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Title
Interim report
Removal of particulate matter by ceramic membranes during surface water treatment

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Summary

This study examines ceramic membranes in pilot scale to remove particulate matter from pretreated dam water, sampled at a full scale water treatment plant. Micro- and ultrafiltration membranes made from different materials such as alum oxide (Al_2O_3) or silicon carbide (SiC) were considered.

The ambition was to examine the influence of membrane pore size and membrane material on operation and on removal of nanoparticles and phages. Moreover, alternative cleaning methods for ceramic membranes were tested.

This report describes interims results of still ongoing examinations.

Available results indicated that SiC/SiO_2 membranes seem to initiate a similar increase of total membrane resistance during filtration of dam water compared to Al_2O_3 membranes. Fouling mechanisms of ceramic and polymeric membranes were found to be different, resulting in lower total membrane resistances for ceramic membranes during filtration of dam water.

Ozone could be a promising alternative method for CIP or CEB of ceramic membranes fouled with organic substances as results of preliminary tests showed.

MS2-phages were removed by ceramic ultrafiltration membranes without dosing a flocculant with an efficiency of about 2 log for 50 nm pore size membranes and about 3 log for 10 nm pore size membranes.

Contents

1 Introduction

Micro- and ultrafiltration membrane applications for particle removal have been rapidly increased in public drinking water supplies in recent years. Among numerous innovations in this sector ceramic membranes are attracting an increasing interest. Ceramic membranes are considered as resistant to mechanical, chemical and thermal stress. A high porosity and a hydrophilic surface are additional advantages which may open various fields for applications in water treatment including the direct treatment of surface waters.

Ceramic membranes are not applied in European public drinking water supply in large scale, today. However, there are a number of producers in Europe, developing and producing ceramic membrane elements for industrial applications.

The objective of this study is to identify advantages and disadvantages of ceramic membranes compared to existing polymeric membranes to remove particles from surface water drinking water treatment. The focus was set to examine the influence of membrane pore size and membrane material on operation and on removal of nanoparticles and phages. Moreover, alternative cleaning methods for ceramic membranes were tested.

2 Materials and Methods

2.1 Membranes

Ceramic membranes, different in pore size, membrane material, channel diameter and producing company were examined in this study. As summarized in Tab. 2.1, microfiltration membranes were made from alum oxide and silicon carbide. Alum oxide ultrafiltration membranes included products with and without an additional TiO_2 membrane layer. Ultrafiltration membrane pore sizes ranged from 50 down to 10 nm. Membranes from four producers were considered in this study.

Tab. 2.1:Characteristics of ceramic membrane elements for pilot examinations

pore size nm	**membrane material**		**channel number per element**	**channel diameter mm**	**area test module m²**	**producer**
200	a-Al_2O_3		7	6	0.13	A
100	a-Al_2O_3		19	3.3	0.20	B
50	a-Al_2O_3		19	3.3	0.20	B
50	a-Al_2O_3	TiO_2	7	6	0.13	A
50	a-Al_2O_3	TiO_2	19	3.3	0.20	C
10	a-Al_2O_3	TiO_2	19	3.3	0.20	C
500	SiC/SiO_2		37	3.4	0.43	D
200	SiC/SiO_2		37	3.4	0.43	D

2.2 Pilot plant

Pilot examinations were conducted in a waterworks using dam water as source water. Fig. 2.1 shows a simplified treatment chain of this waterworks. Treatment steps include a rapid sand prefiltration, ozonation, flocculation, dual media sand filtration followed by limestone filtration and disinfection.

Water from the effluent of the rapid sand prefiltration and from the effluent of flocculation step were used as feed for a ceramic membrane pilot plant (Fig. 2.2). The pilot plant was developed in co-operation with membrane-engineering GmbH Salem, Germany and was operated fully automated. Previous examinations showed that dead-end mode was more relevant for water treatment compared to cross-flow mode. Therefore dead end mode was applied in all runs. Transmembrane pressure was held constant at 2 bar and decline of flux during filtration was monitored online. Membranes were operated without CEB. CIP was conducted as described below:

(1) Alkaline at pH 12-13 with 3 mg/L Chlorine @ 1 h contact time
(2) Acidic at pH 2 with a commercial membrane cleaner containing nitric and phosphoric acid @ 1 h contact time

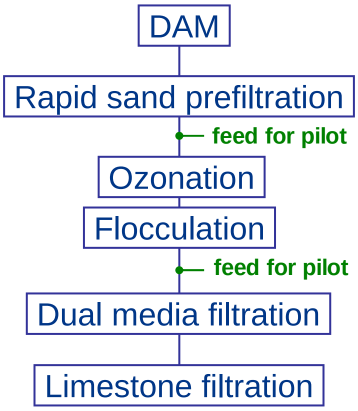

Fig. 2.1: Simplified treatment chain of waterworks, location of pilot examinations

Fig. 2.2: Ceramic membrane pilot plant

2.3 Nanoparticle analysis

Nanoparticles were determined by using a nanoparticle analyzer base on Laser Induced Breakdown Detection (NPA/LIBD). LIBD is a highly sensitive method to detect nanoparticles in the size range between 10 to 1,000 nm. NPA/LIBD measurements were conducted in grab samples from feed and filtrate. Every analysis bases on triple sampling and detection. NPA/LIBD analysis was provided by Research Center Karlsruhe, Germany.

