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Removal of micropollutants in a ceramic membrane bioreactor for the post-treatment of municipal wastewater

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ABSTRACT

Micropollutants, such as pharmaceuticals, endocrine disrupting compounds, and personal care products, have become an emerging environmental issue. In general, they are only partially removed by conventional wastewater treatment plants (WWTPs), and their presence in surface waters may have harmful effects on aquatic organisms and human health. In this study, a pilot-scale ceramic membrane bioreactor (cMBR) was employed as a polishing step in a WWTP to further treat the effluent of the WWTP for 15 months. The removal of chemical oxygen demand (COD) and 29 micropollutants, the process stability, and the development of activated sludge in the cMBR system were investigated. After about 300 days of operation, the cMBR system established stable operating conditions with suspended solids (SS) concentrations and volatile suspended solids (VSS) concentrations at (0.045 ± 0.004) g/L and (0.028 ± 0.005) g/L, respectively. Under these conditions, the cMBR provided stable removal of organic matter and micropollutants. The removal of chemical oxygen demand (COD) was (37.4 ± 3.8)%, and the removal of 29 micropollutants was substance specific and ranged from (−3.6 ± 5.9)% to (42.4 ± 3.0)%. Although the sludge concentration developed in the cMBR was much lower than that in the WWTP aeration tank (SS at 2.3 g/L), the activity of sludge in the cMBR for oxygen consumption and micropollutants removal was more than 10 times higher than that in the WWTP aeration tank. Moreover, as a complement to the cMBR system, an osmosis membrane system was investigated that could completely remove the micropollutants (below detection limits) in the cMBR effluent and achieve high water quality.

1. Introduction

The presence of emerging organic micropollutants including pharmaceuticals, endocrine disrupting compounds, and personal care products, in the aquatic environment has become an environmental issue of growing concern in recent decades [1,2]. Traditional wastewater treatment plants (WWTPs) are designed to remove solids, nutrients, as well as biological and chemical oxygen demand (BOD, COD) from raw wastewater, but not to specifically remove these emerging micropollutants [3–5]. Therefore, the emerging micropollutants have been detected in wastewater effluents, surface water, groundwater, and even drinking water in the range of ng/L to μg/L [6–8]. These micropollutants may have adverse impacts on human health and aquatic organisms, even at trace levels in the environment [9–11]. Thus, additional post-treatment technologies after conventional WWTPs have been investigated to improve the removal of micropollutants, such as ozonation, photocatalytic reactions, activated carbon adsorption, and pressure-driven membrane filtration (such as nanofiltration (NF) and reverse osmosis (RO)) [12–15]. Ozonation has been shown to be very effective in removing micropollutants using hydroxyl radical and ozone, but it may generate harmful by-products, and the removal efficiency is heavily dependent on organic matter, pH, etc., [16,17]. Photocatalytic processes usually consume chemicals such as titanium dioxide (TiO_2) and hydrogen peroxide [18]. Activated carbon can efficiently remove

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micropollutants by physical sorption, but it needs to be regenerated or replaced after some time of use [19]. NF and RO remove micropollutants mainly through molecular sieving. Due to small pore sizes and susceptibility to fouling, high hydraulic pressure is usually required to maintain the flux in these approaches [20,21].

Membrane bioreactor (MBR) technology, combining biodegradation in activated sludge systems with physical membrane filtration, has become a widely accepted, more advanced technology for wastewater treatment compared to conventional activated sludge (CAS) processes, because of its smaller footprint, higher sludge retention time (SRT), lower sludge production, and higher quality effluent with the efficient removal of turbidity, nitrogen, phosphorous, and COD, etc., [1,22–25]. Moreover, a multitude of studies have reported MBR systems can also remove micropollutants efficiently [1,26–29]. As membrane applications are less space demanding and have less risk of biomass washout than gravitational settlers, traditional MBRs can operate at considerably higher sludge concentration (8–12 g/L suspended solids (SS)) and longer SRT (20–100 days) than CAS processes (2–3 g/L SS, 1–2 days SRT, typically), which makes it possible for MBRs to establish an adapted sludge community to enhance micropollutants removal, such as the generation of slowly growing bacteria, e.g., nitrifying bacteria, which may benefit the biodegradation of certain recalcitrant micropollutants [20,30–32]. For example, Radjenović et al. (2009) compared the removal of 26 micropollutants in a CAS and a MBR system operated in parallel treating the same wastewater [33]. 20 of these micropollutants showed higher removal in the MBR than in CAS. Suárez et al. (2012) reported the removal of 16 compounds was related to SRT [34], and Maeng et al. (2013) also showed the biotransformation of some pharmaceuticals (gemfibrozil, diclofenac, bezafibrate, ketoprofen, and 17α-ethinylestradiol (EE2)) was positively correlated with the SRT and possibly linked to the nitrification process by slow-growth nitrifying bacteria in MBRs [35].

Because MBRs have these significant advantages over CAS processes, MBR systems (>10000 m^3/d) have been installed and applied worldwide with the cumulative treatment capacity of more than 20 million m^3/d until the year 2016, and the application is continuously growing [25,36–38]. Most of these installed MBRs are used directly to replace CAS processes to save space and improve the original WWTPs' wastewater treatment efficiency [11,32].

However, little is known about how efficient it is to apply MBR technology as a polishing step for CAS post stream treatment to further remove micropollutants. Different from the traditional MBR process, the post-treatment MBR process would introduce CAS effluent water into reactors instead of raw wastewater from WWTPs. This would provide much less BOD, nitrogen, etc., for sludge growth, thus possibly resulting in different microbial communities established in the reactors, consequently affecting biodegradation of micropollutants and even formation of transformation products [39–42]. Therefore, it is necessary to study and further develop the performance of post-treatment MBRs for wastewater effluent treatment and micropollutants' removal, and to determine whether it is possible to establish biomasses able to degrade compounds that are usually considered to be recalcitrant by co-metabolic processes.

Previous studies have shown membrane fouling to be one of the most critical limitations to the development of MBR technology [11,43]. This can be overcome by sophisticated operations using cross flow with polymeric membranes or by using more resistant materials such as ceramic membranes, which have recently been developed for this purpose [43,44]. In comparison with traditional polymeric membranes, ceramic membranes are less susceptible to fouling and their chemical stability can be exploited by using radical online cleaning procedures [45–47]. In this study, we employed a silicon carbide (SiC) ceramic membrane [48] equipped bioreactor (cMBR) for the removal of micropollutants from wastewater for the first time.

The main objectives of this study were to:

a) Explore the possibilities of sludge adaptation to remove micropollutants in a polishing cMBR with extremely low loading (low carbon, nitrogen sources in WWTP effluent) and a very high SRT (no excess sludge). The removal of 29 micropollutants, commonly detected in wastewater, were investigated for this study: some are neutral, some are positively or negatively charged, some are hydrophilic, some are hydrophobic, with different structures and different molecular weights. Some (such as ibuprofen) are classically defined as rapidly biodegradable, while others (such as carbamazepine, diclofenac, and the iodinated x-ray contrast media) are usually considered to be recalcitrant.
b) To include the determination of 15 metabolites to enable the discrimination between removal and transformation, as well as to explore the fate of human metabolites.
c) To study process stability that can be provided by the cMBR system by exploring the development of biomass, COD removal, and transmembrane pressure.

2. Materials and methods

2.1. Chemicals

29 micropollutants and 15 their biotransformation products were studied in this work. These compounds were purchased from Sigma-Aldrich, Santa Cruz Biotech, Dr. Ehrenstorfer, Toronto Research Chemicals, and LGC Standards at the highest available purity. The isotopic labeled compounds used as internal standards were purchased from Sigma-Aldrich and Toronto Research Chemicals. The main physicochemical properties of these compounds together with their molecular structures are presented in Table S1 of Supporting Information. Compounds included antibiotics, beta-blockers, anticonvulsants, antidepressants, nonsteroidal anti-inflammatory drugs, analgesics, X-ray contrast agents, angiotensin II receptor antagonists, immunosuppressants, and corrosion inhibitors. Molecular weights range from 119.12 to 837.05, pKa from −2.85 to 14.84, log K_{ow} from −2.93 to 3.31 (Table S1, Supporting Information). Formic acid was supplied by Sigma-Aldrich (Munich, Germany), and LC-MS grade water and methanol were obtained from Merck (Darmstadt, Germany).

