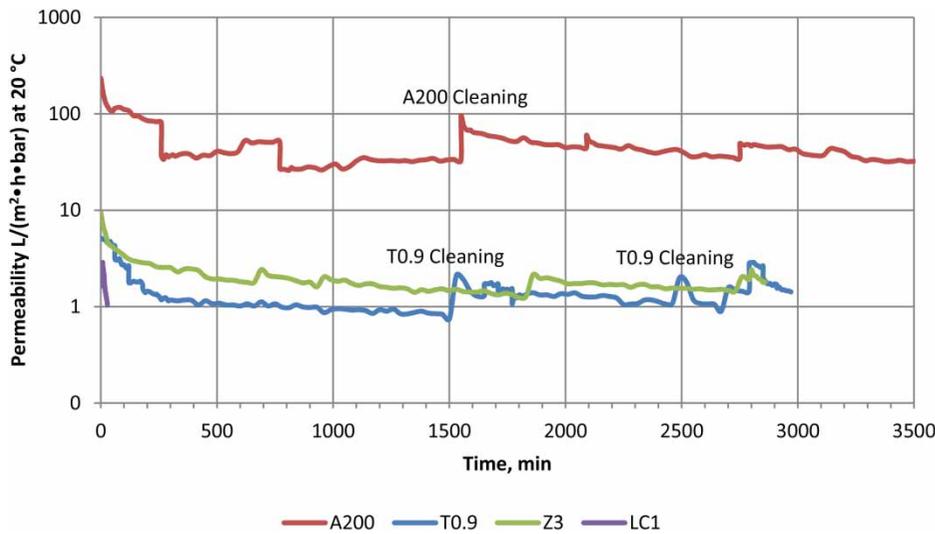


Figure 5 | Hydraulic permeability of all single-channel membranes operated with the inoMini unit.

**Pilot test results with the Atec-TF111**

**COD rejection**

Figure 6 shows the average COD rejection after 16 tests of all the membranes. The membrane combinations were categorized as: A200 + Z3, A200 + T0.9, A200 + LC1, Z3 + T0.9, Z3 + LC1 and T0.9 + LC1. The tests with the A200 as the first stage were performed three times for Z3, T0.9 and LC1-membranes. The inlet wastewater concentration (COD FEED WW) was always different, except for tests 14, 15 and 16, where the wastewater concentrate was used. The COD concentration in the permeate (COD PERM) was taken as the average from two modules, each of which contained three membranes.

The A200 + T0.9 combination showed the highest COD-rejection, from 86 to 96%. The maximum final COD concentration of the permeate was 48 mg/L. As can be seen, the rejection of the T0.9-membranes was always high, even when the inlet COD concentration was low as in Test 1 (17 mg/L).

The A200 + Z3 combination delivers a wider range of COD rejections from 68 to 95%. In Test 7, the COD concentration exceeded 80 mg/L. However, the value of 84 mg/L was taken as an average for both modules, whilst the three C25-Z3-membranes were new and the three C41-Z3-membranes were already used in Tests 2, 3 and 4. These new C25-Z3-membranes, which are designated as C25-Z3 in Figure 7, showed worse COD retention than the used C41-Z3-membranes. Tests 8 and 9

