Effective Treatment of Problematic Process and Wastewater with Ceramic Nano-Filtration Membranes

As part of the production changeover from the former manufacture of electrical porcelain and other silicate ceramics to the production of products made of high-purity oxide ceramics and ceramic filtration membranes, the composition of the wastewater stream changed significantly. As a result, the original wastewater treatment technology could no longer guarantee the required quality criteria. With the development of the following technology, Rauschert Kloster Veilsdorf GmbH/DE broke new ground. The study was conducted within the PAkMem Project no. 02WAV1407C.

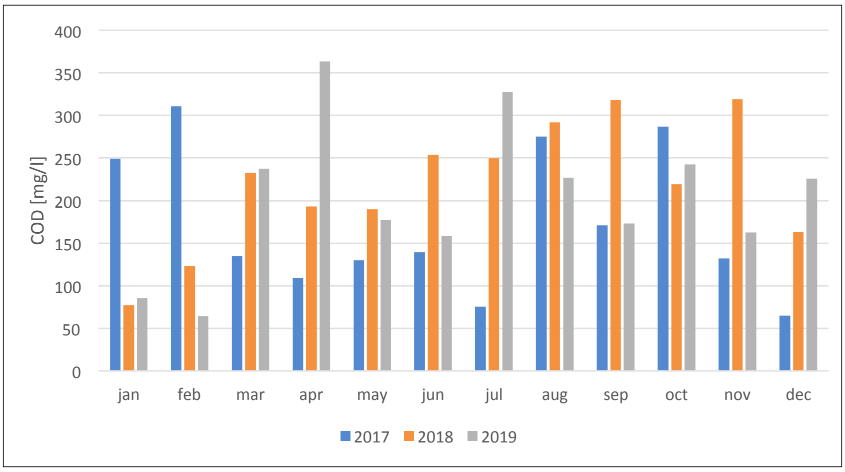

Fig. 1
Average monthly COD values of the feed over three years

1 Current situation and objective

At the Rauschert Kloster Veilsdorf site, the industrial wastewater flows were quantified and qualified. The following key data should be emphasised with regard to the material and volume flows:

- Volume flow of total wastewater maximum: 17,5–20 m³/d;
- Volume flow of total wastewater annual mean: 14 m³/d;
- COD (Chemical Oxygen Demand): approx 50–500 mg/l (measured in sedimentation basins);
- COD level from the current wastewater treatment plant: approx 50–180 mg/l
- Salt load measured as conductivity: approx. 360–820 µS/cm.

The wastewater is made up of the various production substreams. The following substances were present in the wastewater load: ceramic particles from Al_2O_3, TiO_2, and silicate production as well as small amounts of ceramic binder. As can be seen in Fig. 1, the COD load of the wastewater fluctuates monthly and yearly.

The pH value of the feed/wastewater is between 7–8, the temperature is close to ambient temperature (always >0 °C).

According to Annex 17 of the Wastewater Ordinance, a limit value of 80 mg/l must be observed for the chemical oxygen demand. The programme aims to achieve this. A further reduction below 80 mg/l would be a long-term goal. Further information on the quality standard can be found in Tab. 1.

Keywords
process and wastewater treatment, ceramic filtration membranes, microfiltration, nano-filtration, alumina tubes

2 Preliminary examination

Originally, this was started according to the usual project approach at inopor®.

The product/process idea for the solution usually follows the scheme (Fig. 2). The first

Volker Prehn, Christiane Günther, Armin Pabstmann
Rauschert Kloster Veilsdorf GmbH / inopor®
98669 Veilsdorf, Germany

E-mail: v.prehn@rkv.rauschert.de

Tab. 1
Framework conditions for a wastewater quality standard = objective in the project

Quality Standard	**Limit Value**
Chemical Oxygen Demand (COD)	</= 80 mg/l (corresponds to the requirements of the State of Thuringia)
Wastewater quantity:	</= 19 000 m^3/a
COD weight	685 kg/a
Total Suspended Solids (TSS)	</= 50 mg/l
pH range	6–8,5
N total	11 mg/l
P_{ges}	0,8 mg/l

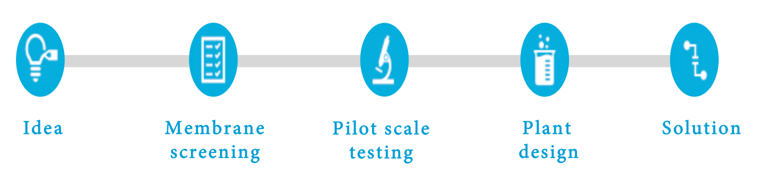

Fig. 2
Scheme of the product/process preliminary examination

Fig. 3
InoMini laboratory cross-flow filter system (also available via inopor®)

