Enhanced removal of micro-pollutants by hybrid processes combining flocculation or adsorption with ceramic flat sheet membrane filtration

Pascal Erdmann [1], Fin Florack [1], Martin Josef Kaschek [1], Miriam Sartor[1*]

[1]*Faculty of Computer Science and Engineering Science, :metabolon Institute, Gustav- Heinemann-Ufer 54, 50968 Cologne, Germany ,*
Email : miriam.sartor@th-koeln.de

ABSTRACT

Hybrid processes combine unit operations in one step to achieve an improved water or wastewater treatment. They overcome the different disadvantages of the individual unit operations. Different approaches to remove micro-pollutants - especially persistent organics as well as phosphate residues - by hybrid processes consisting of ceramic flat sheet membrane filtration combined with flocculation or adsorption were investigated. The target of the studies was to improve the quality of treated sewage effluent (TSE) to protect the ecosystems from micro-pollutants such as pharmaceutical residues and/or forever chemicals like e.g. PFAS and allow a reuse of water. Therefore, ceramic flat sheet membrane filtration was combined with a flocculation process (cake layer filtration) to remove dissolved and colloidal organics from treated sewage effluent and to co-precipitate phosphate. By combining ceramic flat sheet membranes with powdered activated carbon adsorption (active cake layer filtration) persistent trace organics and forever chemicals were efficiently removed from surface water.

Keywords: membrane filtration; ceramic membranes; cake layer filtration; micro-pollutants

1.   INTRODUCTION

Growing awareness for environmental pollution, the poor quality of water bodies and the impairment of the environment as well as contaminations caused by anthropogenic substances are becoming focus of society. This increasing awareness is also driven by the constant improvement of chemical analysis technology: stepwise it is possible to detect and measure even the smallest amounts of chemical substances quantitatively and qualitatively. Due to the continuous improvement of analytical methods, the extent of pollution is becoming drastically clear. The synthesis of various persistent substances, which are released into ecosystems, causes continuously greater problems, e.g. sterilization of fish or the accumulation of harmful substances in food. Microplastics, organic trace substances like drug residues or their metabolites as well as phosphates are proven to accumulate in rivers and deteriorate the quality of the water. [1], [2], [3], [4] To prevent chronic diseases of humans or animals and to avoid the destruction of entire ecosystems these persistent, hazardous, toxic and often bioaccumulating pollutants need to be removed from the water. Often the trace substances were emitted in the past,

where they were released carelessly and partly without knowledge of their environmental hazard. The list of detected dangerous (micro-) pollutants that should not be released into nature or need to be removed thereof is growing continuously. In particular, ingredients used in pharmacy as well as microplastics and even phosphates enter ecosystems through the sewage and the treated sewage effluent (TSE) as the conventional sewage treatment plants cannot retain or mineralize these contaminants. Conventional wastewater treatment plants work with three purification stages [5]:
- Mechanical treatment for the removal of coarse particles and oil,
- Biological treatment for degradation of organic carbons and nitrogen compounds (as well as in some cases biological phosphate elimination, bio-P),
- Chemical treatment for phosphate elimination.

The removal of many of the undesired substances from wastewater is currently not completely possible with the three mentioned conventional clarification stages [2], [3]. The different kinds of micro-pollutant cause severe problems for ecosystem and human health: Although

phosphate removal technologies were installed in sewage treatment plants decades ago, they cannot eliminate phosphate fully [6] and up to 1.0 μg/l are released into the rivers. On average in the years 2012 to 2016 about 22 kilotons of phosphorus per year were discharged into the German water bodies: The share from sewage treatment plants was around 30 % [7] and has hardly decreased in recent years. However, especially in combination with nitrogen compounds the residual phosphate promotes eutrophication in the receiving water bodies leading especially during summer time to a collapse of the entire ecosystem [8]. Persistent organics like e.g. drugs and their metabolites harm the growth of duckweed, lead to sterilization of fishes or have toxic effects on aquatic organisms while other persistent organics like e.g. PFAS are suspicious to cause cancer or other diseases in human [9]. More than 100 medical active substances or their metabolites were detected in German sewage treatment plants. In surface waters approx. 130 pharmaceuticals or their metabolites were found. Isolated concentrations above 1.0 μg/l were measured [10]. Further, microplastics accumulate in rivers and surface waters, which can have far-reaching consequences for organisms [11]. Laboratory studies have shown, for example, that exposure to microplastics reduces the fertility of copepods [2]. Further studies showed that microplastics accumulate in the digestive tracts of mussels and fish and can lead to inflammation [2].

1.1 Overcoming challenges in water supply by micro-pollutants

In order to relieve receiving water bodies from the above-mentioned substances and to avoid further pollution of drinking water sources and impairment of ecosystems, the installation of a fourth purification stage for sewage treatment plants is discussed in Germany since years [4], [7]. However, the optimum treatment in terms of effectiveness and (resource) efficiency is still under investigation. Traditional activated carbon adsorption [12] including fine-powder activated carbon processes [13] or other adsorbents [14] are considered. To increase the removal efficiency of the residual organics also ultra- or nanofiltration steps [15], [16] are investigated. However, the mentioned processes are limited either due to efficiency, material costs (e.g. adsorbents, membranes) or energy consumption and there is a demand to develop treatment processes facing these objections.

In the study presented different approaches to remove micro-pollutants, especially persistent organics as well as phosphate residues, were studied. The approach is the utilization of hybrid processes consisting of ceramic flat sheet membrane filtration in combination with flocculation or adsorption. The target of the investigations was to find approaches to improve the quality of treated sewage effluent to protect the ecosystems from micro-pollutants and surface water for drinking water production.

This research is in line with the discussion in membrane science claiming that for breakthrough implementation of membranes especially in environmental science new processes need to be investigated rather than new materials to be developed. [17].

1.2 Membrane filtration and ceramic flat sheet membranes

In membrane filtration at low pressure (microfiltration and ultrafiltration) there are two options for filtration direction through the membrane [5]. For inside-out-filtration the water is pressed from inside the membrane module through the membrane layer itself to the outer side, while for outside-in-filtration the water flows from the outer side of the membrane module to the inside. In general, both variants offer procedural advantages and disadvantages and their selection is a decisive step for the projection of membrane processes and system integration. As the core difference lies in the direction of the water flow through the membrane and thus the place of accumulation of the separated substances, outside-in-filtration is the relevant filtration direction for the hybrid processes.