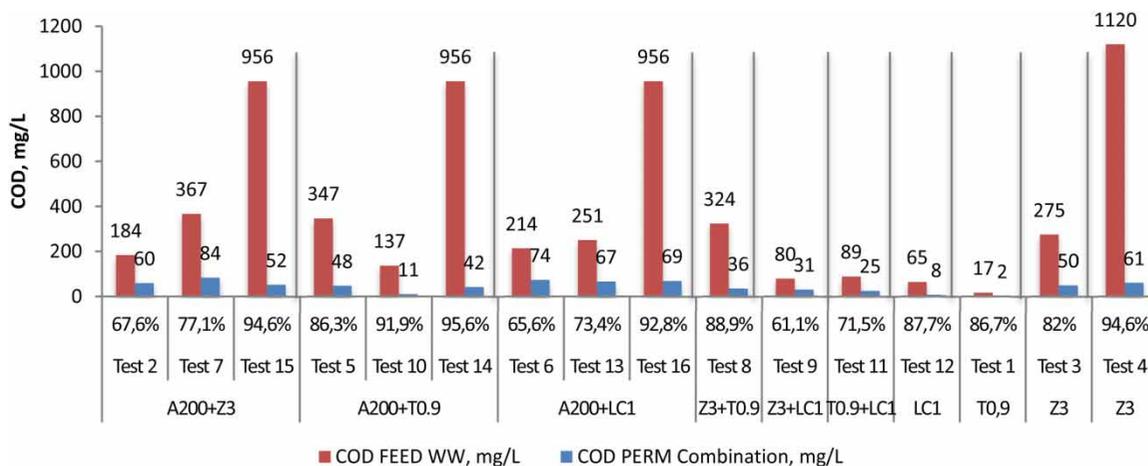


Figure 6 | COD rejection of all tests with multi-channel membranes using the Atec-TF111.

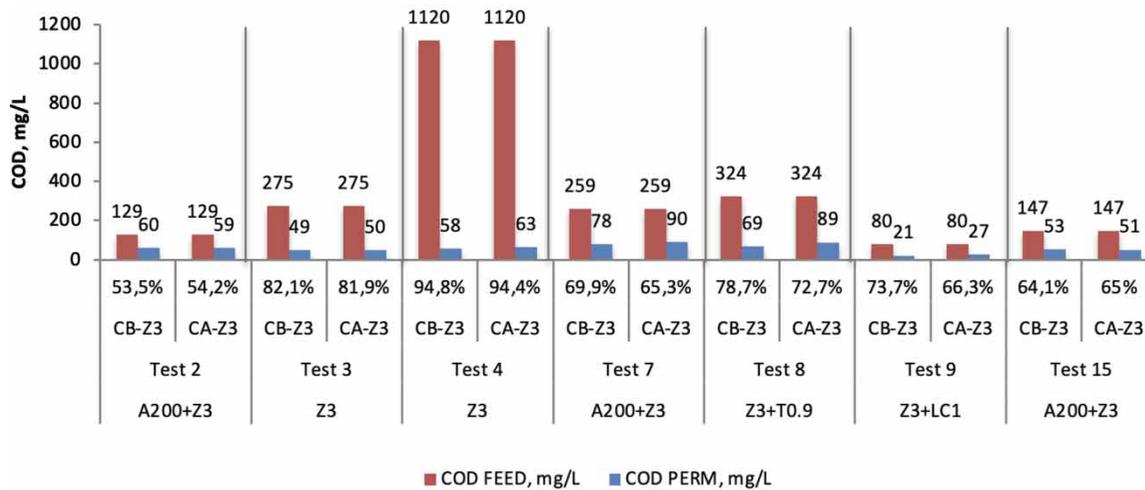


Figure 7 | COD-rejection of C25 and C41 geometries of Z3-membranes.

clearly demonstrate this, with the Z3-membranes working as both the first and second stage of filtration. It is noteworthy that by the 15th test, both types of membranes show almost the same characteristics. There is a possibility that there is a cumulative effect and the COD rejection of Z3-membranes increases after some time of filtration. None of the Z3-membranes have been chemically cleaned during the tests.

The A200 + LC1 combination exhibits a broad spectrum of COD rejections from 66 to 93%. The COD retention is comparable with that of the Z3-membranes but generally even lower. The maximum COD concentration in the permeate from the LC1-membranes was closer to the limit of 80 mg/L in comparison to the Z3-membranes but never exceeded it within the 15 tests.

The most indicative comparison of the combinations mentioned above showed the Tests 14, 15 and 16, where the same permeate of the A200-membrane was used for the second stage, so the T0.9-, Z3- and LC1-membranes worked in nearly the same conditions.

## TOC rejection

Suspended solids, which are present in the feed wastewater in large quantities, caused a lot of difficulties during the TOC measurements. Therefore, the analytical error of the feed is probably higher than of the permeate probes. This disadvantage of the TOC parameter was confirmed by other researchers (Dubber & Gray 2010; Wilderer 2011).