2.4 Characterization of organic foulants

Organic foulants were characterized by Liquid Chromatography Organic Carbon Detection (LCOCD). LCOCD is based on fractionation of background organic matter (TOC). Typical fractions include humic substances, low molecular weight substances, neutral and amphiphilic substances, polysaccharides and natural hydrophobic substances. Polysaccharides are considered as major membrane foulants (Jarusutthirak et al. (2002), Laabs et al. (2003), Kimura et al. (2004)). LCOCD analysis was conducted in feed as well as the alkaline CIP-wastes of membranes. Samples in this study were prefiltered by 1.2 µm.

2.5 Detection of phages

MS2-bacteriophages were cultivated and detected according to DIN EN ISO 10705-1. For spiking a phage stock solution of ca. 10^{12} pfp/mL was prepared. 10 mL of this stock solution was added to 10 L of water with drinking water quality (sampled after rapid sand prefiltration, ozonation and flocculation, dual media filtration) in a 25 L container. After mixing the phage solution was filled into the 200 L raw water tank of the pilot plant containing 150 L of treated dam water, thus resulting in a feed concentration of approximately 10^7 pfp/mL.

A volume of 10 – 20 L of spiked treated dam water was filtered through the ceramic membranes. Phages concentration was measured in the feed and the filtrate. The membrane was backwashed with 10 – 20 L filtrate. For reproducibility this procedure was repeated three times for each membrane tested. Mass balances were applied by considering phages concentration in the spent membrane backwash water, the filtrate and the feed.

3 Results and Discussion

3.1 Membrane resistance of SiC and Al_2O_3 microfiltration membranes

Microfiltration membranes with a pore size of 0.2 µm made from alum oxide and from silicon carbide were compared during filtration of a dam water after ozonation (0.8 mg/L O_3) and Flocculation (1.1 mg/L Al). Alum oxide membrane was operated with a filtration intervall of 5 hours compared to 2.5 hours for the silicon carbide membranes. Conditions of operation were summarized in Tab. 3.1.

Tab. 3.1: Conditions of operation for ceramic microfiltration membranes

parameter		**0.5 µm SiC**	**0.2 µm SiC**	**0.2 µm Al_2O_3**
Clean water flux virgin membrane @ 2 bar	L/m^2/h	1,953	1,674	2,123
Initial feed water flux @ 2 bar	L/m^2/h	749	520	1,056
Filtration interval	s	9,000		18,000
Backwash duration	s	30		60
Backwash media		water pulsed air 2s on /2s off		water pulsed air 2s on /5s off
Backwash flux	L/m^2/h	approx. 5,000		

Total membrane resistance was choosen as parameter to compare silicon carbide and alum oxide membranes. As can be seen from Fig. 3.1 both 0.2 µm membranes showed a similar behaviour during operation. This indicates that isoelectric point (IEP) seems to have a minor influence on organic fouling processes for the feed water tested. However, further studies are required in this field.

Surprisingly, 0.5 µm SiC membrane showed a more rapid increase of total membrane resistance compared to the 0.2 µm SiC membrane. The rapid increase of the 0.5 µm SiC membrane resistance was verified in a second run, which may be also seen in Fig. 3.1. One explanation may be a stronger particle fouling for the 0.5 µm membrane. A determination of the nanoparticle diameter in the feed by NPA/LIBD showed a mean number weighted particle diameter of 192 to 218 nm, which could cause a more comprehensive pore blocking for the 0.5 µm membrane compared to the 0.2 µm membrane. However, further examiniations are necessary to explain this effect.