Furthermore, the driving force as pressure difference for water transport through the membrane can be realized in two ways [5]. Pressure-driven membrane filtration (tubular membranes) apply a pressure on the membrane module while for systems with submerged membranes (hollow fibres, flat sheet membranes) the driving force is a suction pressure. Pressure-driven membrane filtration processes lead to the formation of a relatively dense filter cake. Thus, a high resistance for the water passage lead to an increase of the energy required to continue the filtration. To allow continuous filtration energy consuming cross-flow water stream is used to minimize the cake-layer formation. [18] The operation of membranes as a submerged system with a suction pressure allows the formation an almost non-compressed filter cake leading to a low energy consumption.

For the hybrid processes ceramic flat sheet membranes in the filtration direction outside-in-filtration were selected as submerged system (Figure 1). Thus, the rejected particles in standard filtration for particle removal, flocculants or the adsorbents (active material in case of the hybrid process) form a cake layer on the surface of the membrane. Thus, the water is forced to contact first the flocculation or adsorption before passing the membrane. This specific type of membrane was first produced and patented at the beginning of the 1990s in Germany [19]. Commercial applications with ceramic flat sheet membranes in wastewater treatment (membrane bioreactors, MBR) [20] and demonstrations in fresh water treatment from surface water [21] were realized around 2005. During the last decades several processes and applications for difficult-to-treat effluents were developed, e.g. [22], [23], [24]. The advantages of ceramic flat sheet membranes compared to polymeric

membranes are predominant especially in harsh environments like extreme pH values, aggressive chemicals or high temperature applications as well as for the filtration of abrasive particles. [25].
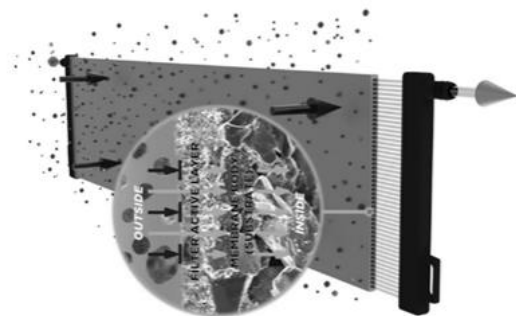

Figure 1: Schematic drawing of submerged filtration with ceramic flat sheet membranes (outside-in filtration), Source: CERAFILTEC®

As the technology has been significantly improved in terms of membrane production capacity, the availability of various membrane materials, module development and process stability it has very good prospects for the future [26]. Especially for applications with fluxes above 400 LMH or under harsh conditions ceramic membranes - which are significantly more expensive than polymer membranes - are now competitive [26], [27]. Especially for drinking water treatment from deep groundwater sources where fluxes of 700 LMH are realized ceramic flat sheet membranes seem to have advantages. Their utilization is especially interesting considering hybrid processes where the material properties of high mechanical strengths and chemical stability are relevant.

2. HYBRID PROCESSES WITH CERAMIC FLAT SHEET MEMBRANES

Surface water as well as treated sewage effluent contains organic particles like microorganisms but also degraded organic material as dissolved or colloidal organics or micro-pollutants which are separated insufficiently. While the particles have a density at approx. 1,000 kg/m³ which makes sedimentation uneconomically due to long residence times or size of the sedimentation basin dissolved organics as well as colloids will not settle at all. Filtration processes in the range of sieving or microfiltration are often inefficient as these particles are very small and pass the filter. In addition, the strong surface charge of the particles also promotes their stabilization in the water. Nanofiltration allows the removal of dissolved organics but suffers from fouling, e.g. [28]. Supportive technologies, especially oxidation processes like e.g. pre-ozonation which are intended to avoid fouling on the membranes [29] need further energy and increase TOC level in the treated water. Especially for the treatment of water with organic micro-pollutants ozonation can be regarded as a critical technology as ozone destroys the organic compounds and forms smaller molecules which are hard to remove from the water and have unknown toxicity.

Typically, fixed bed adsorber with granular activated carbon are applied to remove trace or persistent organic from water sources. Especially for trace substances the effort to remove those substances from water is high as the diffusion path of the molecules into the granular activated carbon grain is comparably long. Thus, the utilization of powdered activated carbon (PAC) is of high interest as the specific surface is maximized and the pathways for the adsorption are comparable short. However, as the small powdered activated carbon particles ($D_{50} < 100\ \mu m$) are hard to reject the removal of the PAC after loading limits its effectiveness. Conventional filter materials block due to the fine particles and polymeric membranes suffer from surface impairments by abrasion.

By combining unit operations like flocculation, precipitation, adsorption or ion exchange with micro- or ultrafiltration the disadvantages of the single unit operation are solved. The new hybrid processes improve water treatment for micro-pollutant removal and reuse of treated water.

2.1 Cake layer filtration (CLF)

Flocculation of organic material allows the conversion of suspended and colloidal contaminants, into larger, separable particles. In combination with a filtration step with ceramic flat sheet membranes an economic approach is chosen as a formation of small flocs is acceptable to form a particle layer on the membrane's surface. Further, dissolved organics can be adsorpt in the flocs during the filtration process. This hybrid process allows the removal of the residual organic material from treated sewage effluent and is called "cake layer filtration" (CLF): The flocculation is done in a separate tank followed by the membrane filtration step (ref. Figure 2). As iron or aluminum salts are used for the flocculation step of the colloidal and dissolved organic substances a co-precipitation of phosphates is possible. Polymeric flocculants should be avoided for the treatment of the treated sewage effluent for reuse as they may increase the organic load of the water when not removed completely.
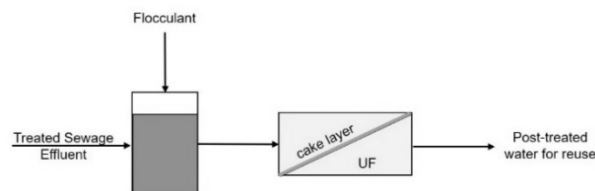