The A200 + T0.9 combination showed the best TOC-rejection from 85 to 93%, reducing the TOC from 161 to

12 mg/L (Test 14). The result is correlated with the COD rejection of the same combination (Figure 6).

The A200 + Z3 combination showed a wide range of TOC rejections from 58 to 87%, reducing the TOC from 161 to 21 (Test 15). The three C25-Z3-membranes in Test 7 were new and they showed a lower retention of the TOC than the used-once C41-Z3-membranes (in Test 8 as well). It is correlated with the COD-rejection results in the same test (Figure 7, Test 7). In Test 15, both geometries showed almost the same TOC retention/rejection. This again indicates the cumulative effect of C25-Z3-membranes.

The Z3 + T0.9 and the Z3 + LC1 combination showed almost the same retention of TOC – 55 and 57% – reduced the TOC from 82 to 37 mg/L and from 40 to 17 mg/L respectively.

The COD/TOC ratio of feed wastewater and permeate was always different, even when the same type of membranes were used. The COD/TOC ratio of the feed ranged from 0.7 to 6 (the highest was in Test 14, when the concentrate was used as the feed). The COD/TOC ratio of the permeate ranged from 0.92 to 2.65 for A200, from 0.57 to 2.53 for Z3, from 0.96 to 4.1 (Test 14) for T0.9 and from 1.13 to 2.89 for LC1-membranes.

## Ion rejection

The total ion rejection was analysed using the EC at 25 °C, which was varied in the range of 555 to 812  $\mu\text{S}/\text{cm}$  on the inlet. All the combinations with T0.9-membranes have the highest EC rejection from 26 to 44%. Test 14 showed the EC reduction from 726 to 479  $\mu\text{S}/\text{cm}$ .

The new C25-Z3-membranes and the used C41-Z3-membranes have different efficiencies in terms of the ion rejection. Certainly, the cumulative effect of C25-Z3-membranes is also present in this case. It should be noted that in case of a low inlet EC, the rejection of all the membranes except T0.9 was also low.

### Permeability

Figure 8 represents the permeability and COD rejections of all the membranes designed in all geometries (see Table 3), which were used with the Atec-TF111 unit. Only the wastewater from the collection basin or its concentrate (Tests 14–16) was used in the experiments. The chemical cleaning was performed once with N41-A200 and B25-A200-membranes before Test 14. The C41-A200-membranes were used only during the first 1,000 min of the filtration, then the new N41-A200 were used instead, until the end of the experiments. Three C25-Z3-membranes were changed after 340 min of filtration.

As can be seen from Figure 8, the permeability is not significantly affected by membrane geometry. The difference is noticeable at the beginning of the experiments, when the membranes are new. In the steady-state regime, the membranes' permeability look very similar. Therefore, the permeability through the membrane is guided by the membrane morphology (structure, pores size, etc.) and the fluid characteristics. This fact enables an average permeability for each membrane type to be taken, which is plotted in Figure 9.

The same pattern is observed for the COD rejection: most points on the chart coincide for different geometries. Small deviations can be observed mainly for the new membranes. The above is true only in the short-term experiments. There can be bigger deviations during the long-term tests, especially for the permeability.

C25 geometry showed a higher permeability in most of the cases, in comparison to the B25 and the N41 geometry; this applies to Z3, T0.9 and LC1-membranes. A decreasing of the COD does not always lead to an increase in the permeability (Figure 9, Tests 10 and 11).

The most stable periods of the membranes' performance were taken to calculate the average permeability. A200: 1,170–1,960 min; Z3: 970–1,080 min; T0.9: 300–1,600 min; and LC1: 560–740 min. The data are recorded in Table 5 together with the permeability of single-channel membranes and the reference data of Mulder (1996). It is clear that the average permeability of the multi-channel membranes is

higher than of the single-channel membranes. Most probably it was higher because of the air backwash. But the hydraulic (filtration) resistance was still relatively high, especially for UF- and NF-membranes.