2.2. cMBR system

A pilot-scale cMBR system was installed at a 350000 PE wastewater treatment plant (BIOFOS A/S, Avedøre, Denmark) operating BOD removal, nitrification, and denitrification in a CAS process. The cMBR was installed as a polishing step treating the effluent from the WWTP, from August 2018 to November 2019. A schematic flow diagram is shown in Fig. 1. The cMBR plant consisted of a 700 L membrane tank (to conduct reactions and separations), a 700 L process tank (to conduct reactions), and a 500 L permeate tank (to collect the cleaned water). The membrane tank contained a submerged membrane unit with forty 0.106 m^2 flat sheet silicon carbide (SiC) ceramic microfiltration membranes (LiqTech Ceramics A/S, Ballerup, Denmark), with a nominal pore size of 0.2 μm, giving a total surface area of 4.24 m^2. The compressed air system provided a constant airflow (5 L/min) from diffusor pipes placed at the bottom of the reactor, to keep aerobic conditions in the tank, and reduce the fouling and formation of cake layer on the membranes. The process tank contained a mechanical mixer ensuring homogeneous mixing of the liquid and preventing the settling of the biomass. The reactor (combined process and membrane tank) was at the start filled with activated sludge from the aeration tank in the WWTP, with initial suspended solids (SS) concentration at 2.3 g/L. No sludge was removed from the system during the entire operation period. The wastewater effluent from the WWTP was pumped into the cMBR system and circulated between the membrane tank and the process tank. In order to keep a constant outflow rate, the operation of the inflow pump was controlled by floating switches in both the process tank and the membrane tank, to ensure the water level

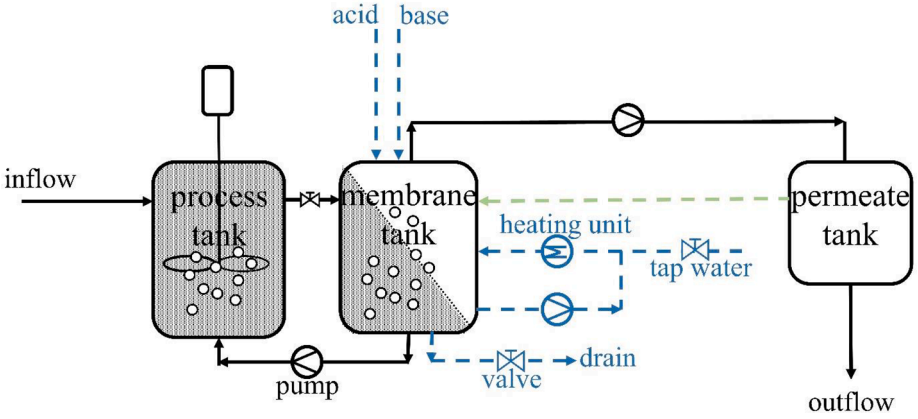

Fig. 1. Flow diagram of the aerated pilot-scale cMBR system. The green dashed line represents backwash of the ceramic membrane, and the blue dashed line represents chemical wash of the ceramic membrane by acid and alkaline solutions (marked with "acid" and "base"), which was operated after emptying the membrane tank. (For interpretation of the references to colour in this Fig. legend, the reader is referred to the web version of this article.)

in the process tank between 59% and 61%, and the level in the membrane tank between 82% and 87%. A vacuum suction pump was used to pump the treated water through the membranes to the permeate tank, and the permeate flow was maintained at 42 L/h (permeate flux ≈ 10 L/m^2/h) via a mass flow controller installed on the permeate stream, which in total controlled the hydraulic retention time (HRT) to be 25 h. Periodic backwash (one minute per 24 h) was performed by recirculating the water from the permeate tank to the membrane modules to remove the fouling layer. Chemical cleaning was performed when the transmembrane pressure (TMP) reached the set upper limit at 0.6 bar. The chemicals used for chemical cleaning were acid solution Ultrasil 75 (Ecolab A/S, Denmark), which is a mixture of nitric acid (10–30%) and phosphoric acid (10–30%), and base solution Ultrasil 115 (Ecolab A/S, Denmark) which consists of potassium hydroxide (10–20%), sodium hydroxide (10–20%), and ethylenediaminetetraacetate (5–10%). The detailed chemical cleaning process is summarized in Table S2 in Supporting Information. A programmable logic controller (PLC) was installed to collect and record the data from all the sensors in the cMBR pilot, such as TMP, water temperature, dissolved oxygen (DO), water flow, and water levels in the tanks.

2.3. Analytical methods

2.3.1. Water quality parameters

Influent water, mixed sludge liquor from the aeration tank, and permeate water samples of the cMBR were taken about once a week or once two weeks for the analysis of water parameters throughout the whole 15 months, with triplicate sampling each time. The detailed sampling schedule is shown in Table S6, Supporting Information. Total COD and filtered COD were measured using the colorimetric method on a spectrophotometer (DR3900, Hach Lange, Dusseldorf, Germany). The only difference between the measurement of total COD and filtered COD was that for the analysis of filtered COD, the samples were filtered by 0.6 μm glass fiber filters (Advantec MFS, Inc., USA) before detection. Total organic carbon (TOC) was determined by a TOC analyzer (Shimadzu, Japan), representing the amount of organic carbon found in the analyzed samples. Suspended solids (SS) and volatile suspended solids (VSS) were measured according to the standard methods for the examination of water and wastewater. In brief: the samples were filtered and the filters were dried at 105 °C weighted and incinerated at 550 °C, and successively weighted again [49]. The pH of water samples was analyzed with a pH meter (WTW pH 537, Xylem Inc., Germany).

2.3.2. Analysis of micropollutants

Water samples were taken from the influent and effluent of the cMBR pilot during the whole period. The raw wastewater and secondary effluent of the WWTP were also collected with a composite sampling strategy (sampling 24 h; n = 24) by an automatic water sampler (BÜHLER 1027, Hach Lange, Dusseldorf, Germany), taking into account the HRT. 29 micropollutants and 15 of their biotransformation products were identified and quantified in these water samples. Their removal was calculated as the percentage of reduction between the concentration in the influent and the concentration in the effluent.

The detection of these compounds was performed on a high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). The HPLC was an Ultimate 3000 HPLC system (Dionex, CAL, USA), and the mass spectrometer was an API 4000 triple quadrupole system (ABSciex, Framingham, MA, USA). An electrospray ionization source (ESI) was installed on the API 4000 system operating in positive mode at 400 °C with a capillary voltage of 5500 V. 100 μL samples, spiked with internal standard were injected into a Synergi polar-RP column (150 × 2 mm, particle size 4 μm, Phenomenex, Torrance, CA, USA), thermostated at 30 °C. The mobile phase was water and methanol, both containing 0.2% formic acid, and the detailed gradient elution is illustrated in Table S3 (supporting information). The precursor ions, product ions, and other HPLC-MS/MS parameters of these compounds are shown in Table S4 in the Supporting Information.

In addition to calculating the apparent removal of micropollutants in the cMBR, we also investigated the sludge activity to degrade micropollutants, i.e., ability of each gram of sludge to remove micropollutants per unit time (see eq. (1)):

$$\frac{\text{Sludge activity}}{[\text{for removal of micropollutants}]} = \frac{Micropollutant removal(\%)}{Sludge amount(g/L) \times Reaction time(h)} \quad (1)$$

Sludge activity is closely related to the otherwise used biomass related first-order reaction rate constant K_{bio} (2).

$$K_{bio} = \frac{\ln\left(\frac{C}{Co}\right)}{Sludge amount(g/L) \times Reaction time(h)} \quad (2)$$

The sludge amount refers to the SS concentration detected in the reactor tank, and reaction time is regarded as the hydraulic retention time, and micropollutant removal was calculated based on the concentrations in the inflow and outflow of the reactor.