Figure 2: Block diagram of cake layer filtration for quality enhancement of treated sewage effluent

2.2 Active cake layer filtration

The combination of the adsorption step with ceramic flat sheet membrane filtration into a hybrid process is called "active cake layer filtration" (ACLF): The ceramic flat sheet membrane is a carrier of a packed bed of "active" material, like e.g. a fine powdered

11

activated carbon as adsorbent (Figure 3). The submerged out-to-in filtration allows a comparable loose powdered activated carbon bed without compression and therefore a high-flux and low-pressure membrane operation (step 1). The formed adsorbent bed layer allows a perfect contact area for adsorption or ion exchange (step 2) and a quick removal of trace pollutants from the water [30], [31]. Thus, this process can be applied for the removal of dissolved micro-pollutants like PFAS or pharmaceuticals from the water.
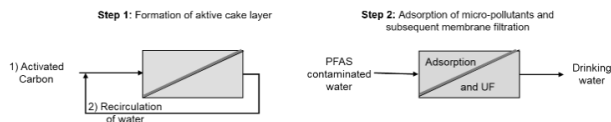

Figure 3: Block diagram of active cake layer filtration for quality enhancement of drinking water - step 1: formation of the active cake layer, step 2: PAC is rejected by UF and micro-pollutants are adsorbed

3. EXPERIMENTAL

The investigations for the two hybrid processes were done in lab scale and followed by technical scale investigations. Selected membranes were ceramic flat sheet membranes. The flocculant applied was ferric chloride ($FeCl_3$) for the lab experiments and aluminum chloride ($AlCl_3$) for the technical scale experiments. As adsorbate different powdered activated carbons (PAC) were used. Experiments were done in lab units as well as technical scale units which were designed and constructed by the company CERAFILTEC®.

3.1 Material and methods

Ceramic flat sheet membranes. The membranes applied for the tests were supplied by CERAFILTEC®. The membranes were ultrafiltration membranes with a pore size of 0.1 µm made of two different materials: Silicon Carbide (SiC) and Alumina Oxide (Al_2O_3). The characteristics are displayed in Table 1.

Table 1: Characteristics of the applied ceramic flat sheet membranes

Type	SiC-1	Al_2O_3-7
Material	Silicon Carbide	Alumina Oxide
Nominal Pore Size [µm]	0.1	0.1
Porosity [%]	42	34
Clean water permeability [l/m²*h*bar]	7,500	1,800

Flocculants. The flocculation was realized with chlorides. During laboratory study $FeCl_3$ and for the technical scale trials $AlCl_3$ was used. Powder activated carbon (PAC). Different PAC were investigated as adsorbents, Table 2.

Table 2: Characteristics of the applied powder activated carbon

Type	H1AK1 (Lab)	H2AK2 (Lab)	Cabot Darco S-51 (Technical)
D_{50} [µm]	20	20	30-42
Iod number [mg/g]	950	n/a	n/a
Methylenblue adsorption [g/100 g]	28	20	n/a
BET [m²/g]	1050	950	650

Analysis. The analysis of the water was done were pH, turbidity, SAK_{254}, Orthophosphate, COD and Extinction. The analysis equipment displayed in Table 3 was used.

Table 3: Laboratory analysis methods applied

Parameter	Equipment	Comments
pH [-]	Parallel analyzer SL 1000, Hach Lange	
Turbidity [NTU]	Turbidimeter 2100 P, Hach Lange	
SAK_{254} [m^{-1}]	Real UV 254, Realtech Incorporation	
COD [mg/l]	Spectrophotometer DR 2800, Hach Lange	Range for COD measurement: 0.0 – 150 mg/l as O_2
PO_4^{3-} [mg/l]	Parallel analyzer SL 1000, Hach Lange	Range for orthophosphates: 0.2 – 4.00 mg/l as PO_4^{3-}
Fe total [mg/l]	Spectrophotometer DR 2800, Hach Lange	Range for Fe total: 0.2 – 6.0 mg/l
Fe^{2+} [mg/l]	Spectrophotometer DR 2800, Hach Lange	
Fe^{3+} [mg/l]	Spectrophotometer DR 2800, Hach Lange	

Extinction [nm]	Spectrophotometer DR 2800, Hach Lange	Maximum of adsorption for brilliant blue: 629 nm (628-630 nm, detection limit: 5 µg/l according to 0) For the calibration a concentration series was prepared.

3.2 Inlet water for investigations

Depending on the investigation target for the CLF filtration and the ACLF different approaches and polluted water were used.

3.2.1 Water for cake layer filtration (CLF)

For the laboratory investigations to remove organics and trace phosphates from sewage effluent, effluent from the municipal sewage treatment plant in Saarbruecken, Germany was used. This is a municipal sewage treatment plant with a daily inlet water of 60,000 m³ of wastewater from households with almost no industrial wastewater [33]. The water for the laboratory investigations was taken after the settling tank prior to discharge the effluent into river Saar. The water is clear with a slightly yellowish color and contains some particles. Table 4 shows the results of the inlet water analysis for the cake layer filtration experiments.

Table 4: Average concentrations of specific water parameter of the feed for the CLF laboratory experiments

Parameter	Unit	Average value of treated sewage effluent
pH	[-]	7.14
Turbidity	[NTU]	1.56
SAK_{254}	[m^{-1}]	0.198
COD	[mg/l]	22.1
PO_4^{3-}	[mg/l]	1.13
Fe total	[mg/l]	0.246
Fe^{2+}	[mg/l]	0.055
Fe^{3+}	[mg/l]	1.191

The technical scale experiments were done with treated sewage effluent of an industrial sewage treatment water plant in Thailand with a COD of approx. 70 mg/l.