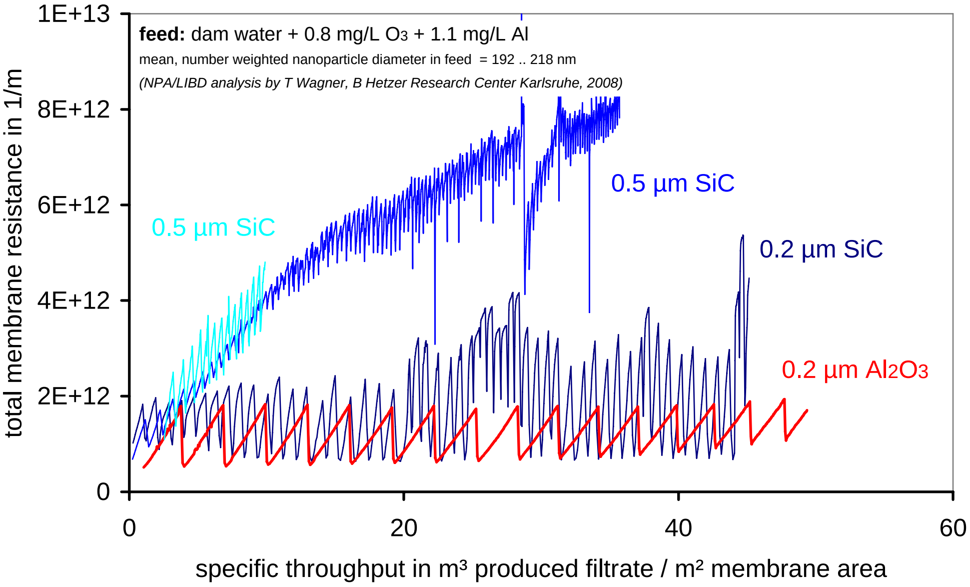

Fig. 3.1: Total membrane resistance of Al_2O_3 and SiC/SiO_2-microfiltration membranes during filtration of preflocculated and preozonated dam water

3.2 Comparison of Al_2O_3 ultrafiltration membranes

Three Al_2O_3-ultrafiltration membranes produced by three different manufactures were compared by total membrane resistance during filtration of clean water (drinking water). Two membranes are characterized by a pore size of 50 nm. (producer A and B). The third membrane had a pore size of 10 nm (producer C). As can be seen from Fig. 3.2, the membrane of producer B is characterized by a higher membrane resistance compared to the membrane with the same pore size from producer A. The better operating behavior of membrane A could be due to general membrane design and production process. The 10 nm ultrafiltration membrane (producer C) shows a somewhat higher resistance compared to the 50 nm membrane of producer A.

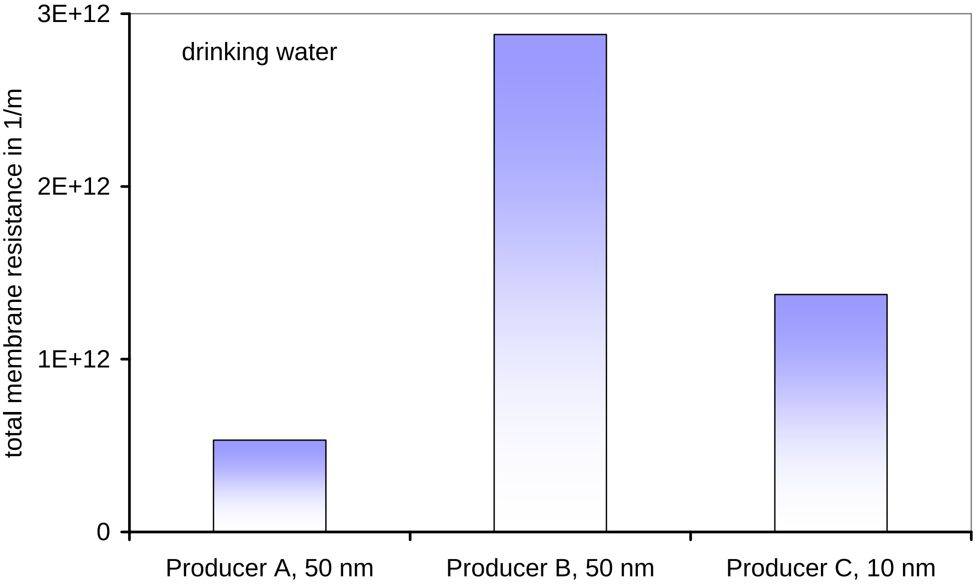

Fig. 3.2: Total membrane resistance of different ceramic ultrafiltration membranes during filtration of drinking water

3.3 Membrane resistance ceramic and polymeric ultrafiltration membranes

Increase of total membrane resistance of a polymeric and a ceramic membrane during filtration of prefiltered dam water was compared by parallel operation of the ceramic membrane pilot plant and an additional pilot plant with polymeric membranes. Ceramic ultrafiltration membrane elements are characterized by a pore size of 50 nm. Channel diameter was 6 and 3.3 mm according to 0.13 and 0.2 m² total membrane area used in a first and in a verification run, respectively. The additional pilot plant includes two modules with polymeric membranes with a pore size of approximately 20 nm and a total membrane area of 8 m². Feed for both pilot plants was dam water after rapid sand prefiltration.