2.4. Kinetic experiment

Sludge samples were taken from the membrane tank of the polishing cMBR pilot, transported to the laboratory within 1.5 h, and used for the degradation kinetic experiments to study the sludge's activity towards degradation of the different micropollutants. The experiments were performed in 1 L reactors under the aerobic condition as triplicate

incubations, and a control reactor filled with tap water. Each reactor was spiked with a mixed solution with 29 micropollutants at initial concentrations of around 10 μg/L, as most of the compounds are present in the water environment in a concentration range of 1–10 μg/L (spiking details in Table S5, Supporting Information). The sludge was fully aerated with 1.5 L air/min using porous stone diffusers in the reactors. The magnetic stirrers (150 rpm) were used to keep a homogenous suspended sludge condition. The reactors were covered by aluminum foil to avoid photodegradation. Samples were taken ten times within 250 h and injected into HPLC-MS/MS. The degradation kinetics of these micropollutants were analyzed, and their degradation rate constants were calculated.

3. Results and discussion

3.1. Development of activated sludge concentration in the cMBR

The development of activated sludge in the reactor during the whole operation period is demonstrated in Fig. 2. In the first 50 days, the SS concentration dropped rapidly from 2.30 g/L (start-up sludge transferred from the CAS-WWTP) to 0.11 g/L. This is due to the scarcity of carbon and nitrogen sources in the cMBR influent (the CAS effluent), leading to autophagy (bacteria eating bacteria), resulting in the decrease in SS concentration [50–52]. After the rapid decrease of the sludge, an increase of BOD loading by feeding the reactor with 0.6% raw wastewater and 99.4% effluent of the WWTP instead of 100% effluent (operable inflow ratios on the cMBR) was implemented from day 60 to attempt to boost/stabilize the sludge concentration in the cMBR. However, the 0.6% raw wastewater did not bring the sludge concentration back to the original level (Fig. 2). Under the new loading condition, the SS concentration first increased and then decreased, varying between 0.004 g/L and 0.594 g/L until the 300th day. After this, the cMBR system operated at a relatively stable condition with the SS and VSS remaining constant at 0.045 ± 0.004 g/L and 0.028 ± 0.005 g/L, respectively. It is worth noting that the blower in the process tank that was not needed to keep this tank aerobic (as the blower in the membrane tank was already sufficient to keep aerobic condition) was turned on, on day 91 until the end of the experiment. The SS value was detected at 0.343 ± 0.042 g/L before turning on the blower, and the value increased to 0.594 ± 0.045 g/L after turning on the blower (on day 91, marked in Fig. 2). This indicates that slight precipitation occurred, and the blower (5 L air/min) was able to increase shear forces and keep homogeneous sludge in the process tank (supplement to the mechanical mixer). Due to the precipitation, the SS data detected before day 91 might be underestimated, but this would not affect the main trend, such as the rapid decrease of SS in the first 50 days. After 91 days, the system remained completely homogenous with no further settlement occurring (several manual cleaning operations without detectable SS increase, data not shown). Thus, the detected data represented actual sludge concentrations in the cMBR system, and stable SS and VSS were indeed established after 300 days of operation. Arriaga et al. (2016) also implemented a post CAS polishing MBR system (hollow-fiber ultrafiltration membranes), which established even lower SS at 0.020 ± 0.002 g/L and VSS at 0.014 ± 0.0006 g/L [5]. Both were considerably lower than concentrations in typical MBRs operating on raw wastewater with SS values in the range of 8–12 g/L [53]. This is probably due to more carbon and nitrogen are available for sludge growth in raw wastewater than in effluent.

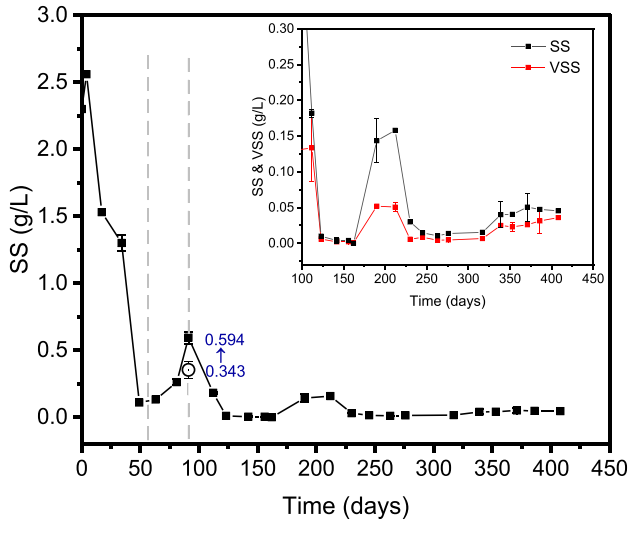

Fig. 2. Evolution of SS (■) and VSS (■) concentrations (representing biomass) in the cMBR system as a function of time. Two vertical grey dashed lines indicate day 60 and day 91, when the cMBR inlet water changed from 100% WWTP effluent to 0.6% raw wastewater and 99.4% effluent, and when the blower in the process tank was turned on (for mixing only). Θ represents the SS value (0.343 g/L) on day 91 before turning on the blower, and the value increased to 0.594 g/L after turning on the blower.

3.2. COD removal

The COD in the inflow of the cMBR (=effluent of CAS) consisted of material that was nondegradable in the CAS, as the easily biodegradable substances would have been consumed in the CAS and only the nonbiodegradable substances remained in the CAS effluent and were loaded into the cMBR. The removal of the COD in the cMBR, and the COD concentration during the whole 15-month experimental period is illustrated in Fig. 3. The COD removal varied from 6.9% to 88.1% during the first 200 days. After that period, the cMBR was able to remove 30–60% COD consistently. The COD concentration in the cMBR influent also varied between 20.4 mg/L and 127 mg/L, as shown in Fig. 3. This might depend on the operation of the main plant, and the operation of the microsieve between the main plant and the cMBR pilot [54,55]. However, it can be seen from Fig. 3 that the COD concentration in the outlet of the cMBR was much more stable, with an average value of 21.5 ± 7.6 mg/L in the whole period. The relatively constant COD in cMBR effluent might represent the residual non-biodegradable organic matter that could not be utilized by the activated sludge in the cMBR pilot. These results are in agreement with previous ones that have studied COD removal in different MBRs loaded with raw wastewater reporting high COD removal (80% – 98.7%), but the COD outlet concentrations in these MBRs outlet were similar (28 mg/L to 35 mg/L) to those determined in ours [5,56]. The higher COD removal in the literature is due to the fact that raw wastewater contains more easily biodegradable organic matter than effluent water, i.e., raw wastewater COD has a higher

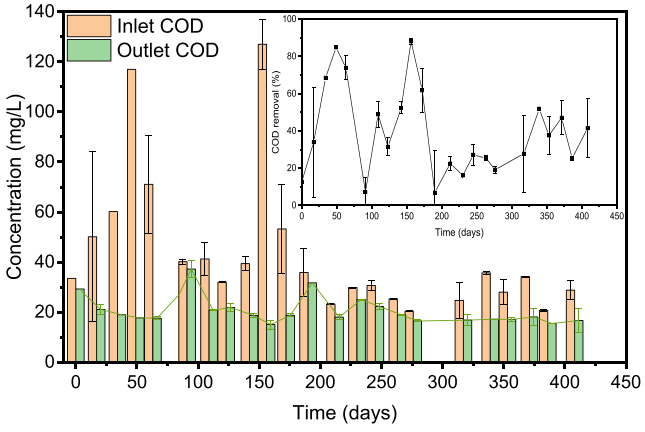

Fig. 3. COD concentrations in cMBR influent and effluent, and the removal of COD by cMBR as a function of time.

proportion of BOD [57].