3.2.2 Water for active cake layer filtration (ACLF)

Laboratory investigations were done with a model organic (dye - brilliant blue FCF, E133, [32]) which allows a quick characterization of the process due to short analysis times. This approach was selected as analysis of trace organic contaminants takes several days and is not allowing a quick change of process parameter during the process development. Brilliant blue was selected as it is easy to handle, not harmful and has a high solubility in water. Due to the solubility the dye is not rejected by the ultrafiltration membrane and need to be adsorbed on the activated carbon for removal from the water. Brilliant blue is a comparable complex organic material with a high molecular weight (792.8 g/mol). The more complex structure may lead to a poorer adsorption behavior than the traditional methylene blue which is used to characterize activated carbon adsorption. The structure consisting of different benzol rings shall allow to simulate persistent pharmaceuticals. As no Fluoride is contained in the structure of brilliant blue the non-adhesive properties of the forever-chemicals of the PFAS group are not simulated. Nevertheless, to allow a process development with short development cycles brilliant blue was selected as a good first approach model for dissolved trace, persistent organics. Experiments were done with a concentration of brilliant blue of 1 mg/l. This concentration is in the typical trace concentrations of persistent organic at contaminated sites which normally show concentrations in the same range of several µg/l. Surface water concentrations are lower and found in the range of several ng/l. However, it was expected, that these experiments will give a first indication and proof of functionality of the ACLF process.

The technical scale experiments were done with a groundwater contaminated with 1.3 ng/l PFAS as trace organic micro-pollutant. The water was from a drinking water plant in the City of Rome, USA.

3.3 Lab filtration systems

For the filtration tests a lab filtration unit was used consisting of a filtration tank, a pump for filtration and backwash, a blower and a data log unit [34]. The flux is set by the pump speed and the pressure is detected by a pressure sensor (Figure 4). The filtration tank of the laboratory system is designed in correspondence to the dimensions of a ceramic flat sheet filtration module. The membrane of 0.01 m² is mounted in a membrane adapter and stands upright in the filtration tank for batch filtration tests (volume of 5 litres). The distance between the membrane and the wall corresponds to that of two mounted membranes (5 mm) in a filtration module.
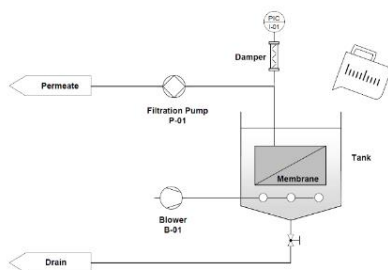
Figure 4: P&ID of the laboratory unit
Source: CERAFILTEC®

For continuous operation a pressure vessel was connected to the filtration tank as a storage tank in order to continuously convey feed water into the filtration tank. A level sensor controlled the feeding. As a result, the hydrodynamic pressure as an error variable for long-term measurements can be omitted.

3.4 Plants for technical scale experiments

The technical scale experiments were done in full-scale technical units with full membrane modules. The modularized plant for the technical scale ACLF experiments was installed inside a 40-feet-sea-container (Figure 5) while the technical scale plant for CLF was fixed onsite. Both plants have a control unit for data storage (flux, pressure, pH, conductivity) including remote control [35]. For the mixture of powder activated carbon into the water as well as the addition of the flocculants separate tanks were applied.
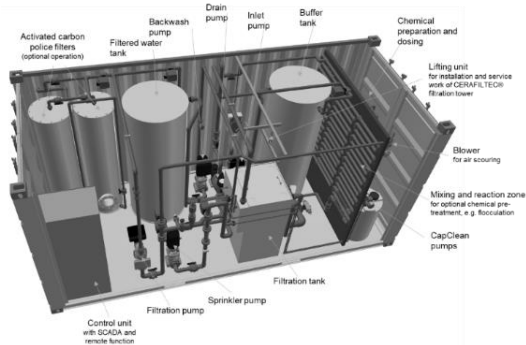

Figure 5: 3D-drawing of a mobile, containerized unit (right)
Source: CERAFILTEC®

4. RESULTS

The results are presented separately for cake layer filtration (CLF) and active cake layer filtration (ACLF).

4.1 Cake layer filtration (CLF)

Targets of the cake layer filtration experiments were to improve the quality of the treated water from the sewage treatment plant in terms of removal of residual organic material by flocculation and to remove residual phosphates by co-precipitation. As known from basic literature the application of flocculants leads to three sub-processes [36]:

- First during the coagulation: the electrostatic rejection of the suspended and colloidal organic substances is overcome and agglomerates are formed.

- Second during flocculation: the flakes formed adsorb further organic material and even the removal of dissolved organic substances is possible.

- Third: $FeCl_3$ leads to a precipitation as the ferric and the orthophosphates form sparingly soluble ferric phosphate ($FePO_4$) (eq. 1).

$$[PO_4]^{3-} + FeCl_3 \rightarrow FePO_4 \downarrow + 3\,Cl^- \quad \text{(eq.1)}$$
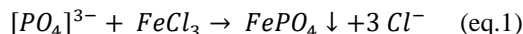
Aluminum containing salts like used for the technical scale experiments lead to the formation of sparingly soluble aluminum phosphates ($AlPO_4$) (eq. 2).

$$[PO_4]^{3-} + AlCl_3 \cdot 6\,H_2O \rightarrow FePO_4 \downarrow + 3\,HCl + 3\,OH^- \text{ (eq.2)}$$
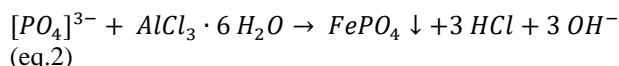
4.1.1 Lab results CLF

The experiments were divided in two different steps. In a first step the optimum concentration of the flocculant in terms of organic removal (measured as SAK_{254}) and phosphate precipitation were determined. In a second step the combined process of flocculation and ultrafiltration was investigated. Figure 6 shows the results of the determination of the optimum flocculant concentration.
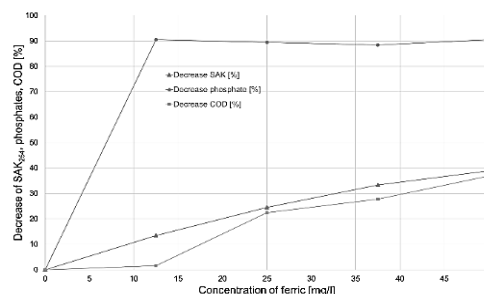

Figure 6: Decrease of organics and phosphate concentration by addition of $FeCl_3$ depending on the concentration

The investigations showed, that the maximum phosphate concentration is already achieved with a ferric concentration of 25 % while the organic removal can be improved with rising concentrations of the flocculant.