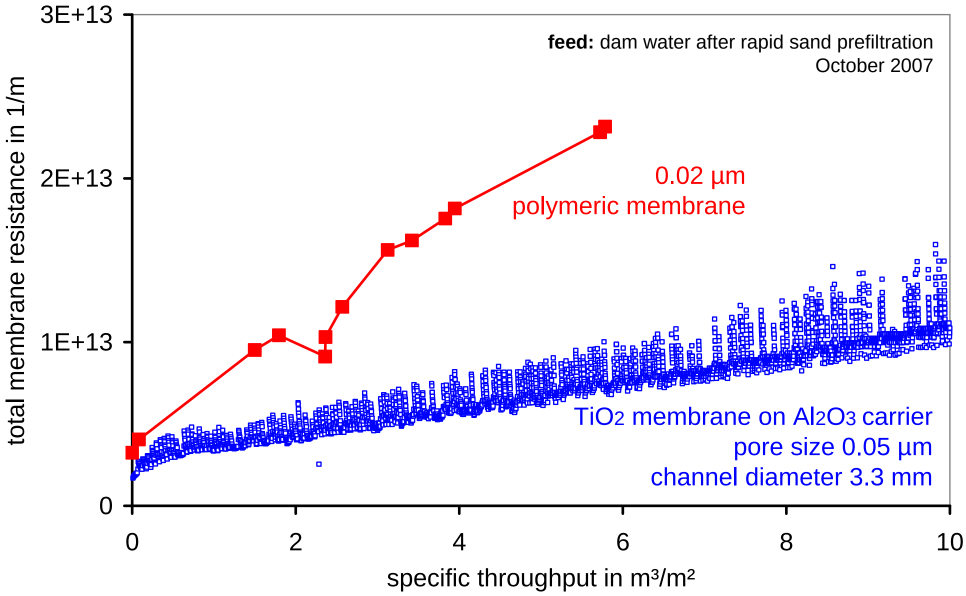

Fig. 3.3: Comparison of total membrane resistances of a ceramic and polymeric ultrafiltration membrane

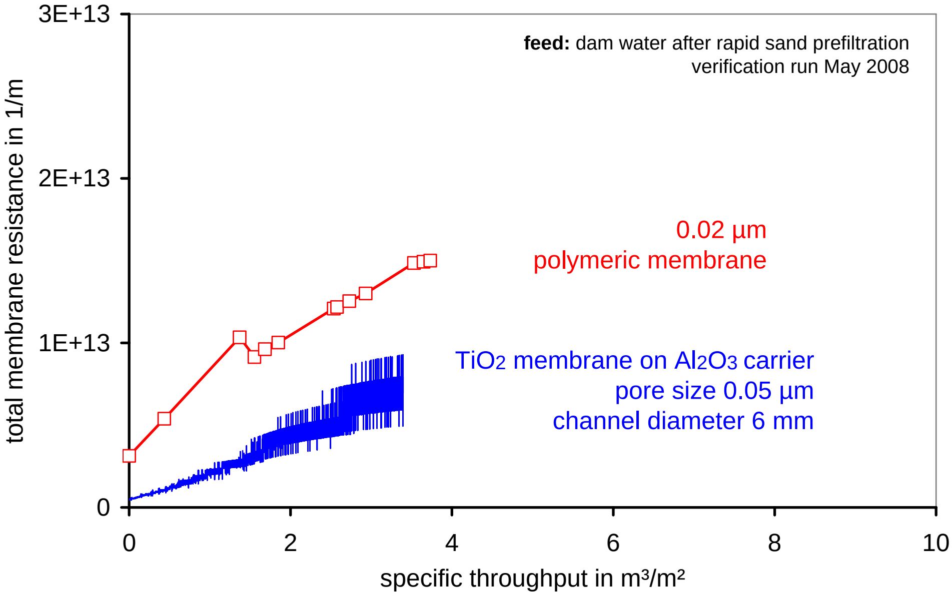

Fig. 3.4: Comparison of total membrane resistances of a ceramic and polymeric ultrafiltration membrane (verification)

Fig. 3.3 shows the total membrane resistance for ceramic and polymeric membranes in dependence of specific throughput. The increase of total membrane resistance was higher for the polymeric compared to the ceramic membrane. The results were verified with another ceramic membrane element with the same material and pore size as described above and the same polymeric membrane modules after CIP (Fig. 3.4). To illustrate the filtered water volumes, fluxes of polymeric and ceramic membranes were contrasted in Fig. 3.5. Opposite to the previous discussed comparison on the basis of total membrane resistence comparison of fluxes is limited, due to somewhat different transmembrane pressures (TMP) during operation. TMP of the ceramic membrane was helt constant at 2 bar. TMP of polymeric membrane fluctuated with an average of 1.5 bar. Nevertheless, the flux of the polymeric membrane is much lower compared to ceramic membrane. It is to consider, that the polymeric membrane has a smaller pore size and probably a lower porosity. However, pore size specified by manufacturers may be difficult to compare, due to various methods available to characterize pore size. Nanoparticle removal is comparable for both membranes, which will be discussed in Chapter 3.6.