Fig. S2 (Supporting Information) demonstrates the concentration and removal of filtered COD and TOC during the cMBR operating period. Compared with the result of COD, the concentration and removal of filtered COD and TOC were more stable, again suggesting that the changing of COD over time might be related to the particles that occasionally appeared in the wastewater effluent (instabilities in the microsieve operation). As can be seen from Fig. S2, within 300 days of the cMBR operation, the removal of filtered COD and TOC showed variation to some extent, but after 300 days, their removal tended to be constant at 36.1 ± 5.5% and 34.7 ± 1.8%, respectively, which was consistent with the sludge development trend (Section 3.1.1), indicating this cMBR pilot probably reached a stable operation after about 300 days, providing stable sludge concentration and also removal of organic matter. It is worth noting that during the stable operating period, the pH value in the cMBR effluent (7.1 ± 0.1) was lower than that in the influent (7.8 ± 0.1) (data from the last month operating, Table S7 in Supporting Information). This phenomenon has also been seen in a previous paper that pH of the MBR (treating raw wastewater) outlet was about 7.18, while pH of the MBR inlet was about 7.67 [56]. The decrease of pH value by MBR system was explained that the nitrifying bacteria inside MBR systems would produce protons during the nitrification process, which would lead to the acidification of the solution [56]. However, this might not be the main reason for our post-treatment MBR, because our MBR inflow was mainly the WWTP effluent, with ammonia nitrogen at 1.14 ± 0.82 mg/L, much less than it in the raw wastewater at 42.80 ± 11.6 mg/L.

3.3. Micropollutant removal

The concentrations of the 29 micropollutants were monitored in the cMBR influent (secondary effluent of the CAS) for 15 months (Fig. S1 and Table S6, Supporting Information). The detected concentrations were compound-specific and ranged from 0.017 μg/L to 8.190 μg/L. Some micropollutants were present with relatively high concentrations in the WWTP effluent, such as iomeprol (3.8 ± 1.9 μg/L), gabapentin (3.1 ± 1.6 μg/L), and iohexol (2.5 ± 1.6 μg/L). The concentrations of pharmaceuticals were stable at the inflow of the cMBR (normally day to day deviation less than 10%) except for a) x-ray contrast media as the x-ray facilities in the catchment closed down over the weekends and b) other variations traceable to rain events.

The removal of the 29 micropollutants in the cMBR during the whole operating period is demonstrated in a heatmap (Fig. 4(a)), and the details of each compound's removal over time are illustrated in Fig. 4(b) and Fig. S3 (supporting information). Taking atenolol as an example (Fig. 4(b)), the initial removal was about 40.9%, gradually decreasing to 20.2% (in 50 days), then increasing again to 65.0% (the highest level e.g., on day 91 when sludge concentration reached a temporary maximum (Fig. 2)), then varying between 3.5% and 55.5% until the 300th day, after which the removal stabilized at 19.5 ± 2.1%. It can be seen from Fig. 4(a) and S3 (supporting information) that most of the compounds (17 out of the 29 investigated compounds, including atenolol, erythromycin, irbesartan, clarithromycin, propranolol, mycophenolic acid, citalopram, diatrizoic acid, losartan, benzotriazole, sulfadiazine, oxazepam, iopromide, trimethoprim, iomeprol, iohexol, sulfamethoxazole) showed a similar removal pattern as atenolol, with relatively high removal at the beginning, then varying to some extent, and in the end (about 300 days later), reaching relatively stable compound specific removal which was ranging from about 0 to 43% (Table 1 and Table S8 in Supporting Information). The changes in removal with time might be related to activated sludge's development (amount and composition) (Fig. 2) in the cMBR. Day 0: the high concentration sludge (2.3 g/L SS) produced high removal of micropollutants; Day 0–50: the rapid reduction of sludge (autophagy from 2.3 to 0.11 g/L SS) led to the decrease of micropollutant removal (sludge decreasing and sludge mainly consuming bacterial death cells as nutrition); Day 50–300: the sludge

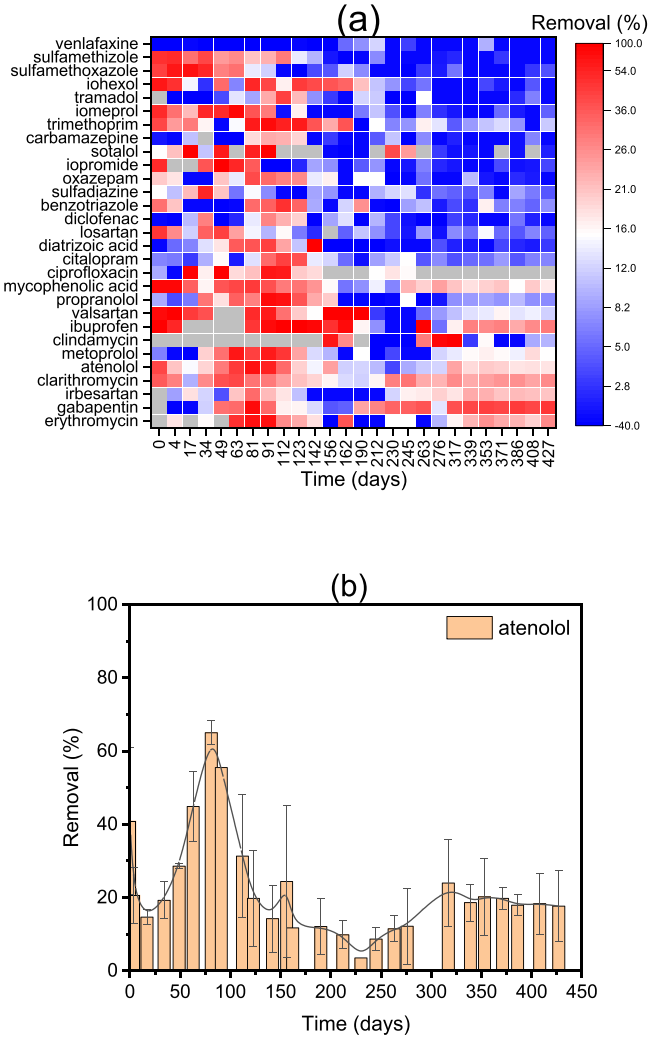

Fig. 4. (a) Heat map of the removal of 29 micropollutants in the cMBR pilot in the whole experimental period. (b) The removal of atenolol by the cMBR as a function of time.

concentration varying at low levels (0.004 – 0.59 g/L SS) resulted in the increased but changing removal of micropollutants (low concentration sludge starting to consume some micropollutants as C and possible N sources as well as the source for energy); After day 300: The sludge concentration tended to be stable (0.045 g/L SS), which could result in stable removal of micropollutants. For the remaining 12 compounds, seven (gabapentin, metoprolol, diclofenac, carbamazepine, tramadol, sulfamethizole, venlafaxine) followed a different pattern. This may be because these compounds had biological reaction processes that were different from other compounds. Five compounds (clindamycin, ibuprofen, valsartan, ciprofloxacin, sotalol) were not detected all the time thus there were no enough data points to establish trends. However, at the current state of knowledge, it seems impossible to predict the complex ecological changes in the microbial communities that then had vast effects on the degradation of micropollutants. However, it is worth noting that after 300 days, when the cMBR reached stable system operation, the removal of all the 29 compounds tended to be stable, with removal ranging from 0 to 43% (Table 1). – Probably micropollutant removal could have been established quicker by either inoculating with a suitable sludge (which does not exist at this moment) or by more dedicated process control from the beginning, but this was out of the scope of this study, though.

Table 1 summarizes the removal of the 29 micropollutants in the

Table 1
Removal rates of 29 micropollutants and COD in the WWTP and the cMBR system, and the degradation kinetics results of these micropollutants in the sludge incubation experiment. The data are given as mean ± relative standard deviation.