Fig. 4
Various membrane geometries that are manufactured by Rauschert Kloster Veilsdorf GmbH (brand inopor®)

Tab. 2
Membrane geometries and their properties (see also www.inopor.de)

Geometry	**Flow Channel Diameter [mm]**	**Number of Flow Channels**	**Outside Diameter [mm]**	**Filtration Area $[m^2/m]$**
AA	7	1	10	0,022
BA	6	7	25	0,132
CA	3,5	19	25	0,209
CB	6	19	41,4	0,358
EE	3,4	61	41	0,722
HA / NA	2	163 / 151	41	1,098 / 1,072

series of tests with 1-channel geometry were carried out on the InoMini laboratory system (Fig. 3). After successful tests with the inopor® nano-filtration membrane, the trials and tests for the process development began.

3 Pilot plant trials

3.1 Variation/membrane geometry / process temperature / cross flow velocity and pressure

Inopor® offers alumina tubes (Al_2O_3) in a wide variety of geometries (see also www.inopor.de), which could be used here. As standard, pipes are manufactured with a number of channels from 1–163 (Fig. 4).

Various membrane geometries were tested with the wastewater from the reservoir (production wastewater) – the aim of this step is to preselect the membrane geometry and the main parameters of the filtration technology for a later production plant (Tab. 2):

- No significant difference in flux could be determined for the various geometries.
- The influence of temperature on the flow through a membrane with A3 carrier and LC1 membrane is applied. When the temperature is increased from 23° C to 60° C, an increase in the flux from around 11 $l/(m^2 \cdot h)$ to around 15 $l/(m^2 \cdot h)$ can be observed.
- The pressure has almost no effect on the retention.

3.2 Systematic experiments on membrane backwashing and cleaning

Ceramic membranes have a particularly high chemical resistance to acids and alkalis compared to polymeric membranes [1]. Cleaning tests were carried out with acidic and alkaline membrane cleaners. Cleaning with the alkaline cleaner has proven to be effective. Cleaning with the acidic cleaner and subsequent alkaline cleaning was similarly effective.

3.3 Process combination for feed pretreatment and retention preparation

The expansion of the membrane filtration to include a flocculation process was also evaluated, but was proven to be impractical due to the requirements of the chemically different flocculants (acidic and basic). This path was therefore not pursued any further.

4 Field trials

4.1 Filtration tests with real process waters under production conditions

The pilot plant has been in operation since the end of November 2017 and automatically carries out backwashing. In Fig. 5, the times at which the membranes were cleaned are shown. As a rule, cleaning was carried out using acidic and then alkaline cleaning.

As expected, the cleanings caused the increasing of fluxes, but did not affect the retention. This basically confirmed the cleaning technology.

In the pilot plant, two different membrane geometries were tested in parallel over two periods as shown in Tab. 3. Three identical membranes were installed per module. The tests were carried out at 20 bar trans-membrane pressure in feed-batch mode. The storage container is completely emptied about twice a week, and the concentrate is transferred to a waste container. The system is neither heated nor cooled.

Fig. 6 shows the COD retention of the membranes tested. All membrane types show retention in the range >90 % over the majority of the measurement period. Values >95 % are often achieved, but this is heavily dependent on the initial concentration of organic matter (COD values) in the wastewater. No influence of the geometry (CA vs. NA) was found, regarding the retention. In this way, a comparable retention can be achieved with geometries with a large membrane area and up-scaling is successful.

Likewise, there was no significant influence detected by the choice of membrane (T09 vs. LC1) on the retention. It follows from this that the main impurities are so large that they are retained equally well by both types of membrane.

Fig. 7 shows the fluxes through the membranes. In Test 1, the NA geometry made from A4 material has a significantly lower flux than the CA geometry made from A3 material. In Test 2, the CA and NA geometries (both from A4) showed almost the same fluxes (based on the membrane area). Therefore, the flux differences to Test 1 are due to the different support materials.

In Test 2 only a slight influence of the geometry can be observed. In the first 20 days and after about 120 days, the flux of the CA geometry is slightly higher than for the NA

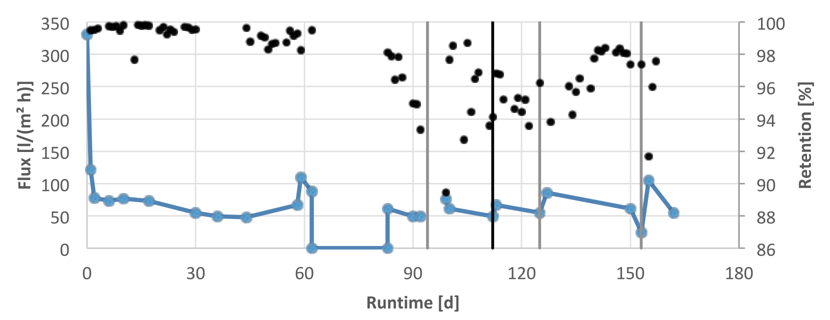

Fig. 5
Flux and retention of the CA geometry in the pilot plant against time

Tab. 3
Overview of the long-term tests carried out

Test	Date / Duration	Module 1	Module 2
(1)	2017-11-21 – 2018-04-27	CA A3 T09	NA A4 LC1
(2)	2018-06-27 – 2019-03-13	CA A4 T09	NA A4 T09
(3)	2019-09-10 – 2020-02-27	CA A3 T09	NA A3 T09