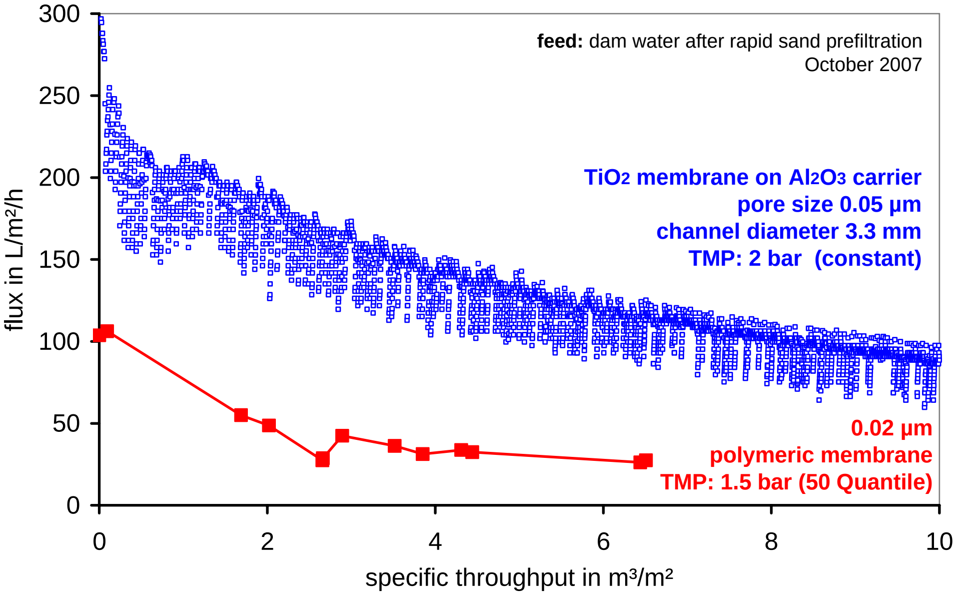

Fig. 3.5: Comparison of fluxes for a ceramic and polymeric ultrafiltration membrane

3.4 Characterization of fouling behaviour of ceramic and organic membranes

Polymeric and ceramic membranes were loaded during filtration with prefiltered dam water as described in the previous chapter. Both membranes were cleaned at pH 11. Alkaline CIP-waste was examined for composition of organic substances by LCOCD.

According to Fig. 3.6 CIP-waste of polymeric membrane contained a higher polysaccharides fraction compared to CIP-waste of the ceramic membrane. Humic substance fraction was higher in the CIP waste from the ceramic membrane compared to the polymeric membrane.

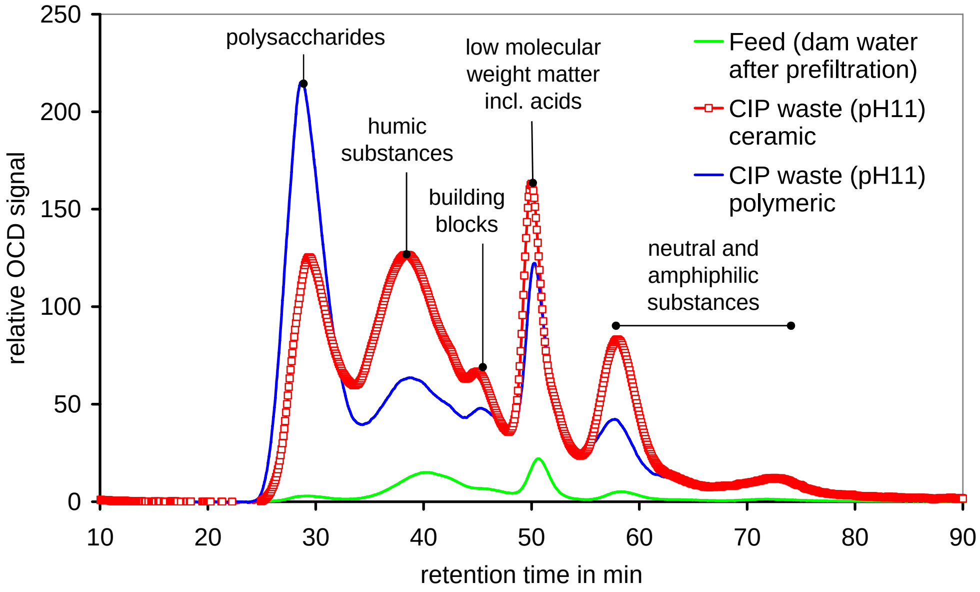

Fig. 3.6: LCOCD examination of alkaline CIP-waste from a ceramic and a polymeric ultrafiltration membrane