Micropollutants	Removal (%)		Sludge incubation experiment			
	WWTP	cMBR	pseudo first order k ($\times10^{-3}h^{-1}$)	R^2	p-value	predicted removal in cMBR (%)
Ciprofloxacin	100		1.92 ± 0.09	0.98	7.34E−10	4.7 ± 1.2
Ibuprofen	96.6 ± 0.9	25.1 ± 4	4.01 ± 0.14	0.99	4.23E−10	9.5 ± 2
Mycophenolic acid	89.7 ± 1.2	18.9 ± 2.1	3.41 ± 0.16	0.98	1.12E−09	8.2 ± 0.6
Gabapentin	87.6 ± 2.3	42.4 ± 3	13.22 ± 0.37	0.99	6.18E−12	28.1 ± 3.2
Valsartan	72 ± 4.2	12.9 ± 1.8	3.59 ± 0.23	0.96	2.48E−08	8.6 ± 1.1
Atenolol	58.6 ± 9.7	19.5 ± 2.2	6.01 ± 0.11	1	1.28E−13	14 ± 0.5
Clarithromycin	41.8 ± 31.9	25 ± 1.2	6.78 ± 0.46	0.95	3.88E−08	15.6 ± 1.2
Erythromycin	18.8 ± 8.7	22.1 ± 3.4	17.86 ± 0.39	0.99	5.27E−13	36 ± 1.2
Propranolol	8.1 ± 13.2	7.9 ± 1	3.52 ± 0.29	0.93	3.08E−07	8.4 ± 1.2
Irbesartan	3.3 ± 26.3	21.3 ± 1.7	7.57 ± 0.17	0.99	7.29E−13	17.2 ± 0.8
Metoprolol	2.5 ± 17.8	15.6 ± 1.9	5.48 ± 0.74	0.83	2.24E−05	12.8 ± 0.2
Clindamycin	−55 ± 65.3	4.7 ± 7.9	4.87 ± 0.18	0.98	1.36E−10	11.5 ± 1.6
Diatrizoic acid	−66.6 ± 54.1	2 ± 1.4	0.66 ± 0.3	0.26	5.25E−02	
Iohexol	76 ± 2.5	−1.1 ± 4.5	−0 ± 0.14	0.1	9.81E−01	
Iomeprol	62.3 ± 2.2	1.1 ± 3	0.07 ± 0.16	0.08	6.68E−01	
Sulfamethoxazole	49.7 ± 30.4	−0.8 ± 4.8	−0.62 ± 0.32	0.21	7.66E−02	
Sulfamethizole	46.9 ± 16.4	−1.7 ± 3.7	−0.73 ± 0.33	0.26	5.32E−02	
Venlafaxine	−12.5 ± 7.2	−3.6 ± 5.9	−0.91 ± 0.57	0.12	1.43E−01	
			zero order k ($\times10^{-3}$ μg L^{-1} h^{-1})	R^2	p-value	predicted removal in cMBR (%)
Sotalol	16 ± 31.5	0.9 ± 0.9	2.82 ± 0.91	0.99	3.08E−02	0.9 ± 0.1
Iopromide	73.9 ± 6.4	1.1 ± 2.3	15.93 ± 5.14	0.99	1.13E−02	1.0 ± 0.3
Sulfadiazine	14.8 ± 23	4.3 ± 3.6	4.47 ± 1.24	0.99	4.86E−03	1.1 ± 0.3
Trimethoprim	45 ± 9.5	7.3 ± 5.4	5.65 ± 1.75	0.98	8.91E−03	0.8 ± 0.2
Tramadol	−18.9 ± 46.6	−1.7 ± 4.6	3.45 ± 0.94	0.99	3.76E−02	0.9 ± 0.0
Benzotriazole	34.5 ± 23.1	6.7 ± 4.6	4.84 ± 0.96	0.98	1.06E−03	1.1 ± 0.2
Citalopram	6 ± 16	5.6 ± 1.4	11.19 ± 1.50	0.95	2.11E−05	2.9 ± 0.4
Carbamazepine	−6 ± 31.8	−1.1 ± 4.5	2.69 ± 0.00	0.99	3.52E−04	0.7 ± 0.1
Oxazepam	17.9 ± 10.3	0.9 ± 4.7	7.55 ± 0.00	0.98	7.39E−06	1.8 ± 0.2
Diclofenac	−0.5 ± 12.3	0.9 ± 3.3	4.80 ± 1.04	0.99	4.02E−02	1.2 ± 0.5
Losartan	54.4 ± 2.8	6.7 ± 3.6	6.75 ± 0.51	0.97	2.27E−02	1.5 ± 0.5
COD	92.8 ± 4.6	37.4 ± 3.8				

WWTP and the cMBR system during the stable operation conditions (after 300 days). Among the 29 micropollutants investigated, gabapentin had the highest removal in the cMBR at 42.4%. Four compounds, ibuprofen, clarithromycin, erythromycin, and irbesartan, were removed by more than 20%, and four compounds, mycophenolic acid, valsartan, atenolol, and metoprolol, were removed by less than 20%, but higher than 10% in the cMBR. The removal of other compounds was less than 10% in the cMBR. In conclusion, different compounds had different removal, which may be due to their different structural and biochemical properties, leading to their different biodegradability in the microbial community developed in the cMBR. In general, hydrophobic compounds with electron-donating groups are more likely to be biodegraded (e.g., ibuprofen: 96.6% removal in the WWTP, and 25.1% removal in the cMBR), while hydrophilic compounds with strong electron-withdrawing groups are hard to decompose in biological processes (e.g., diclofenac: 0.5% removal in the WWTP, and 0.9% removal in the cMBR). The removal of gabapentin was the highest in the cMBR (42.4%) and 87.6% removal in the WWTP. Some papers have reported an almost complete removal of gabapentin during biological wastewater treatment processes, due to presence of specific heterotrophic microorganisms able to degrade this compound [58–60]. The occasionally observed significant negative removal of some compounds (Table 1) were usually attributed to microbial deconjugation of pharmaceutical conjugates from human metabolism in sludge incubations. For example, conjugated glucuronides of carbamazepine presenting in water have been reported to be converted back to carbamazepine in biological reactions [4,36], which also showed negative removal of carbamazepine in this study. For some compounds, negative removal was also found due to the large concentrations variation in the inflow: e.g., diatrizoic acid and tramadol in the CAS.

Table S8 (Supporting Information) compares the removal of these 29 micropollutants in this cMBR study (stable removal after 300 days operation) with previous MBR studies, showing the removal was relatively lower in this study. For example, the removal of atenolol was 19.5% in this study, but the removal was between 69.5% and 87.1% in 21 highly loaded MBRs (treating 100% raw wastewater) and around 86.3% in a polishing ultrafiltration MBR system [5,11]. However, on top of the different loadings, these systems were operated under different HRT, SRT, etc., than our system, making the results difficult to compare. Moreover, it can be seen that although the apparent removal of micropollutants was not high in our post-treatment cMBR system, the established sludge concentration (0.045 g/L SS) was much lower than that in the traditional MBRs (8–10 g/L SS) and CAS processes (2–3 g/L SS). Therefore, it is worth further investigating the activity per gram of sludge in the cMBR to degrade micropollutants.

3.4. Sludge activity

Fig. 5 compares the sludge activities concerning micropollutant degradation and oxygen consumption on day 0 and day 427 of the operation of the cMBR (in triplicate). The sludge activity on day 427 represented the performance of the sludge eventually established in the cMBR system (due to the sludge stabilized at 0.045 g/L SS after 300 days cMBR operation). The sludge activity on day 0 represented the performance of the initial sludge from the CAS system (due to the initial sludge (2.3 g/L) transferred from the WWTP aeration tank).

Table S11 (Supporting Information) shows the removal of micropollutants in the cMBR on day 0 and day 427. It can be seen that although the sludge concentration on day 0 was 51.1 times higher than on day 427 (2.3 g/L and 0.045 g/L SS on day 0 and 427), the removal of micropollutants on day 0 was only 6.3 times (average for 29 compounds) higher than that on day 427. This was because the sludge activity (ability of each gram of sludge to degrade micropollutants) on day 427 was about ten times higher than that on day 0.