The filtration experiments were done in order to evaluate the interrelations of the flocculant with the membrane and – which is most important – to determine the improvement of water clarification by this combined process. The flocculant is added with a concentration of 0.075 ml/l to the flocculation tank with a stirring velocity of 4.7 m/min which is applied for 30 seconds, after for 15 minutes the pre-treated water is stirred with a velocity of 0,3 m/min. The filtration flux applied was 200 LMH while the backwash flux was 700 LMH. The filtration cycle was 45 minutes followed by a 30 second backwash which was

enhanced by shear forces due to aeration. Total filtration time was 1.5 h (two cycles). During filtration the tank volume was kept constant. The results of the filtration experiments in terms of permeability of both investigated membrane types is shown in Figure 7.
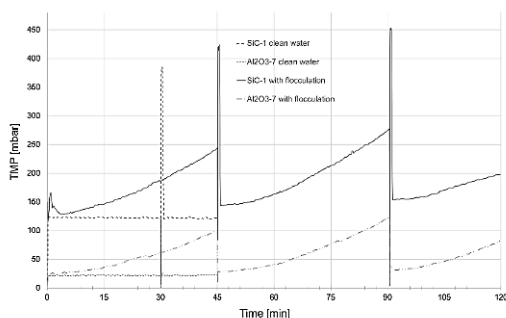

Figure 7: Permeability of the investigated membranes with flocculation (FeCl₃) in comparison with clean water flux

The investigations showed, that FeCl₃ causes only a low decrease of permeability. However, the membrane is not recovering fully during backwash which indicates a slight fouling. The effect on the membranes is comparable although the permeability of the SiC-1 membrane is significantly higher than the Al₂O₃-7 membrane. No severe difference could be determined for the filtered water quality between the two different membrane types, Table 5. However, due to the higher permeability the efficiency of the SiC-1 membrane is significantly higher.

Table 5: Decrease of organic and phosphate concentration in treated sewage effluent

Parameter	Decrease [%]	
	SiC-1	Al₂O₃-7
Turbidity	88.4	86.2
SAK₂₅₄	39.3	38.4
PO₄³⁻	91.1	89.6
COD	58.5	60.0

During a long-term filtration test of 24 h a volume 60 l of treated sewage effluent was post-treated. The results achieved during the 2 h filtration tests were confirmed. Phosphate concentration was reduced below 0.2 mg/l and organic concentration below 15 mg/l (as COD) or below 0.065 m⁻¹ (as SAK₂₅₄).

4.1.2 Technical scale results CLF

A technical scale plant was realized at a soy bean production plant in Prachinburi, Thailand. As state-of-the-art the water was collected in open ponds. However, the residual nitrogen and carbon concentration as well as the oily residues increases the eutrophication resulting in bloom of algae. Recovery of the water for reuse is challenging as it leads to strong membrane fouling. Cake

layer filtration allowed to overcome this challenge and allows a recovery of the water. For the flocculation and cake formation an aluminum-based flocculant is used. The filtration is operated with a flux of 215 LMH. The plant treats a water volume of 15.5 m³/h. After the filtration time of 1.93 h a backwash is done to remove the cake layer. The backwash including a short chemical cleaning takes 3 min/h. The water parameter turbidity, total suspended solids (TSS) and oil are reduced below detection limits allowing a reuse of the treated water in chillers (Table 6). The plant is constantly in operation since December 2019.

Table 6: Water quality before (feed water) and after (filtrate) treatment with CLF, data extracted from 0

Parameter	Unit	Feed water	Filtrate
Turbidity	[NTU]	11.2	< 0.5
COD	[mg/l]	68	30
TSS	[mg/l]	18	< 1 (nil)
Oil	[mg/l]	7.2	< 0.2

4.2 Results active cake layer filtration (ACLF)

Persistent organic trace material can be removed by adsorption on activated carbon 0. Especially per- and polyfluorinated alkyl substances (PFAS) have recently received increasing attention in connection with contamination of the soil and groundwater and the associated risk of contamination of drinking water. The group of PFAS are artificial, industrial chemicals that comprise about 4,700 substances. They are persistent, toxic and accumulate in the food chain. Worldwide, contaminated drinking water is one of the main sources of adverse effects on humans caused by PFAS; among other things, PFAS is suspected of being carcinogenic and toxic in reproduction. [39], [49], [41]

For the lab experiments suspension with a concentration of 2.5 g/l of PAC was mixed in a beaker and the suspension was given into the lab unit. The PAC layer was formed by high filtration speed of 1,000 LMH. After the layer was formed uniformly to avoid local breakthrough, the filtration started at lower filtration flux. With the filtration flow as the driving force, the activated carbon adheres to the membrane surface. Nevertheless, approx. 15 % of PAC is lost during this process and not fixed on the membrane's surface. The thickness of the PAC layer was measured by light microscopy in a cross section of the coated membrane. The average thickness is between 178 up to 155 µm (Figure 8).
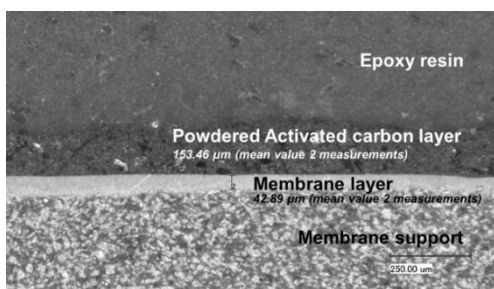
Figure 8: Cross-section of ceramic flat sheet membrane and PAC