Certainly, the permeability of any membrane is better appraised based on long-term test data, which is time consuming. However, the long-term test together with an evaluation of the power consumption was performed for the B25 and N41 geometries of the A200-membrane.

### Long-term test of A200-membranes

Figure 10 represents the first 100 hours of the 7-day test with the B25 and N41 geometries of A200-membranes. The chemical cleaning was performed before the test. As can be seen from the graph, the permeability differs more. Except for the first 1,300 hours of operation after the cleaning, the average permeability equals 68 and 48.7 L/(m<sup>2</sup>h·bar) for B25 and N41 membranes accordingly. So, the average permeability, which was calculated during the short-term test, (50.64) was a bit underestimated, in comparison to the long-term average permeability of 58.35 L/(m<sup>2</sup>h·bar).

The energy consumption in kWh per 1 m<sup>3</sup> was relatively high – 20.3 kWh/m<sup>3</sup> on average within 7 days. The cross-flow processes need between 2 kWh/m<sup>3</sup> and 10 kWh/m<sup>3</sup> (for MF and UF); and the dead-end processes consume much less energy (between 0.1 and 0.3 kWh/m<sup>3</sup>) (Pinnekamp & Friedrich 2003). Such a high energy demand is more likely to be comparable to RO, which typically consumes 18.2 kWh/m<sup>3</sup> ((Metcalf & Eddy 2003). On the other hand, Atec-TF111 is not intended for long-term operations. Besides, the Agitator R1, which maintained the cross-flow through the modules, but not the low- or high-pressure pumps, consumed most of the energy, which corresponds to Mulder (1996). It must be considered that the energy consumption depends on the membrane surface area as well. Potentially, the higher surface area of membranes provides the higher permeate permeability, so the spent energy per cubic meter of liquid is less in this case.

The COD feed concentration was 201 mg/L and it was increased in the working tank B2 after 4,270 min up to 5,200 mg/L. The COD concentration of the permeate was quite constant: it ranged from 86 to 122 mg/L for the B25 and from 85 to 123 mg/L for the N41 geometry. It is noteworthy that as the COD concentration in the B2 tank increased, the COD of the permeate decreased. Probably,