TOC fractions as determined by LCOCD were summarized in Fig. 3.7 for the run discussed above and an additional run for verification. The fraction, which was not detectable by LCOCD was described here as "hydrophobic TOC". Both runs showed similar results. According to thus the relative polysaccharide fraction in CIP-waste was higher for the polymeric membrane compared to the ceramic membrane. Polysaccharides are assumed to be a major foulant. This indicates that the ceramic membrane show a lower potential for organic fouling compared to the polymeric membrane for the water tested in this study.

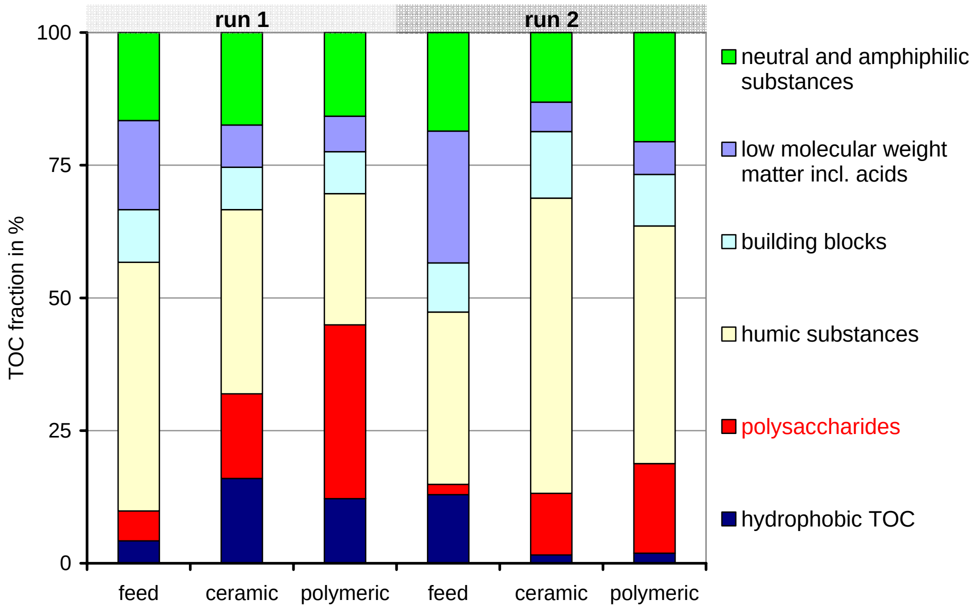

Fig. 3.7: TOC-fractions determined by LCOCD of alkaline CIP-waste from ceramic and polymeric ultrafiltration membranes

3.5 Alternative cleaning methods for ceramic membranes

Ceramic membrane characteristics include a resistance against chemical, mechanical and thermal exposures. For an efficient use of these features, alternative methods for cleaning (CIP) or chemical enhanced backwash (CEB) including chemical or physical practices could be developed. Advantages and disadvantages of hypothetical practices are summarized in Tab. 3.2.

Tab. 3.2:Hypothetical methods for CEB and CIP of ceramic membrane

Principle	Example	Advantage	Disadvantage
Chemical	– Ozone – AOP	without chlorinated by-products	– efficiency depends on foulant type – resistant housings / pipes required
Physical	Heat up	high efficiency	– energy consumption
	Ultrasound	without by-products	– complex design – membrane damage – wave injection
	Mechanical (e.g. Abrasive media)	without by-products	– complex operation – limited efficiency

Preliminary tests were conducted with preloaded membranes. Objective was to identify directions for further, more detailed examinations.CIP was performed by some methods mentioned above. Effect of CIP was compared to total membrane resistance of virgin membrane. Total membrane resistance was always determined by filtration of drinking water.

CIP by ozone was started by preparing an ozone containing water. Ozone containing water was transferred carefully in a narrow container similar to a membrane housing. Preloaded membrane was inserted into the container. The membrane was soaked in ozone containing water for certain contact times. Ozone concentrations were determined before inserting and after removing the membrane from the container. Ozone dosages were reported as average of both concentrations.