4.2.1 Lab results ACLF

Comparable to the experiments with the flocculation first experiments were done for adsorption of the organics in stirred beakers. The residual concentration of the dye brilliant blue was measured after 24 h and 48 h. The results showed, that after 24 h 99.98 % and after 48 h 100 % of the dye was removed by both activated carbons. The idea of active cake layer filtration is to increase the adsorption time drastically by applying a cake layer formed by PAC on the surface of the membrane. The fine particles are rejected by the membrane and the polluted water is forced to move through this thin packed bed layer. The investigated aspects were the pressure drop caused by the PAC layer on the membrane and the adsorption ability of the thin PAC layer for the trace organic. The membrane applied was SiC-1 and the PAC layer was formed from with 400 ml suspension with 2.5 mg/l PAC with a flux of 1,000 LMH. The filtration velocity (flux) was varied between 400 up to 1,000 LMH to find the optimum operation parameter. The formation time for the PAC layer (precoating time) was 2 minutes. Regarding permeability or pressure drop respectively it was found that there is almost no influence on the membrane filtration caused by the PAC. However, for finer particle grains a slight increase of filtration pressure is found as the transport distance through the layer (tortuosity) arises. The contact time within the PAC layer was calculated by the flow through the porous bed (eq. 3). This was done

as empty tube velocity $t = \frac{h*A}{\dot{V}}$ (eq. 3)

with
t = contact time [s]
h = thickness of powdered activated carbon bed [m]
A = surface area of activated carbon bed [m²]
$\dot{V}$ = Volume flow [m³/s]

with correction factors of porosity ε [%] and tortuosity τ. Porosity was estimated based on basic literature to ε = 0.4 and for the tortuosity values of τ = 2 and τ = 4 were selected [42].

The calculation shows, that the contact time in the thin fixed bed is less than 2 seconds, Table 7.

Table 7: Calculation of contact time in the thin fixed bed at different filtration fluxes

Flux [LMH]	Average layer thickness [µm]	Contact time [s]			
		without ε and τ	with ε	with ε and τ=2	with ε and τ=4
700	193.63	0.98	0.39	0.79	1.57
800	177.77	0.79	0.32	0.63	1.26
900	147.25	0.58	0.23	0.47	0.93
1,000	239.25	0.85	0.34	0.68	1.36

Both investigated activated carbons were able to retain the dye at a concentration of 1 mg/L and a flux of 1,000 LMH completely over a period of 5 h. After 5 h, the retention decreased to 99.7% for the H1AK1 and to 99.5% for the H1AK2 (Table 8). Due to the very slow surface diffusion, the activated carbon in the precoat layers is only partially loaded. The adsorption experiments with contact times between 24 h to 48 h showed that 150 mg/l dye could be adsorbed on the PAC while only 65 g/l were adsorbed with a filtration speed of 1,000 LMH. However, the tank volume and retention time is lower and therefore the process is interesting for the treatment of high-volume water streams like e.g. removal of persistent organic from drinking water.

Table 8: Retention of brilliant blue by ACLF

Filtration time [h]	Retention [%]	
	H1AK1	H1AK2
1	100,0	100,0
2	100,0	100,0
3	100,0	100,0
4	100,0	100,0
5	100,0	100,0
5.5	99,7	99,5

4.2.2 Technical scale results ACLF

The technical scale experiments were done in a period of three months with a containerized unit in the City of Rome, Georgia, USA. The city's drinking water supply is affected by a contamination of PFAS in the range of 1.3 ng/l. The turbidity of the influent water was 0.1 to 0.3 NTU. A full-scale membrane module of CERAFILTEC® with 6 m² of membrane area was covered by a thin powdered activated carbon layer. After covering the membranes with powdered activated carbon (PAC), the filtration was operated with a flux of approx.

16

200 LMH. The plant treated a water volume of 1.2 m³/h. After the filtration time of 23.75 h a backwash was done to remove the loaded PAC and a new cycle started. Four different water sources were tested during the technical scale trials. Water samples were taken and analyzed by the laboratory of the City of Rome almost every week. The results are displayed in Table 9.

Table 9: Mean values in the different months of technical scale trials, data extracted from [43]

Water Source	PFAS [ng/l] before treatment	PFAS [ng/l] after treatment	Removal [%]
1	0.85	0.06	93.1
2	0.74	0.00	99.3
3	0.34	0.00	99.5
4	0.05	0.00	99.7

The results show that a removal of PFAS was achieved for three of the four sources for 99 to 100 %. The results from water source 1 were poorer as it was the first attempt for the formation of the PAC layer. After PAC layer formation was optimized, the PFAS was removed from the water to detection limit.

5. DISCUSSION OF THE RESULTS

The laboratory experiments showed, that the hybrid process of flocculation with co-precipitation followed by ceramic flat sheet membrane (cake layer filtration, CLF) is suitable to remove dissolved and colloidal organics from treated sewage effluent and to reduce the phosphate concentration in this water. It should be noted that the performance of filtration varies greatly due to the type of membrane, flocculant and inlet surface water. Overdosing flocculants might lead to membrane fouling. Therefore, the interactions of flocculants with membrane surfaces need further investigation. The hybrid process with precoated powdered activated carbon on the ceramic flat sheet membrane (ACLF) for adsorption of trace organic material showed high removal efficiencies. For this process the selection of the suitable activated carbon is a crucial step for the removal of the targeted organics. Nevertheless, the mechanisms of the adsorption process need to be studied in detail as it cannot be explained by exiting fixed bed models. The technical scale trials proved that the hybrid processes developed in laboratory scale improve the treatment of water with residual and trace organics: combination of flocculation and ceramic flat sheet membrane filtration (CLF) reduces membrane fouling caused by organic residuals and allows a reuse of treated sewage effluent while reaching fluxes of 215 LMH, combination of adsorption and membrane filtration (ACLF) allows the efficient removal of trace organic components from drinking water. The technical scale trials showed that ACLF can remove hazardous

micro-pollutants like PFAS constantly > 99 % and the suitable operation flux is 200 LMH. Further experiments with the hybrid process of an active cake layer formed by PAC on the ceramic flat sheet membrane is perspective to remove trace organic components from surface water. This process is interesting as due to the high surface area of the PAC compared to granular activated carbon it is more efficient than typical fixed bed adsorber and the ultrafiltration process itself is more energy efficient than nanofiltration / reverse osmosis processes currently applied for trace organic removal. By combining the ceramic flat sheet membranes successfully with the respective PAC, the process of ACLF will allow the removal of a broad range of dissolved trace organic materials – not only forever chemicals from the PFAS group but also e.g. persistent pharmaceuticals. Furthermore, PAC layer avoids membrane fouling. [44]

6. CONCLUSION AND PERSPECTIVES

Within the scope of this work, it could be shown that hybrid processes combining ceramic flat sheet membrane ultrafiltration with a flocculation or adsorption process is valuable for the treatment of surface water contaminated with micro-pollutants. The combination of activated carbon adsorption and ceramic flat membrane is suitable for removing trace organic substances from the treated effluent and by combination of ceramic flat sheet membrane with flocculation, colloidally dissolved and finest suspended organic water constituents are converted into separable flakes which allow a high-flux membrane filtration. Part of the latter process is a co-precipitation of phosphate.