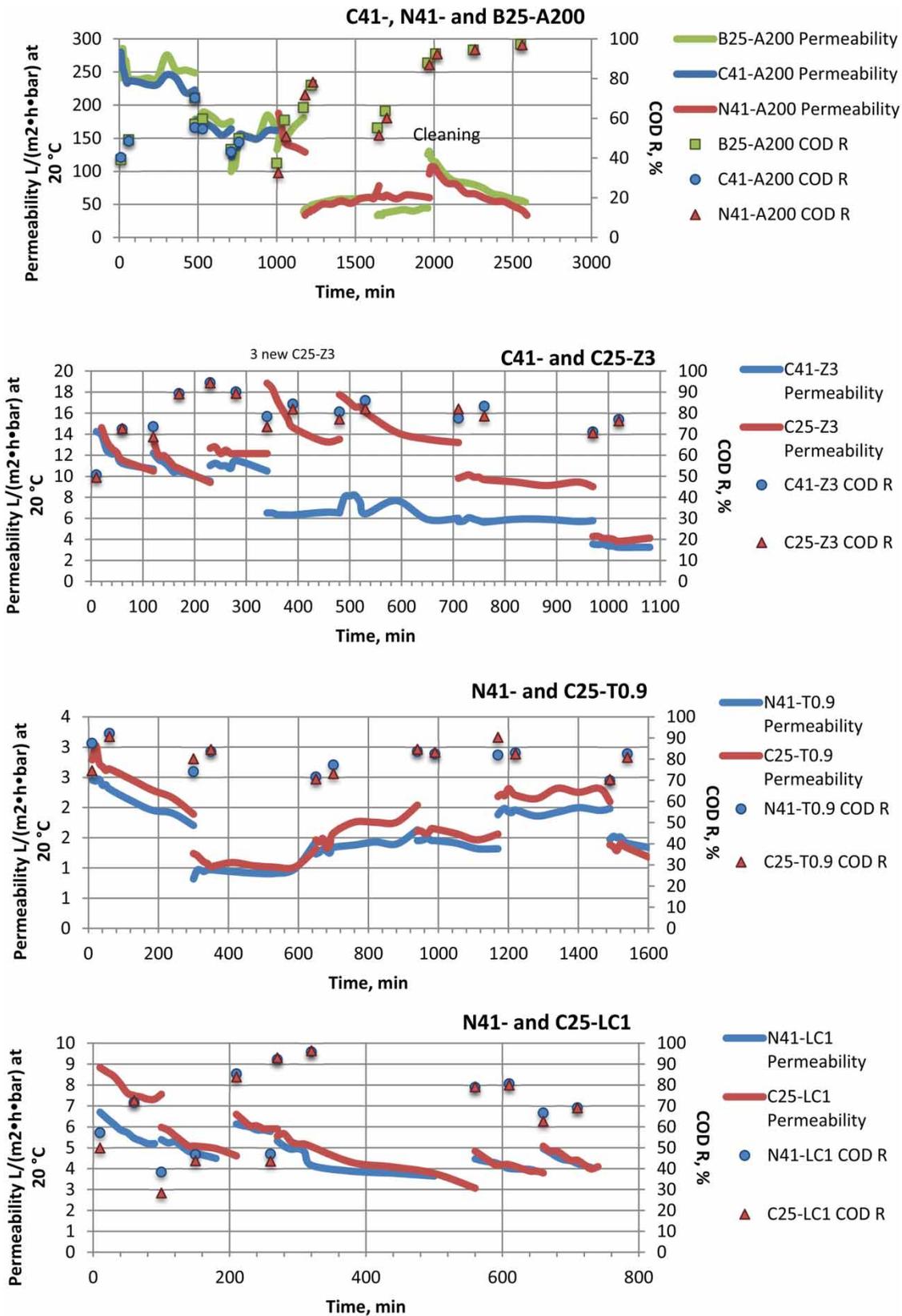


Figure 8 | Hydraulic permeability and COD rejection of all tested multi-channel membranes.

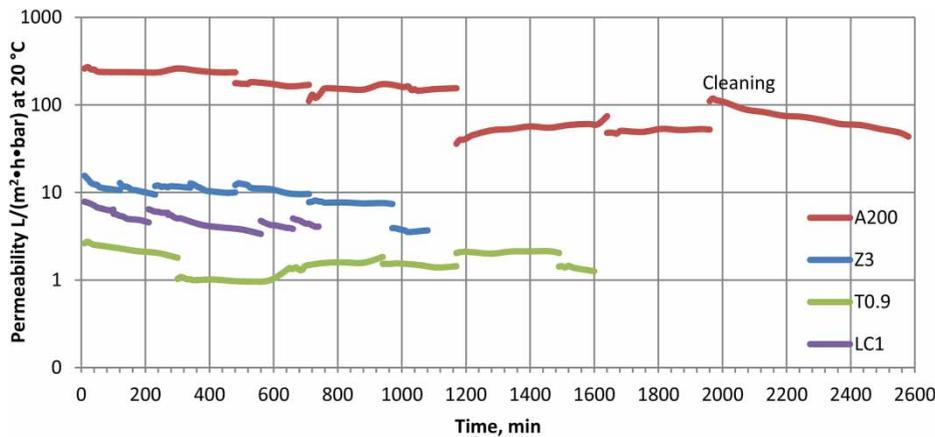


Figure 9 | Average hydraulic permeability of multi-channel membranes.