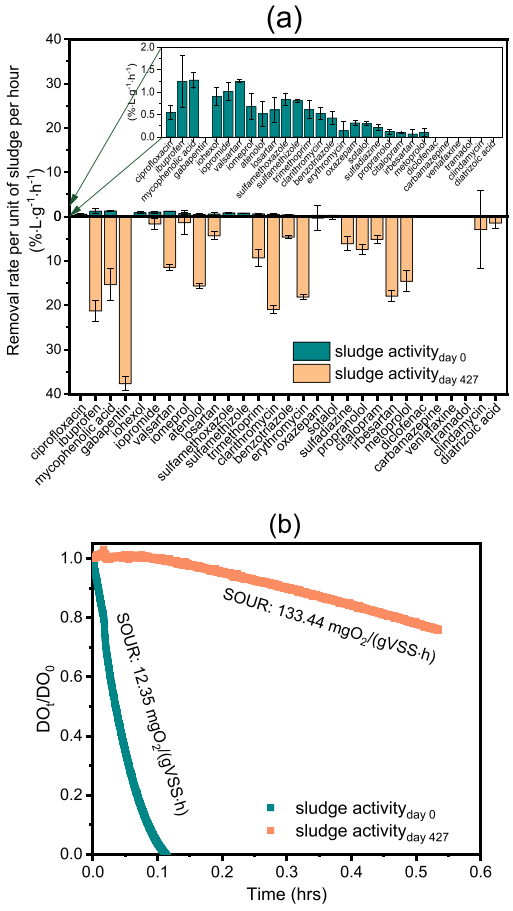

Fig. 5. Comparison of sludge activity in the cMBR system on day 0 (first day of MBR operation with sludge concentration at 2.30 g/L) and day 427 (last day of MBR operation with sludge concentration at 0.045 g/L), with triplicate sampling. (a) The sludge activity regarding the ability to remove micropollutants, expressed as the removal of micropollutants per unit concentration of sludge in unit time (% L g^{-1} h^{-1}). The inner green bar graph is the $sludge_{day\ 0}$ result with the scaling of the y-axis. (b) The sludge activity concerning the relative dissolved oxygen (DO) consumption rate and specific oxygen uptake rate (SOUR) of activated sludge. (For interpretation of the references to colour in this Fig. legend, the reader is referred to the web version of this article.)

Fig. 5(a) and Table S10 (Supporting Information) summarize sludge activities to degrade micropollutants based on micropollutants removal and first-order reaction rate constants, and it can be seen that the sludge activity (to degrade micropollutants) at day 427 was considerably higher than at the beginning (day 0). For example, the removal of atenolol by 1 g/L sludge per hour was 0.6 ± 0.2% L g^{-1} h^{-1} on day 0 (K_{bio} = 0.00751 ± 0.00293 L g^{-1} h^{-1}), and 15.6 ± 0.5% L g^{-1} h^{-1} on day 427 (K_{bio} = 0.17190 ± 0.00501 L g^{-1} h^{-1}). This is indicating that the developed sludge in the cMBR was 20 times more active to remove atenolol than the initial sludge from the CAS. This is probably due to the higher fraction of less opportunistic and more specialized microorganisms (towards micropollutants) in the polishing MBR biomass compared to the CAS (competitive inhibition theory in [61,62]). Similar findings have been reported by Arriaga et al. (2016): a 10–100 times higher micropollutant removal (degradation per gram sludge, per hour, for ketoprofen, diclofenac, ibuprofen, naproxen, and gemfibrozil) by the sludge from a post-treatment MBR than from a CAS or a traditional MBR (treating raw wastewater) [5]. These authors interpreted that, in addition to the adaptation of the microbial communities in the post-treatment MBR, the higher sludge activity toward micropollutants' removal might be due to the higher ratio of oxygen vs. biomass in the polishing MBR in comparison to the CAS system and the traditional MBR. This could lead to a higher mass transfer of oxygen into the biomass (which is needed for the mineralization of the micropollutants) in the polishing MBR than in the CAS and traditional MBR.

Fig. 5(b) shows sludge activity regarding oxygen consumption rates to demonstrate the changed oxygen turnover in the cMBR. The oxygen consumption by the sludge established in the cMBR was slower than the sludge from the CAS, in which oxygen was completely consumed within 0.12 h, which was consistent with previous studies in order of magnitude [63,64]. However, the calculated specific oxygen uptake rate (SOUR) showed the opposite result. SOUR represents the biometabolic activity of aerobic bacteria, and it was expressed as mg/L of oxygen used per gram of activated sludge per hour [63,64]. SOUR was calculated at 12.35 mgO_2/(gVSS•h) with the sludge from the CAS, while the SOUR value was more than 10 times higher at 133.44 mgO_2/(gVSS•h) with the sludge in the cMBR (values marked in Fig. 5(b)). This demonstrated that the sludge activity (micropollutants removal and oxygen consumption) of the sludge established in the cMBR was higher than the initial sludge activity from the CAS, even though the sludge concentration in this cMBR system was much lower.

3.5. Degradation kinetics of micropollutants

After the cMBR system reached stable operation conditions, a sludge sample from the cMBR was transferred to the laboratory (October 2019), and a sludge incubation experiment was conducted with 29 spiked micropollutants (details in Section 2.4). The results are illustrated in Fig. S5 (Supporting Information). The degradation of most compounds followed pseudo-first-order degradation kinetics, and the rate constants together with the fitting R^2 and significance level p-value are summarized in Table 1. Some compounds such as erythromycin and gabapentin showed a relatively fast degradation with pseudo-first-order rate constants at (17.86 ± 0.39) × $10^{-3}h^{-1}$ and (13.22 ± 0.37) × $10^{-3}h^{-1}$, respectively. For some other compounds, degradation was better described by a zero-order kinetic model, and the zero-order rate constants were also shown in Table 1, e.g., citalopram had a zero-order rate constant of (11.19 ± 1.50) × 10^{-3} μg $L^{-1}h^{-1}$. Six compounds did not degrade significantly (p-values greater than 0.05) and thus their concentrations followed neither pseudo-first nor zero-order degradation (Table 1).

Assuming the degradation of the 29 micropollutants in the cMBR system followed the same degradation rate constants obtained above, under the reaction time HRT, their removal in the cMBR could be predicted, and the predicted values are shown in Table 1. It can be seen that the predicted removal of most of the compounds was lower than the actual removal values in the cMBR. For example, the removal of atenolol was about 19.5% in the cMBR, but the predicted value was 14.0%. It might be due to the prediction underestimating i) the membrane effect (separation or sorption of micropollutants by membranes) or ii) the reaction time (sorption of some micropollutants on sludge, leading to bioreaction time longer than HRT) or iii) the absence of co-degradates in the batch incubations.

3.6. Process stability and influence on the removal of micropollutants

The mechanical data of the cMBR were monitored during the whole operation period, and the results are illustrated in Fig. S4 (Supporting Information), including water temperature, DO, flow rate, HRT, and TMP. The flow rate and HRT were set and stabilized at 42 L/h and 25 h during the entire experiment. The water temperature varied with the seasons from 7 to 25 °C. The DO concentration was about 2 mg/L at the beginning, and then it gradually increased with the rapid decrease of the sludge concentration, reaching 8 mg/L on day 50. The DO was kept saturated until the end of the experiment. The TMP never exceeded 0.6 bar (maximum threshold) before 300 days, as long as the cMBR conducted hydraulic backwash regularly. The TMP exceeded 0.6 bar twice

after 300 days of operation, showing fouling and cake layers formed on the membranes, thus chemical washes were performed automatically. After the chemical cleaning, the TMP always returned to normal conditions, indicating the high performance of the ceramic membranes for long-term use.

It is worth noting that after 300 days of operation of the cMBR, the micropollutants removal remained stable in spite of the chemical washes. Generally, the mechanism of micropollutant removal in MBRs includes biodegradation, sorption on sludge, and membrane separation process, which mainly refers to the rejection/sorption of micropollutants by the foulants and cake layers on membranes (microfiltration/ultrafiltration membranes) [11,36]. In our system, sludge was not removed during the whole experimental period, thus sorption on sludge would not contribute significantly to micropollutants' removal. Fig. S4 (Supporting Information) shows that a cake layer started to build up on the ceramic membranes after 300 days, but this had no obvious effect on the removal of micropollutants, indicating that the effect of membrane separation (rejection/sorption by membrane foulants) on the removal of micropollutants was insignificant.

3.7. Performance of the integrated membrane system

Complementing the cMBR, we investigated the performance of a three-stage integrated wastewater treatment system (CAS + cMBR + FO/RO) to remove micropollutants for water reuse. The detailed description of the FO/RO is in a previous paper [65] and the process of this integrated system is in Text S1 (Supporting Information), and the results are shown in Fig. S8, S9 (Supporting Information). In addition to the 29 micropollutants, their 15 common metabolites were also studied (Table S9, Supporting Information). 1) Within the CAS, the 44 compounds had removal ranging from −163.0% (formation) to 100% (complete removal as concentration dropped below detection limits after CAS). Negative removal indicated towards the formation of these metabolites or the deconjugation effect of parent compounds [4,36]. 2) in the cMBR, the 44 compounds had removals ranging from −53.9% to 42.4% (based on cMBR influent and effluent). 3) In the FO process, the removal ranged from 86.7% to 100% (no compounds detected after RO process). Therefore, the FO/RO could be used as an effective supplement to the cMBR to further remove micropollutants, but the construction and operational costs of the integrated membrane system should be further calculated and considered.