The combination of flocculants and ceramic flat sheet membranes contribute to a good post-treatment of treated sewage effluent by removing organics and phosphates. This will on the one hand protect the ecosystems from eutrophication and on the other hand allow a reuse of the treated sewage effluent as rinsing water, for gardening or agricultural irrigation. The hybrid process of ACLF showed a high-potential for trace organic removal from surface water. This contributes especially to the improvement of drinking water security.

The biggest advantage of using the hybrid processes with ceramic flat sheet membranes is the modularity of the process. Existing sewage and drinking water treatment plants can be equipped with a very low degree of upgrade to improve water quality. This is particularly interesting when the concentration of the pollutants in the feed is subject to strong seasonal fluctuations, which means that the need for flocculation / co-precipitation or adsorption is not always present. Such fluctuations can occur in surface waters due to heavy rain or supplied meltwater and introduce significant amounts of pollutant into the water. In an application for industrial wastewater, such fluctuations are also conceivable, for example due to large time intervals between individual batches of problematic products. Existing constrains are

poor knowledge on the details of the interactions of flocculants with the membranes and the adsorption mechanism during the short contact time. These aspects will be part of future research to improve the hybrid processes constantly in order to contribute to water reuse and cleaner water resources.

7. CONFLICT OF INTERESTS

There are no conflicts to declare.

8. ACKNOWLEDGEMENTS

ABBREVIATIONS

ACLF	Active cake layer filtration
A	Surface area of PAC layer [m²]
AlCl₃	Aluminium chloride
AlPO₄	Aluminium phosphate
BET	Surface area (Brunauer, Emmet, Teller)
CLF	Cake layer filtration
COD	Chemical oxygen demand
D₅₀	Average particle size (50 %)
ε	Porosity [%]
Fe	Iron
Fe²⁺	Iron (II)
Fe³⁺	Iron (III), Ferric
FePO₄	Ferric phosphate
FeCl₃	Ferric chloride
H	Thickness of PAC layer [m]
l/m²*h*bar	Permeability – liters per area, hour and pressure
LMH	Flux – liters per square meter and hour
MBR	Membrane bioreactor
NTU	Nephelometric turbidity units
PAC	Powdered activated carbon
PFAS	per- and polyfluorinated alkyl substances
PO₄³⁻	Orthophosphate
SAK₂₅₄	Specific adsorption coefficient at 254 nm
TSE	Treated sewage effluent
TSS	Total suspended solids
T	Contact time [s]
τ	Tortuosity
$\dot{V}$	Volume flow [m³/s]

REFERENCES

[1] German Federal Ministry of the Environment: Umweltbewusstsein in Deutschland (Report on Environmental Awareness in Germany), https://www.bmuv.de/fileadmin/Daten_BMU/Pools/Broschueren/umweltbewusstsein_2020_bf.pdf , (accessed 28 March 2022)

[2] J. G. Gesamp, Sources, fate and effects of microplastics in the marine environment: Part two of a global Assessment, London, 2016

[3] P. E. Stackelberg, E. T. Furlong, M. T. Meyer, S. D. Zaugg, A. K. Henderson, D. B. Reissman, Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant, Sci. Total Environ, 2004, 329 (1–3), 99-113. https://doi.org/10.1016/j.scitotenv.2004.03.015

[4] B. Klauer, Pharmaceutical residues in drinking water and water bodies, TAB-Fokus, 2019, 22, 183, ISSN: 2364-2645

[5] J. C. Crittenden, J. R. Trussel, D. W. Hand, et.al., MHW's Water Treatment, New Jersey, 2012

[6] D. L. Correll, The Role of Phosphorous in the Eutrophication of Receiving Waters: A Review, J. Environ. Qual., 1998, 27, 261-266, https://doi.org/10.2134/jeq1998.00472425002700020004x

[7] German Federal Ministry of the Environment: Einträge von Nähr- und Schadstoffen in die Oberflächengewässer (Nutrients in surface water) https://www.umweltbundesamt.de/daten/wasser/fliessgewaesser/eintraege-von-naehr-schadstoffen-in-die#nahrstoffeintrage-sinken-wieder-langsam (accessed 17 November 2021)

[8] A. J. P. Smolders, E.C.H.E.T. Lucassen, R. Bobbink, How nitrate leaching from agricultural lands provokes phosphate eutrophication in groundwater fed wetlands: the sulphur bridge, Biogeochemistry, 2010, 98, 1-7, DOI 10.1007/s10533-009-9387-8

[9] A. Chohan, H. Petaway, V. Rivera-Diaz, A. l. Day, O. Colaianni , M. Keramati, Per and polyfluoroalkyl substances scientific literature review: water exposure, impact on human health, and implications for regulatory

reform, Rev. Environ. Health, 2021, 36 (2), pp. 235-259, https://doi.org/10.1515/reveh-2020-0049

[10] T. aus der Beek, F.-A. Weber, A. Bergmann, S. Hickmann, I. Ebert, A. Hein, A. Küster, Pharmaceuticals in the environment—Global occurrences and perspectives, Environ. Toxicol. Chem., 2016, 35 (4), 823–835. https://doi.org/10.1002/etc.3339

[11] M. Wagner, S. Lambert, (ed.), Freshwater Microplastics – Emerging Environmental Contaminants?, Cham, 2018, DOI 10.1007/978-3-319-61615-5

[12] E. Worch, E., Adsorption technology in water treatment – Fundamentals, Processes, and Modelling, Berlin, Boston, 2012 https://doi.org/10.1515/9783110240238

[13] Y. Matsui, H. Hasegawa, K. Ohno, T. Matsushita, S. Mima, Y. Kawase, T. Aizawa, Effects of super-powdered activated carbon pretreatment on coagulation and trans-membrane pressure buildup during microfiltration, Wat. Res., 2009, 43 (20), 5160 – 5170. DOI: 10.1016/j.watres.2009.08.021