Table 5 | The average permeability in L/(m²·h·bar) of multi- and single-channel membranes

Membrane	Average permeability, L/(m²·h·bar) at 20 °C		
	Tests for B25, C41, C25 and N41	Tests for A10	Mulder (1996)
A200 (MF)	50.64	38.8	> 50
Z3 (UF)	3.76	1.76	10–50
T0.9 (NF)	1.51	1.08	1.4–12
LC1 (NF)	4.37	–	1.4–12

that the bacteria depleted oxygen but its consumption was still going on, since there was no ‘stationary phase’. Probably, the ‘longer-term’ BOD test was necessary. The measured wastewater parameters on day 0 are as follows: COD – 432 mg/L; TOC – 75.6 and NH<sub>4</sub>-N – 1 mg/L. The COD/BOD<sub>5</sub> ratio reached 3.82, which means that the wastewater is poorly biodegradable. However, the degradation is not completed. Moreover, the BOD<sub>5</sub> test was performed just once, which makes it impossible to judge the wastewater biodegradability accurately.

it is related to the contamination of the membranes and their partial pores blocking.

**BOD<sub>5</sub> test**

The BOD<sub>5</sub> was measured externally at KIT laboratory. The degradation curve had a rising shape, which confirmed

**CONCLUSIONS**

The following can be stated for single-channel ceramic membranes of 500 mm length and 7 mm internal diameter, which combinations were tested with an InoMini filtration test unit with ceramic wastewater:

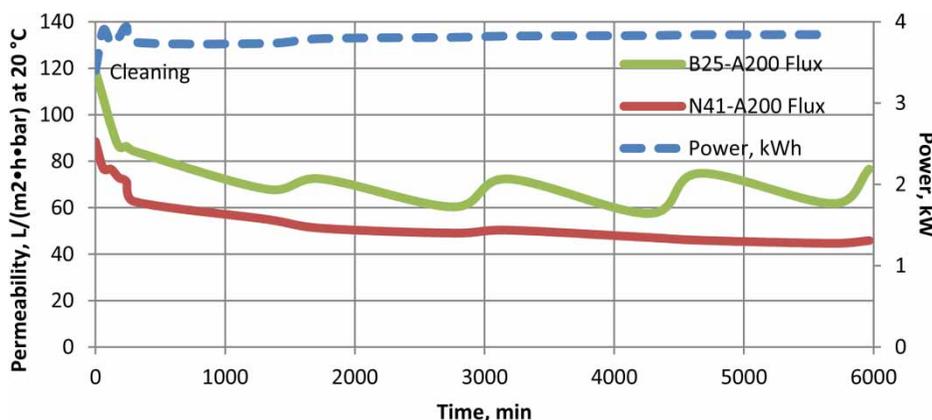


Figure 10 | Long-term test permeability of BA- and NA-A200-membranes.

1. The membrane combinations demonstrated high COD-rejection from 83.8 to 99.9% with a feed concentration from 34 to 7,300 mg/L and a permeate concentration from 2 to 51 mg/L.
2. The combinations of Z3 + T0.9, A200 + Z3 and A200 + T0.9-membranes showed the highest and very similar COD rejections at different feed concentrations. So, other evaluation criteria are needed to select the best combination: average permeability, chemical cleaning frequency or required pressure. The Z3-membrane provided the appropriate level of COD rejection and the second stage of filtration (T0.9) might be unnecessary.
3. The average permeability for A200-, Z3- and T0.9-membranes was 38.8, 1.76 and 1.08 L/(m<sup>2</sup>h·bar) at 20 °C accordingly. If 20 bar is considered for Z3- and T0.9- and 1 bar for A200-membrane, as it was set during the most of the experiments, the permeability of Z3 + T0.9, A200 + Z3 and A200 + T0.9 combinations will be 56.8, 74 and 60.4 L/(m<sup>2</sup>h) at 20 °C, which makes the A200 + Z3 combination the best.
4. In terms of the chemical cleaning, the combination of A200 + Z3 is the best because the Z3-membrane was never cleaned during the experiments in contrast to the T0.9-membrane, which was cleaned twice.
5. All the combinations demonstrated good ion rejection from 43.5 to 70%. The Z3 + T0.9 combination had the best performance and reduced the EC from 623 to 187 µS/cm. The A200-membrane also showed small ion rejection from 2.3 up to 6.5% probably due to the chemical bonding between the cations and negatively charged organic matter or due to fouling.