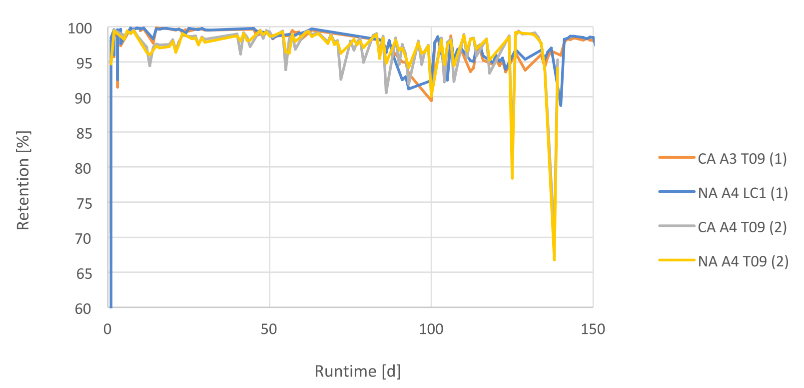

Fig. 6
COD retention during the long-term Tests 1 and 2

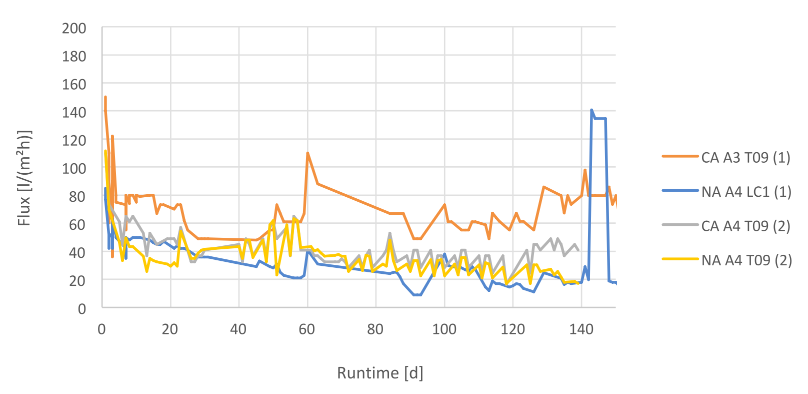

Fig. 7
Fluxes through the membrane during long-term Tests 1 and 2

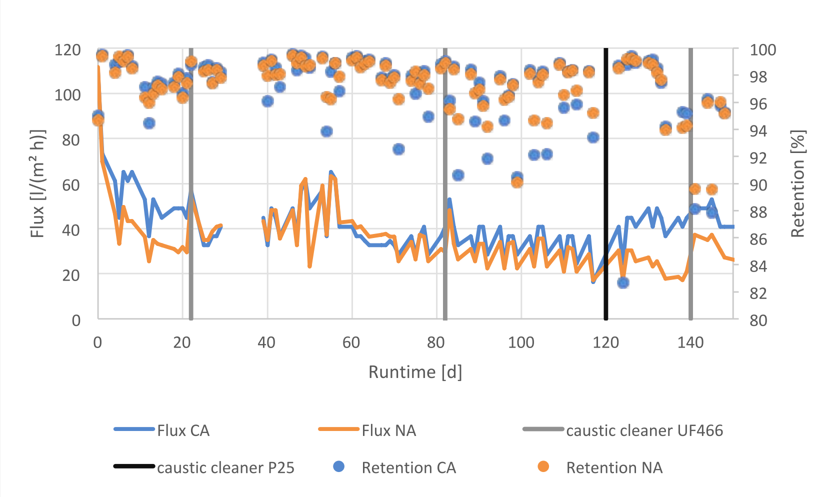

Fig. 8
Cleaning on Test 2

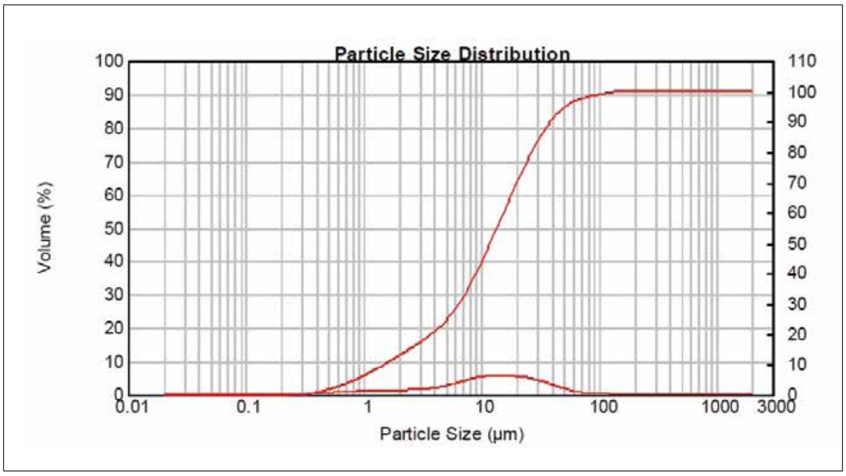

Fig. 9
Particle size distribution of the wastewater

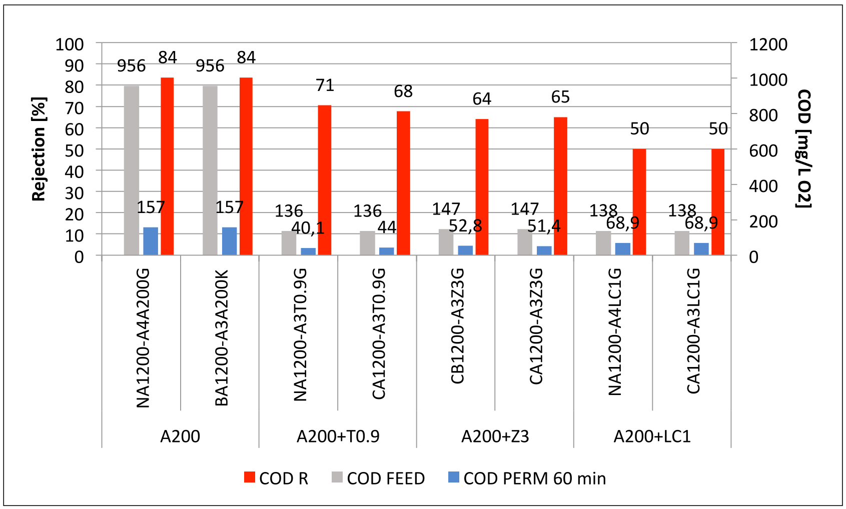

Fig. 10
Retention of the tested ultra-filtration and nano-filtration membranes after 60 min

geometry. As can be seen in Fig. 8, the differences were seen mostly after cleaning. Both support materials, both tested geometries and both layers are potentially suitable for the application. The NA geometry, however, has the larger membrane area and is therefore preferable. The T09 membrane is chosen because it is less costly than LC1. This results in the optimised final variant: NA A4 T09.

A two-stage filtration concept was considered helpful to further reduce the COD value. Tests were again started in the laboratory and continued on a pilot scale. The particle size analysis of the wastewater shows that the particles in the wastewater are over 200 nm in size (Fig. 9). Therefore, a membrane with a pore size of 200 nm was used for the first filtration stage.

The permeate of the first filtration stage was then filtered in the second stage with the 3 nm, T09 and LC1 membrane (Fig. 10). In the first stage, only as much permeate was produced as was necessary for the next stage. The following diagram shows the results of the tests.