[14] R. Awual, Efficient phosphate removal from water for controlling eutrophication using novel composite adsorbent, J. Cleaner Prod., 2019, 228, 1311-1319. https://doi.org/10.1016/j.jclepro.2019.04.325

[15] J. Radjenović, M. Petrović, F. Ventura, D. Barceló, Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment, Wat. Res., 2008, 42 (14), 3601-3610. https://doi.org/10.1016/j.watres.2008.05.020

[16] B. van der Bruggen, C. Vandecasteele, Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry, Environ. Poll., 2003, 122 (3), 435-445, https://doi.org/10.1016/S0269-7491(02)00308-1

[17] U. Beucher, E. J. Kappert, J. G. Wijmans, Membrane research beyond material science, J. Mem. Sci., 2022, 643, (1-5). https://doi.org/10.1016/j.memsci.2021.119902

[18] K. W. Böddeker, Liquid Separations with Membranes – An Introduction to Barrier Interference, Berlin, 2008

[19] H. Chmiel, Druckstabile anorganische Membranen (pressure resistent inorganic membranes), DE 4329473 C1, 1993 – expired

[20] C. Blöcher, Einsatz getauchter keramischer Mehrkanal-Flachmembranen in Bioreaktoren (utilization of submerged ceramic flat sheet membranes in bioreactors), upt-Schriftenreihe, volume 1, Saarbruecken, 2004

[21] M. Sartor, B. Schlichter, H. Gatjal, V. Mavrov, Demonstration of a new hybrid process for the decentralised drinking and service water production from surface water in Thailand, Des., 2008, 222, 539-551

[22] C. Gränitz, M. Kaschek, O. Binkle, Process for the separation of radioactive nuclides by ceramic filtermembranes, EP 2 754 158 B1

[23] C. Gränitz, K. G. Gabriel, Filter unit for treating water and other liquid media and process for producing the same, EP 2 310 115 B1

[24] M. W. Hakami, A. Alkhudhiri, S. Al-Batty, S., M.-P- Zacharof, J. Maddy, N. Hilal, Ceramic Microfiltration Membranes in Wastewater Treatment: Filtration behaviour, Fouling and prevention, Mem. 2020, 248 (10), 1-34. doi:10.3390/membranes10090248

[25] M. B. Asif, Z. Zhang, Ceramic membrane technology for water and wastewater treatment: A critical review of performance, full-scale applications, membrane fouling and prospects, Chem. Eng. J., 2021, 418, 1-18. doi.org/10.1016/j.cej.2021.129481

[26] GWI -Global water Intelligence: Market Map – Ceramic membranes: high expectations for cracking the market, GWI, 2017, 6, 43-49

[27] Interview Keil, R.R., Hi-tech solutions are 'need of the hour', Gulf construction, 2018, 10, 87-89

[28] D. Liu, J. Cabrera, L. Zhong, W. Wang, D. Duan, X. Wang, S. Liu, Y. F. Xie, Using loose nanofiltration membrane for lake water treatment: A pilot study, Front. Environ. Sci. Eng. 2021, 15 (4):69, 1-11. DOI:10.1007/s11783-020-1362-6

[29] W. Yu, T. Liu, J. Crawshaw, T. Liu, N. Graham, Ultrafiltration and nanofiltration membrane fouling by natural organic matter: Mechanisms and mitigation by pre-ozonation and pH, Wat. Res., 2018, 139, 353-362. doi: 10.1016/j.watres.2018.04.025.

[30] M. Sartor, M. Kaschek, Membrane Filtration and Flat Sheet Membrane Technology, MTAIC, Cairo, Egypt, 15.-17.08.2021, Keynote Lecture on invitation of National Research Center, NRC Cairo, 2021

[31] M. Kaschek, M. Sartor, K. G. Gabriel, High Flux Operation of Ceramic Membrane System in Drinking Water Application, Industrial Water 2018, Frankfurt am Main, (2018)

[32] National Library of Medicine, Information on brilliant blue, https://pubchem.ncbi.nlm.nih.gov/compound/Brilliant-Blue-FCF, (accessed 23 May 2022)

[33] Entsorgungsverband Saar, Information on sewage treatment plants in Saarland, Germany, https://www.evs.de/evs/oeffentlichkeitsarbeit/infomaterial/abwasser , (accessed 23 May 2022)

[34] CERAFILTEC, Lab test units, https://www.cerafiltec.com/lab-test-units/ (accessed 23 May 2022)

[35] CERAFILTEC, Container pilot units, https://www.cerafiltec.com/container-pilot-unit/ (accessed 23 May 2022)

[36] C. E. Mortimer, U. Müller, Basiswissen Chemie (Chemistry - The basic knowledge of chemistry), Stuttgart 2001

[37] CERAFILTEC, Case Studies, https://www.cerafiltec.com/case-industrial-tse/ , (accessed 23 May 2022)

[38] S. Metzger, Einsatz von Pulveraktivkohle zur weitergehenden Reinigung von kommunalem Abwasser, Use of powdered activated carbon for advanced treatment of municipal wastewater, München, 2010

[39] OECD, Portal on Per and Poly Fluorinated Chemicals, http://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/, (accessed 26 March 2021)

[40] US: AWWA Briefing on PFAS, Denver, Washington, 2019

[41] UBA: PFAS – gekommen um zu bleiben (PFAS – came to stay), Studies on PFAS in Germany, https://www.umweltbundesamt.de/sites/default/files/medien/2546/publikationen/uba_sp_pfas_web_0.pdf , (accessed 26 March 2021)

[42] M. Stieß, Mechanische Verfahrenstechnik - Partikeltechnologie 1 (mechanical process engineering, particle technology), 3rd ed., Berlin, 2009

[43] N.N. ravenvolt: Pilot Test Summary Report, City of Rome, Georgia, PFAS Mitigation Technologies, 2021, https://www.cerafiltec.com/pfas-report-2021/ (accessed 9 April 2022)

[44] N.N., PFAS treatment market concentrates on waste reduction and total destruction, GWI, CTO report, 2020, 5, 40-45