The experiments with multi-channel ceramic membranes of 1,200 mm length and 6, 3.5 or 2 mm internal diameter (7-, 19- or 151-channel tube accordingly), which were performed with an Atec-TF111 filtration test unit with ceramic wastewater, showed the following results:

1. The membrane combinations showed a COD rejection from 61.1 to 95.6% with a feed concentration from 80 to 1,120 mg/L and a permeate concentration from 11 to 84 mg/L.
2. The best COD rejection from 86.3 to 95.6% showed the A200 + T0.9 combination. Its permeate exhibited a COD concentration from 11 to 48 mg/L. The combination of A200 + Z3 showed similar results; however, the Z3-membranes showed rejections near the tolerance limit (80 mg/L) and the new Z3-membranes even exceeded it. In the same test conditions with the same permeate of A200-membranes used as the feed, both

Z3- and T0.9-membranes demonstrated similar COD values of the permeate – 52 and 42 mg/L – accordingly. The accumulation effect takes place and the Z3-membrane rejection increases due to the residues from the previous tests. The Z3 + T0.9 combination provided only 88.9% of COD rejection with a concentration of 36 mg/L in the permeate, which is comparable with the A200 + T0.9 combination; however, the last one provides more advantages in terms of the permeability and the pressure requirements.

3. All the combinations showed a TOC retention range from 54.5 to 92.7%. The best performance showed the A200 + T0.9 combination, which rejected 92.7% of the TOC with 12 mg/L in the permeate. The A200 + Z3 combination showed a little worse but comparable results at the same test conditions – 86.9% rejection with 21 mg/L in the permeate. The accumulation effect was also noticeable: new Z3-membranes had a lower TOC rejection than the used ones, similar to the COD rejection.
4. The average permeability for A200, Z3 and T0.9-membranes was 50.64, 3.76 and 1.51 L/(m<sup>2</sup>h·bar) at 20 °C accordingly. The permeability was taken on average for both geometries, which were used in the tests. The additional long-term test of six A200-membranes during 100 hours showed a higher difference between the B25-A200 and N41-A200 – 68 and 48.7 with an average of 58.35 L/(m<sup>2</sup>h·bar) at 20 °C.
5. All the membrane geometries of the same types of membranes showed similar permeability (L/(m<sup>2</sup>h·bar) at 20 °C) during the tests. For all types of membranes, the C25 geometry showed slightly higher permeability than the C41 geometry and the N41 geometry. The higher permeability of the C25 geometry in comparison to C41 can be explained by the higher volume of ceramic material in between the channels, which increases the permeability resistance. A large number of channels can also increase resistance, as the flow between the channels increases, so the permeability of N41 was lower than that of the C25 geometry.
6. The membrane combinations showed EC rejection from 5.2 to 43.7%. The best performance showed the A200 + T0.9 combination. All the combinations with T0.9-membranes demonstrated high EC rejection. The cumulative effect of the Z3 is also applicable to the ion rejection as it was in the case of COD and TOC.
7. The energy consumption during the MF filtration with A200-membranes per 1 m<sup>3</sup> of permeate was relatively high (20.3 kWh/m<sup>3</sup>) and comparable with RO. Usually, it is 2–10 kWh/m<sup>3</sup> (for MF and UF).

8. The BOD test result and the COD/BOD ratio, which equalled 3.82, showed the low biodegradability of the wastewater from the ceramic factory. However, the test was performed only once, the COD concentration was relatively high and the BOD test itself was performed during 5 days only. Roughly it can be estimated that bacteria can decrease the COD in the 5 days, but only in the amount of 113 mg/L from 432 mg/L (COD). Therefore, the efficiency of the biological process is about 26%. On the other hand, during the complex treatment even this efficiency can be used. It gives a lot of opportunities for the coupling of the membranes treatment with the traditional biological treatment. Moreover, the BOD test was done for the raw wastewater but how the bacteria behave themselves in the permeate or in the concentrate of the A200-membrane, is an interesting subject for new research.

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Ms. Dr. rer. nat. Gudrun Abbt-Braun.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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