Although the same feed was used for the Z3, T09 and LC1 membrane, the COD is slightly different. However, a slight change in COD over time is normal. The tests were carried out as quickly as possible in order to keep any change in the feed as small as possible.

The combination of A200 and T09 gave the best results. In relation to the COD of the output feed, the retention was 96 %. The COD of the concentrate of the first stage was about 4000 mg/l. In relation to this, the retention was 99 %.

4.2 Definition of operating regimes for continuous operation

The framework conditions for the operating regime are specified in Tab. 4.

5 Operation of pilot plants

5.1 Determination of the optimal operating point

The optimum operating point for the pressure was determined to be 20 bar. Tests have shown that if the pressure is increased by 100 % from 10–20 bar, the flux also increases by 100 % (Fig. 11). When the pressure was increased by 50 % from 20–30 bar, the flux increased by only 26 %. The retention was almost unaffected by the pressure.

5.2 Continuous test operation

In the preliminary tests, the two-stage filtration provided promising COD retention values, although only a few cubic meters of wastewater were filtered in these tests. In continuous test operation, the two-stage filtration was carried out with a significantly larger volume of wastewater. The filtration lasted several days for each test before conclusion, at which stage the concentrate container was emptied. Strictly speaking, this mode of operation is not a continuous operation but rather a batch operation with regular repetition, as is customary and can also be used in industrial applications.