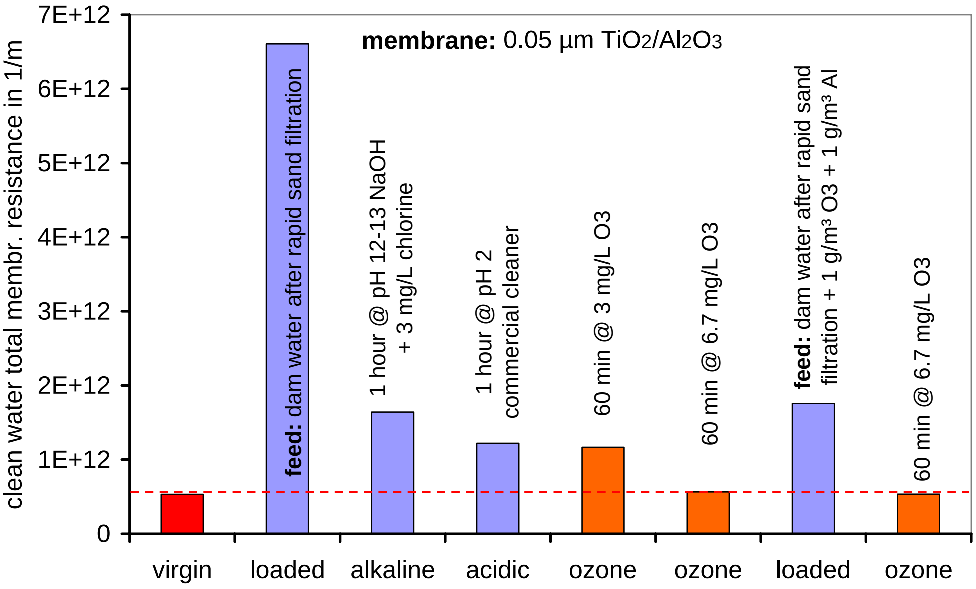

Fig. 3.8: Effect of different CIP-methods for a ceramic ultrafiltration membrane

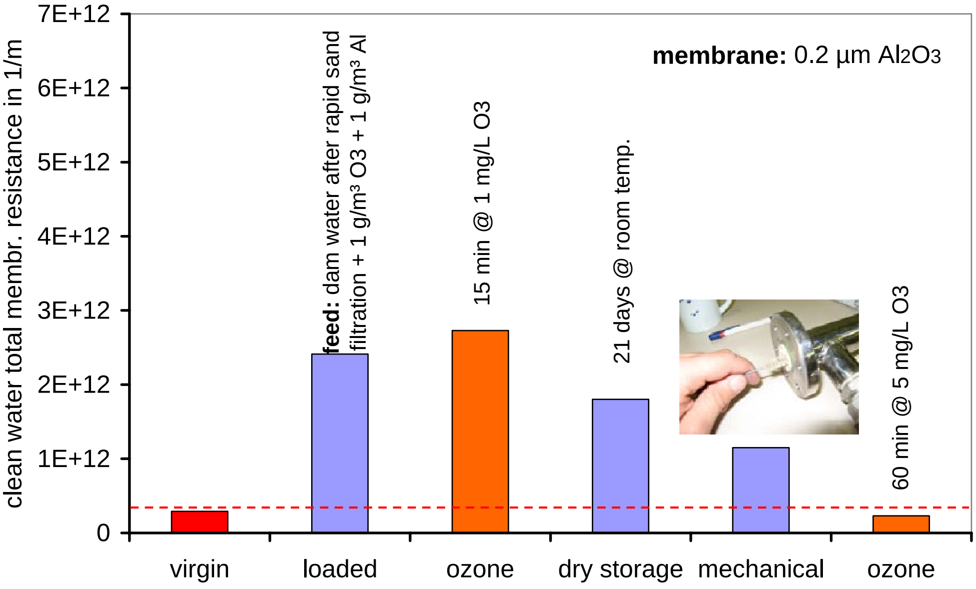

Fig. 3.9: Effect of different CIP-methods for a ceramic microfiltration membrane

Fig. 3.8 shows total membrane resistance for a ceramic ultrafiltration membrane. Virgin membrane was characterized by a total membrane resistance of $5.3*10^{11}$ m^{-1}, which was increased by loading with prefiltered dam water to $6.6*10^{12}$ m^{-1}. Due to the elevated concentration of humic substances in feed water (about 2 mg/L TOC) alkaline CIP was much more effective compared to acidic CIP. An ozone dosage of 3 mg/L for one hour contact time was considered as too low for CIP. However, increasing ozone dosage to about 7 mg/L decreased the total membrane resistance to the amount of the virgin membrane. The same effect of CIP by ozone was found for the membrane loaded with prefiltered, preozonated and flocculated feed water.