4. Conclusions

This was the first study of a silicon carbide cMBR as a post-treatment for operation in a wastewater effluent environment. In addition to studying the removal of micropollutants, the sludge activities were also investigated, and biotransformation products/metabolites were also included for the first time in a cMBR study. The results lead to the following conclusions:

Implementation of the polishing cMBR to remove micropollutants is feasible. Even though the sludge concentration established in the polishing cMBR (0.045 g/L) was much lower than that in the CAS system (2.30 g/L), the biomass related sludge activity towards micropollutants removal and oxygen consumption in the cMBR was more than 10 times higher than that in the CAS system (the WWTP aeration tank). Slightly increasing the proportion of raw wastewater loaded into the cMBR (from 0% to 0.6% raw wastewater) resulted in a stabilized biomass while maintaining the activity of the sludge.

The removal of the 29 micropollutants in the cMBR was compound specific and ranging from 0 to 43%. Different compounds had different removal due to their different structural and biochemical properties, leading to their different biodegradability. The removal of micropollutants was also influenced by the changes of microbial communities caused by the changes in loading (adaptation of C, N sources, etc.,) to the cMBR, which was worthy of further study.

The silicon carbide ceramic microfiltration membrane was operated within the runtime of this project (15 months) without problems, with stable TMP and stable system operation, as long as regular (automatic) hydraulic backwash and chemical cleaning (acid and alkali) was applied.

Although some micropollutants could be removed to a certain extent in the WWTP and the cMBR, some of their biotransformation products were formed. A cMBR combined with a FO/RO membrane system was able to remove micropollutants and their biotransformation products and could be used for direct water reuse. However, the integrated system needs a lot of further process optimization and energy optimization for a final application for micropollutant removal.

As the future perspective, it is worth investigating more sophisticated balancing of BOD loading to increase the amount of biomass while starving the biomass to maintain activity and selectivity to degrade recalcitrant compounds.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.131458.

References

[1] R. Reif, S. Suárez, F. Omil, J.M. Lema, Fate of pharmaceuticals and cosmetic ingredients during the operation of a MBR treating sewage, Desalination 221 (1-3) (2008) 511–517, https://doi.org/10.1016/j.desal.2007.01.111.

[2] A. Arias, T. Alvarino, T. Allegue, S. Suárez, J.M. Garrido, F. Omil, An innovative wastewater treatment technology based on UASB and IFAS for cost-efficient macro and micropollutant removal, J. Hazard. Mater. 359 (2018) 113–120, https://doi.org/10.1016/j.jhazmat.2018.07.042.

[3] J.L. Santos, I. Aparicio, E. Alonso, Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. a case study: Seville city (Spain), Environ. Int. 33 (4) (2007) 596–601, https://doi.org/10.1016/j.envint.2006.09.014.

[4] N. Vieno, T. Tuhkanen, L. Kronberg, Elimination of pharmaceuticals in sewage treatment plants in Finland, Water Res. 41 (5) (2007) 1001–1012, https://doi.org/10.1016/j.watres.2006.12.017.

[5] S. Arriaga, N. de Jonge, M.L. Nielsen, H.R. Andersen, V. Borregaard, K. Jewel, T. A. Ternes, J.L. Nielsen, Evaluation of a membrane bioreactor system as post-treatment in waste water treatment for better removal of micropollutants, Water Res. 107 (2016) 37–46, https://doi.org/10.1016/j.watres.2016.10.046.

[6] T.L. Zearley, R.S. Summers, Removal of trace organic micropollutants by drinking water biological filters, Environ. Sci. Technol. 46 (17) (2012) 9412–9419, https://doi.org/10.1021/es301428e.

[7] P. Verlicchi, M. Al Aukidy, E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: removal, mass load and environmental risk after a secondary treatment-a review, Sci. Total Environ. 429 (2012) 123–155, https://doi.org/10.1016/j.scitotenv.2012.04.028.

[8] T.A. Ternes, Occurrence of drugs in German sewage treatment plants and rivers, Water Res. 32 (1998) 3245–3260, https://doi.org/10.1016/S0043-1354(98)00099-2.

[9] P. Kovalakova, L. Cizmas, T.J. McDonald, B. Marsalek, M. Feng, V.K. Sharma, Occurrence and toxicity of antibiotics in the aquatic environment: a review, Chemosphere 251 (2020) 126351, https://doi.org/10.1016/j.chemosphere.2020.126351.

[10] S. Lin, X. Yu, J. Fang, J. Fan, Influences of the micropollutant erythromycin on cyanobacteria treatment with potassium permanganate, Water Res. 177 (2020) 115786, https://doi.org/10.1016/j.watres.2020.115786.

[11] Y. Gu, J. Huang, G. Zeng, L. Shi, Y. Shi, K. Yi, Fate of pharmaceuticals during membrane bioreactor treatment: status and perspectives, Bioresour. Technol. 268 (2018) 733–748, https://doi.org/10.1016/j.biortech.2018.08.029.

[12] X.T. Bui, T.P.T. Vo, H.H. Ngo, W.S. Guo, T.T. Nguyen, Multicriteria assessment of advanced treatment technologies for micropollutants removal at large-scale applications, Sci. Total Environ. 563–564 (2016) 1050–1067, https://doi.org/10.1016/j.scitotenv.2016.04.191.

[13] I. Schneider, A. Abbas, A. Bollmann, A. Dombrowski, G. Knopp, U. Schulte-Oehlmann, W. Seitz, M. Wagner, J. Oehlmann, Post-treatment of ozonated wastewater with activated carbon and biofiltration compared to membrane bioreactors: toxicity removal in vitro and in Potamopyrgus antipodarum, Water Res. 185 (2020) 1–14, https://doi.org/10.1016/j.watres.2020.116104.

[14] S. Dogruel, Z. Cetinkaya Atesci, E. Aydin, E. Pehlivanoglu-Mantas, Ozonation in advanced treatment of secondary municipal wastewater effluents for the removal of micropollutants, Environ. Sci. Pollut. Res. 27 (36) (2020) 45460–45475, https://doi.org/10.1007/s11356-020-10339-5.

[15] T. Wintgens, T. Melin, A. Schäfer, S. Khan, M. Muston, D. Bixio, C. Thoeye, The role of membrane processes in municipal wastewater reclamation and reuse, Desalination 178 (1-3) (2005) 1–11, https://doi.org/10.1016/j.desal.2004.12.014.

[16] G. Knopp, C. Prasse, T.A. Ternes, P. Cornel, Elimination of micropollutants and transformation products from a wastewater treatment plant effluent through pilot scale ozonation followed by various activated carbon and biological filters, Water Res. 100 (2016) 580–592, https://doi.org/10.1016/j.watres.2016.04.069.

[17] S.G. Zimmermann, M. Wittenwiler, J. Hollender, M. Krauss, C. Ort, H. Siegrist, U. von Gunten, Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: micropollutant oxidation, by-product formation and disinfection, Water Res. 45 (2) (2011) 605–617, https://doi.org/10.1016/j.watres.2010.07.080.

[18] R. Cai, Y. Kubota, A. Fujishima, Effect of copper ions on the formation of hydrogen peroxide from photocatalytic titanium dioxide particles, J. Catal. 219 (1) (2003) 214–218, https://doi.org/10.1016/S0021-9517(03)00197-0.

[19] M. El Gamal, H.A. Mousa, M.H. El-Naas, R. Zacharia, S. Judd, Bio-regeneration of activated carbon: a comprehensive review, Sep. Purif. Technol. 197 (2018) 345–359, https://doi.org/10.1016/j.seppur.2018.01.015.

[20] P. Krzeminski, C. Schwermer, A. Wennberg, K. Langford, C. Vogelsang, Occurrence of UV filters, fragrances and organophosphate flame retardants in municipal WWTP effluents and their removal during membrane post-treatment, J. Hazard. Mater. 323 (2017) 166–176, https://doi.org/10.1016/j.jhazmat.2016.08.001.