5.2.1 Test 1

In a first Test, only the first stage (200 nm) was tested to find out how far the wastewater can be concentrated without problems. About 32 m³ was filtered within 7 days. As can be seen in Fig. 12, both the permeate volume flow and the COD of the permeate were at a relatively constant level, so the Test could have been carried out even longer. A very satisfactory result was achieved with the concentration factor of 140.

5.2.2 Test 2

In the second Test, the combination of micro-filtration (200 nm membrane) and nano-filtration (0,9 nm membrane) was tested, with intermediate buffering of the permeate before the second stage. Strictly speaking, this process involves two batch processes carried out one after the other, as shown in Fig. 13.

In Fig. 14, the permeate volume flow and the concentration factor of the micro-filtration stage are shown. At the end of the Test, the nano-filtration was started at a concentration factor of 110 (the MF level).

Fig. 15 shows the change of the COD in the concentrate and permeate over time. The COD in the concentrate no longer rose after 4 days and remained at a level of around 2000 mg/l. The retention based on the concentrate was thus just under 95 %. The COD in the permeate fluctuated around 100 mg/l.

Only the last two measurements showed increased values. The COD in the permeate seems to be independent of the concentration in the concentrate.

Fig. 16 shows the permeate volume flow and concentration factor during the subsequent test with the 0,9 nm membrane. The

Tab. 4
Overview of various parameters for continuous operation

Parameter	Value	
Pressure	>/= 20 bar	The preliminary tests have shown that a further increase in permeance is achieved at 20 bar compared to 15 bar
Temperature		The pilot plant is not cooled because the flux is better at higher temperatures without the COD retention being weakened
Operating mode		Feed batch

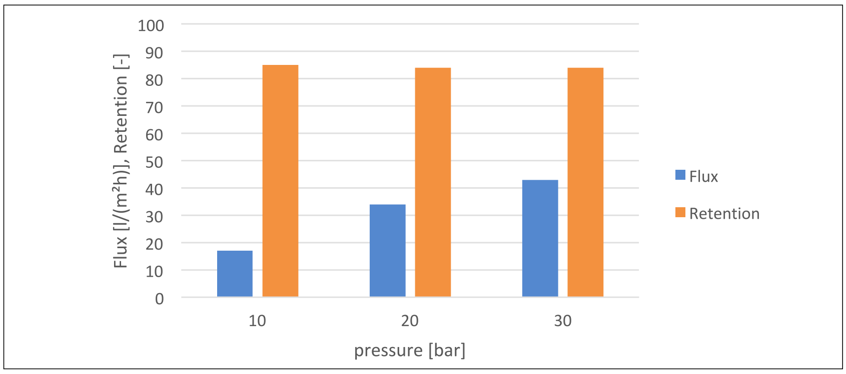

Fig. 11
Retention and flux of the T09 membranes at different pressures

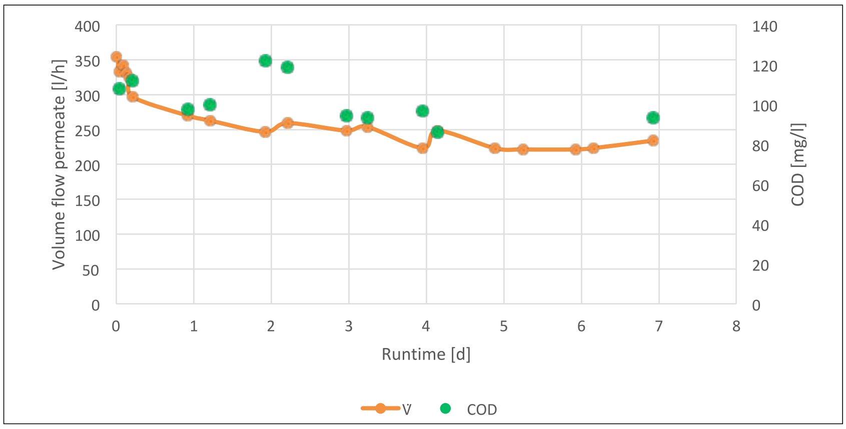

Fig. 12
Generated permeate volume flow and COD of the permeate during concentration with a 200 nm membrane (Test 1)