For CIP of a ceramic microfiltration membrane an ozone dosage of 1 mg/L at a contact time of 15 min showed no effect as can be seen in Fig. 3.9. Full capacity of the membrane was restored by applying 5 mg/L ozone for one hour contact time. Mechanical cleaning was simulated by scrubbing each membrane channel with a brush. Effect on total membrane resistance was relatively low, indicating that fouling occurred not only on the membrane surface.

3.6 Removal of nanoparticles

Nanoparticles were determined in filtrates of ceramic and polymeric ultrafiltration membranes. Nanoparticles were detected using a Nanoparticle Analyzer based on Laser Induced Breakdown Detection (NPA/LIBD).

Tab. 3.3 summarizes mean nanoparticle diameters and nanoparticle volumes in filtrate of a ceramic membrane. They base on a 50 nm TiO_2/Al_2O_3 membrane during filtration of dam water, prefiltered by a conventional rapid sand filter. To extend the database analytical data from additional polymeric ultrafiltration membranes operated in various pilot and full scale plants were included in this comparison. Nanoparticle diameters and volumes in filtrates tend to show similar efficiencies for polymeric and ceramic membranes.

Tab. 3.3:Nanoparticles in filtrates of ceramic and polymeric ultrafiltration membranes (Analysis by T Wagner and B Hetzer, Research Center Karlsruhe)

Membrane	Mean particle diameter in nm	Nanoparticle volume in nL/L	Number of readings
0.05 µm TiO_2/Al_2O_3	12 - 16	0.044 - 0.18	2
various polymeric UF membranes	12 - 176	0.1 - 9.7	15

3.7 Removal of phages

Different ceramic membrane materials (SiC/SiO_2, TiO_2/Al_2O_3 und Al_2O_3) with pore diameters of 200 nm, 50 nm und 10 nm were tested for phage removal efficiency. The 200 nm SiC/SiO_2 and the 50 nm Al_2O_3 membranes were also tested after preloading with prefiltered dam water. The results are summarized in Tab. 3.4. Feed had drinking water quality (dam water after prefiltration, ozonation, flocculation, dual media filtration) and was spiked with *MS2*-phages.

Tab. 3.4:Removal efficiency of MS2 phages depending on membrane material, pore diameter and preloading

Membrane characterization				**Removal efficiency of *MS2* phages**		
Material	**Manu-facturer**	**Pore diameter**	**Condition**	**Feed**	**Filtrate**	**Removal**
		nm		**pfp/mL**	**pfp/mL**	**log**
SiC/SiO_2	D	200	after CIP	1.50E+05	7.80E+04	0.3
SiC/SiO_2	D	200	preloaded	9.33E+06	1.20E+07	-0.1
TiO_2/Al_2O_3	A	50	after CIP	2.43E+07	7.20E+05	1.5
Al_2O_3	B	50	virgin	2.41E+07	3.27E+05	1.9
Al_2O_3	B	50	preloaded	2.04E+07	1.85E+05	2.0
TiO_2/Al_2O_3	C	10	virgin	2.81E+07	2.20E+04	3.1

The average size of the *MS2*-phage is about 24 nm in diameter. For the 200 nm SiC/SiO_2 membrane (after CIP) no significant phage removal was obtained and preloading of the membrane had no effect on phage retention. This is already known from Al_2O_3 microfiltration membranes indicating that membrane surface charge should be negligible compared to pore size for phages removal.

Among the 50 nm membranes a removal of 1.5 to 2.0 log was calculated. This difference in the log-removal between the 50 nm membranes tested is considered to be not significant, however. Preloading the Al_2O_3 membrane had also no effect on removal efficiency.

The highest removal efficiency of 3.1 log was achieved for the virgin 10 nm TiO_2/Al_2O_3 membrane. However, considering the theoretical pore diameter of the membrane and the size of the *MS2*-phages higher removal rates were expected. Further examinations to this topic will be undertaken to verify these results.

4 Conclusion

The report describes interims results of ongoing examinations.

Available results indicate that a SiC/SiO_2-microfiltration membrane tend to cause a similar increase of total membrane resistance during filtration of dam water compared to an Al_2O_3-microfiltration membrane. The understanding of the influence of ceramic membrane material on particle removal requires further examinations, however.

Fouling mechanisms of ceramic and polymeric ultrafiltration membranes were estimated to be different, resulting in lower total membrane resistances for ceramic membranes during filtration of dam water tested in this study. A lower potential for organic fouling of ceramic membranes compared to polymeric membranes is considered as an additional advantage for the introduction of ceramic membranes for treatment of natural waters.

Removal of *MS2*-Phages by ceramic ultrafiltration membranes showed removal rates between 2 and 3 log without dosing a flocculant. Further investigations on this topic are in progress.

5 Acknowledgements

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