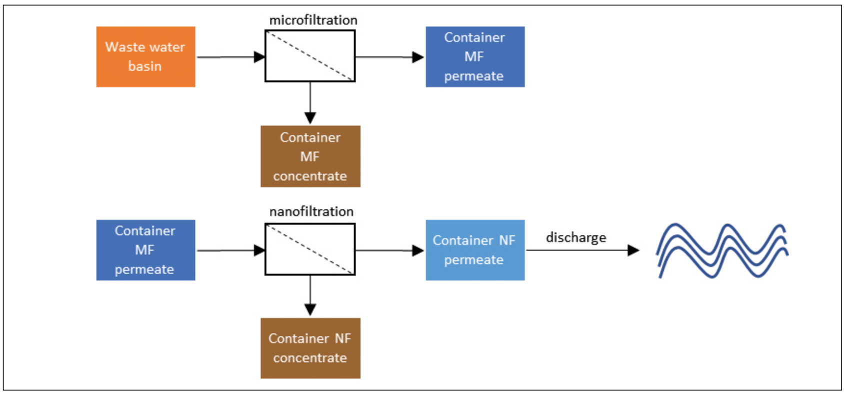

Fig. 13
Two-stage filtration scheme

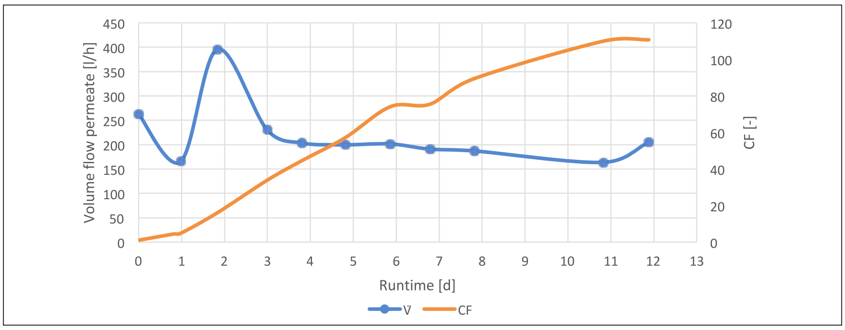

Fig. 14
Generated permeate volume flow and concentration factor CF during concentration with 200 nm membrane (Test 2, MF)

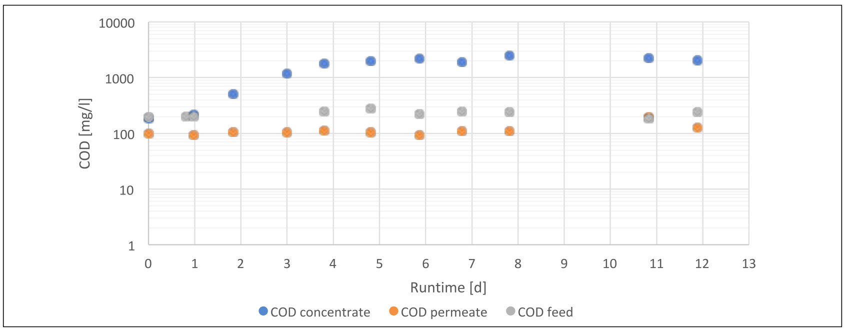

Fig. 15
COD in the concentrate and permeate with a 200 nm membrane (Test 2, MF) against time

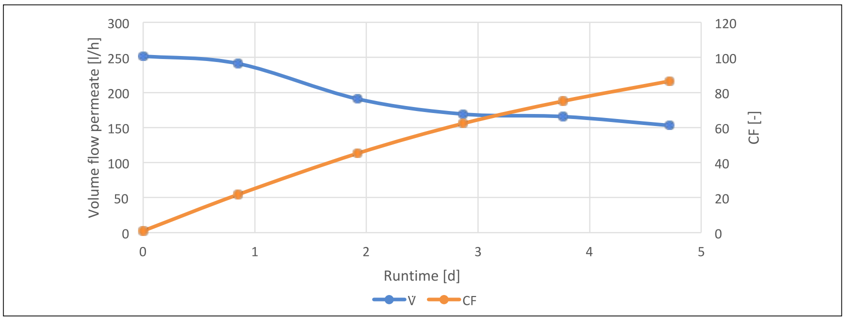

Fig. 16
Generated permeate volume flow and concentration factor CF during concentration with 0,9 nm membrane (Test 2, NF)

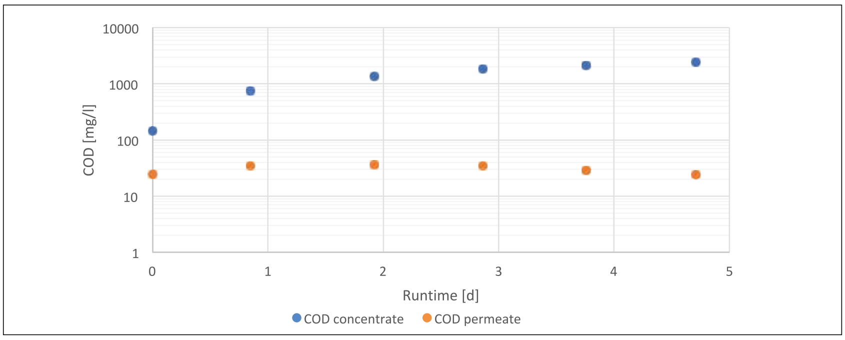

Fig. 17
COD in the concentrate and permeate with 0,9 nm membrane (Test 2, NF) against time

permeate volume flow decreased sharply from the first to the second day and then fell more slowly. A longer-term view would be interesting here; it can be assumed that the flow would stabilise similarly to the previous single-stage long-term filtration attempts. In the second stage of the two-stage filtration, the flow moves at a level similar to that in the single-stage filtration.
The COD values in the permeate after the second stage averaged 30 mg/l and are thus significantly better than the mean value for the single-stage nano-filtration (Fig. 17).

5.2.3 Test 3

In the third attempt, a repeat attempt for the two-stage filtration was carried out. After nano-filtration, an average COD value of only 6,1 mg/l was achieved in the permeate, which corresponds to a total retention of 97 %.
However, this retention is not exclusively due to the filtration, but is also due to a biological degradation in the collecting basin for the permeate. A growth of biomass in the collecting tanks was already noted in the preliminary test, hence the COD value in the collecting containers was monitored in the third attempt.
As can be seen in Fig. 18, the COD drops in the collecting basins and is thus below the mean COD value of the permeate produced. Tab. 5 shows the retention for the individual process steps. For the sake of completeness, the biological degradation of the COD in the collecting basins was considered as a single process step, but this was not the subject of the current investigations. In a filtration system on an industrial scale, this step would probably not occur, or be shorter in time, due to the large storage volume required for the permeate.
Therefore, a theoretical retention was calculated without the biological degradation in the collecting basins. This would still be 95 %, which would correspond to a COD of around 10 mg/l.
The calculation is based on the assumption that the bio-degrading has no influence on the retention of the subsequent NF.
However, the biological degrading may have a positive effect on the NF by breaking down membrane-permeable molecules or combining them to form larger molecules through chemical, biological or physical processes.

5.2.4 Comparison of the trials

The focus here is on COD retention, as this is the most important parameter. The retention was related to the COD of the feed (in contrast to the previous, above-mentioned reports, which were related to the concentrate). This improves comparability:

$$R = 1 - \frac{COD_{Permeate\_discharge}}{COD_{Feed}}$$

The two two-stage tests showed very good retention. A long-term test with two pilot systems is therefore very interesting for two-stage filtration.

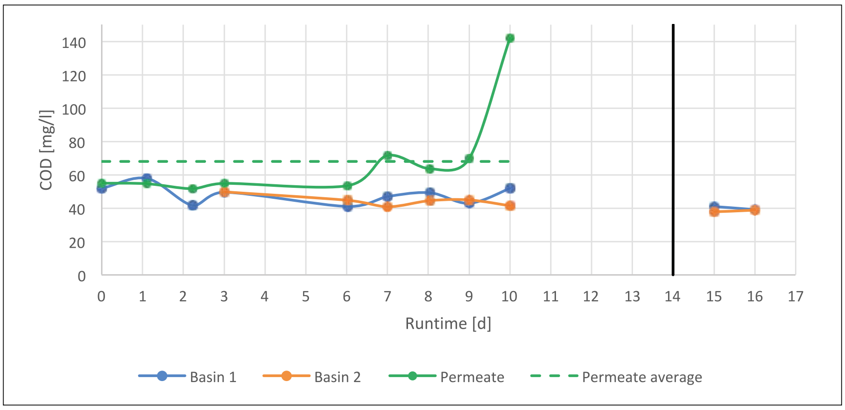

Fig. 18
COD values in the collecting basins in Test 3 against time

Tab. 5
Overview of the retention of the individual process steps of Test 3

Process Step	**COD Feed**	**COD Permeate**	**Retention (COD)**	**Retention without Basin (COD)**
	mg/l	mg/l	%	%
MF	200	68	66	66
Basin	68	40	41	
NF	40	6,1	85	85
Total			97	95

Tab. 6
Overview of the COD retention of various tests

Test	**COD Feed**	**COD Permeate MF**	**COD Permeate Discharge**	**Retention**
	mg/l	mg/l	mg/l	%
2 (MF+NF)	225	117	30,4	86
3 (MF+NF)	200	68	6,1	97

5.3 Optimisation

The strong fluctuations in wastewater quality mask the effects of subtle changes in the parameters so much that no causal change could be determined. The parameters as shown in chapter 6.1 are therefore considered to be the optimum.

5.4 Use and evaluation of the water

Regular reuse of the treated wastewater, e.g. as rinsing water is not sensible in the given structural circumstances, since large amounts of the permeate would have to be kept and the supply to the supply points requires additional investments. In the case of new or expansion investments, it makes sense to consider this approach, as the purity of the wastewater allows it to be reused in certain washing steps.

6 Recovery and recycling

6.1 Deriving and creating a process description

There are several conceivable methods that can be considered for wastewater treatment. The piloted option here is nano-filtration with upstream micro-filtration (Fig. 19). For the micro-filtration, 200 nm membranes of the EE geometry are used, with a channel diameter of 3,4 mm, because the solids load in the micro-filtration and the targeted concentration factor of 100 should be relatively high. The trans-membrane pressure will be 1,5 bar in normal operation. At this pressure, a good permeate flow with a low tendency for blockage can be expected. The backwash is set at intervals.

T09 membranes are used for nano-filtration. The HA variant is selected as the pipe geometry, as it offers the largest filtration surface and the solids load is low. The trans-membrane pressure will be 20 bar in normal operation.

Both systems are operated without cooling, as a higher temperature would increase the permeate flow without significantly affecting the COD retention. In a plant on an industrial scale, the use of a heat exchanger to heat the cold feed from the storage tank by means of the warmer permeate is worth considering.

According to the results of the preliminary tests, a concentration factor of around 100 should be achievable in both filtration stages. With an automatic filtration system, the concentrate will be pumped out when the appropriate amount of permeate has been generated.

A corresponding long-term test is currently running (beyond the scope of the project).

6.2 Economic/ecological evaluation

From an ecological point of view, the two-stage filtration reduces the amount of waste to be removed, the cleaned wastewater is returned to the natural water cycle without additional treatment if it is discharged directly or, if used as rinsing or production water, reused. From an economic point of view, a two-stage cross-flow filtration is cost-intensive, especially on the investment side.

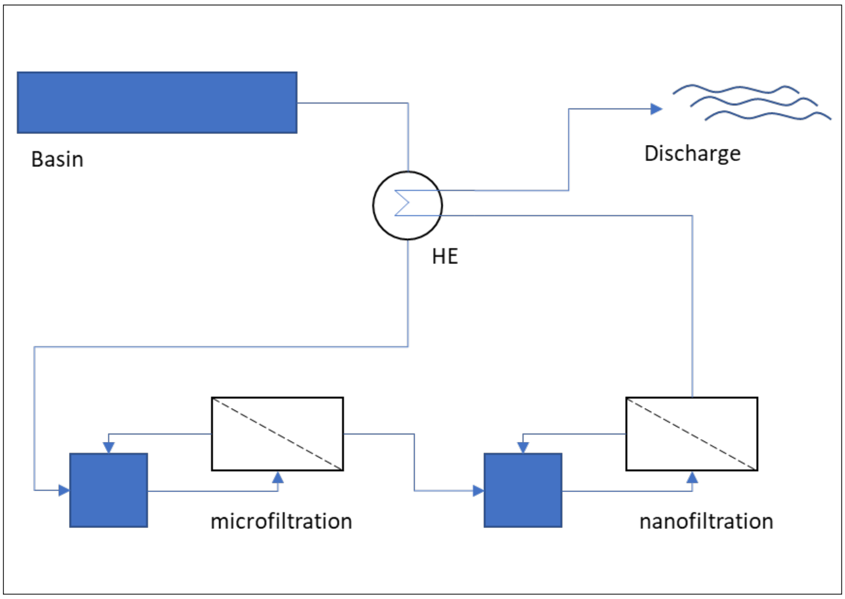

Fig. 19
Process principle of two-stage filtration

To reduce the investment costs, depending on the local conditions – if holding basins or tanks are available – a lower cost microfiltration stage based on the use of ceramic flat membranes can be implemented.

7 Summary

The functionality of the process could be clearly demonstrated through the project described. The procedure can be transferred to similar wastewater requirements, though in individual cases, some of the tests (chapter 2) must be carried out to allow verification and adjustments if needed. In both micro-filtration and single-stage nano-filtration, the membranes were run under “heavy” conditions (wastewater with mineral as well as biological load). Even under these conditions, the fouling could be kept at a commercially acceptable level by regular cleaning. The advantages and disadvantages of the tested method are summarised again here. Depending on the operational and local conditions, use in membrane bio-reactors can be offered as a supplement or alternative.
Advantages and disadvantages are:

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- No use of chemicals such as flocculants (exception: membrane cleaning cycles);
- Small footprint, especially compared to biological water purification;
- Compact construction;
- Long service life of the system/s and membranes;
- Automatic operation with little need for service personnel is possible;
- Fluctuations in the wastewater are tolerated;
- Operating downtimes can be planned without problems;
- The investment costs will break even over the operating time.

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- Transferability of the process requires wastewater analysis and possibly process adjustments;
- Relatively high investment costs.

Acknowledgment

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