[21] G. Crini, E. Lichtfouse, Advantages and disadvantages of techniques used for wastewater treatment, Environ. Chem. Lett. 17 (1) (2019) 145–155, https://doi.org/10.1007/s10311-018-0785-9.

[22] D. Serrano, S. Suárez, J.M. Lema, F. Omil, Removal of persistent pharmaceutical micropollutants from sewage by addition of PAC in a sequential membrane bioreactor, Water Res. 45 (16) (2011) 5323–5333, https://doi.org/10.1016/j.watres.2011.07.037.

[23] S. Buetehorn, C.N. Koh, T. Wintgens, D. Volmering, K. Vossenkaul, T. Melin, Investigating the impact of production conditions on membrane properties for MBR applications, Desalination 231 (1-3) (2008) 191–199, https://doi.org/10.1016/j.desal.2007.12.008.

[24] T. Melin, B. Jefferson, D. Bixio, C. Thoeye, W. De Wilde, J. De Koning, J. van der Graaf, T. Wintgens, Membrane bioreactor technology for wastewater treatment and reuse, Desalination 187 (1-3) (2006) 271–282, https://doi.org/10.1016/j.desal.2005.04.086.

[25] A. Santos, W. Ma, S.J. Judd, Membrane bioreactors: two decades of research and implementation, Desalination. 273 (1) (2011) 148–154, https://doi.org/10.1016/j.desal.2010.07.063.

[26] F.I. Hai, K. Tessmer, L.N. Nguyen, J. Kang, W.E. Price, L.D. Nghiem, Removal of micropollutants by membrane bioreactor under temperature variation, J. Membr. Sci. 383 (1-2) (2011) 144–151, https://doi.org/10.1016/j.memsci.2011.08.047.

[27] T. Alvarino, S. Suárez, M. Garrido, J.M. Lema, F. Omil, A UASB reactor coupled to a hybrid aerobic MBR as innovative plant configuration to enhance the removal of organic micropollutants, Chemosphere 144 (2016) 452–458, https://doi.org/10.1016/j.chemosphere.2015.09.016.

[28] A.T. Besha, A.Y. Gebreyohannes, R.A. Tufa, D.N. Bekele, E. Curcio, L. Giorno, Removal of emerging micropollutants by activated sludge process and membrane bioreactors and the effects of micropollutants on membrane fouling: a review, J. Environ. Chem. Eng. 5 (3) (2017) 2395–2414, https://doi.org/10.1016/j.jece:2017.04.027.

[29] T. Alvarino, N. Torregrosa, F. Omil, J.M. Lema, S. Suarez, Assessing the feasibility of two hybrid MBR systems using PAC for removing macro and micropollutants, J. Environ. Manage. 203 (2017) 831–837, https://doi.org/10.1016/j.jenvman.2016.03.023.

[30] S.-Y. Leu, L. Chan, M.K. Stenstrom, Toward long solids retention time of activated sludge processes: benefits in energy saving, effluent quality, and stability, Water Environ. Res. 84 (1) (2012) 42–53, https://doi.org/10.2175/106143011X12989211841052.

[31] K. Ma, A preliminary comparative analysis of MBR and CAS wastewater treatment systems, Int. J. Water Wastewater Treat. 3 (2017), https://doi.org/10.16966/2381-5299.138.

[32] M.F. Tay, C. Liu, E.R. Cornelissen, B. Wu, T.H. Chong, The feasibility of nanofiltration membrane bioreactor (NF-MBR)+reverse osmosis (RO) process for water reclamation: comparison with ultrafiltration membrane bioreactor (UF-MBR)+RO process, Water Res. 129 (2018) 180–189, https://doi.org/10.1016/j.watres.2017.11.013.

[33] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Res. 43 (3) (2009) 831–841, https://doi.org/10.1016/j.watres.2008.11.043.

[34] S. Suárez, R. Reif, J.M. Lema, F. Omil, Mass balance of pharmaceutical and personal care products in a pilot-scale single-sludge system: influence of T SRT and recirculation ratio, Chemosphere 89 (2) (2012) 164–171, https://doi.org/10.1016/j.chemosphere.2012.05.094.

[35] S.K. Maeng, B.G. Choi, K.T. Lee, K.G. Song, Influences of solid retention time, nitrification and microbial activity on the attenuation of pharmaceuticals and estrogens in membrane bioreactors, Water Res. 47 (9) (2013) 3151–3162, https://doi.org/10.1016/j.watres.2013.03.014.

[36] J. Ma, R. Dai, M. Chen, S.J. Khan, Z. Wang, Applications of membrane bioreactors for water reclamation: micropollutant removal, mechanisms and perspectives, Bioresour. Technol. 269 (2018) 532–543, https://doi.org/10.1016/j.biortech.2018.08.121.

[37] S.J. Judd, The status of industrial and municipal effluent treatment with membrane bioreactor technology, Chem. Eng. J. 305 (2016) 37–45, https://doi.org/10.1016/j.cej.2015.08.141.

[38] B. Teychene, C. Guigui, C. Cabassud, G. Amy, Toward a better identification of foulant species in MBR processes, Desalination 231 (1-3) (2008) 27–34, https://doi.org/10.1016/j.desal.2007.12.006.

[39] S.M. Abtahi, M. Petermann, A. Juppeau Flambard, S. Beaufort, F. Terrisse, T. Trotouin, C. Joannis Cassan, C. Albasi, Micropollutants removal in tertiary moving bed biofilm reactors (MBBRs): contribution of the biofilm and suspended biomass, Sci. Total Environ. 643 (2018) 1464–1480, https://doi.org/10.1016/j.scitotenv.2018.06.303.

[40] P. Champagne, P.J. Van Geel, W.J. Parker, A proposed transient model for cometabolism in biofilm systems, Biotechnol. Bioeng. 60 (1998) 541–550, https://doi.org/10.1002/(SICI)1097-0290(19981205)60:5<541::AID-BIT4>3.0.CO;2-Q.

[41] K. Fischer, M. Majewsky, Cometabolic degradation of organic wastewater micropollutants by activated sludge and sludge-inherent microorganisms, Appl. Microbiol. Biotechnol. 98 (15) (2014) 6583–6597, https://doi.org/10.1007/s00253-014-5826-0.

[42] M. Escolà Casas, K. Bester, Can those organic micro-pollutants that are recalcitrant in activated sludge treatment be removed from wastewater by biofilm reactors (slow sand filters)? Sci. Total Environ. 506–507 (2015) 315–322, https://doi.org/10.1016/j.scitotenv.2014.10.113.

[43] J. Teng, L. Shen, G. Yu, F. Wang, F. Li, X. Zhou, Y. He, H. Lin, Mechanism analyses of high specific filtration resistance of gel and roles of gel elasticity related with membrane fouling in a membrane bioreactor, Bioresour. Technol. 257 (2018) 39–46, https://doi.org/10.1016/j.biortech.2018.02.067.

[44] H.-S. Shin, S.-T. Kang, Characteristics and fates of soluble microbial products in ceramic membrane bioreactor at various sludge retention times, Water Res. 37 (1) (2003) 121–127, https://doi.org/10.1016/S0043-1354(02)00249-X.

[45] Y. Jeong, S.W. Hermanowicz, C. Park, Treatment of food waste recycling wastewater using anaerobic ceramic membrane bioreactor for biogas production in mainstream treatment process of domestic wastewater, Water Res. 123 (2017) 86–95, https://doi.org/10.1016/j.watres.2017.06.049.

[46] J. Xue, Y. Zhang, Y. Liu, M. Gamal El-Din, Treatment of oil sands process-affected water (OSPW) using a membrane bioreactor with a submerged flat-sheet ceramic microfiltration membrane, Water Res. 88 (2016) 1–11, https://doi.org/10.1016/j.watres.2015.09.051.

[47] P. Banerjee, T.K. Dey, S. Sarkar, S. Swarnakar, A. Mukhopadhyay, S. Ghosh, Treatment of cosmetic effluent in different configurations of ceramic UF membrane based bioreactor: toxicity evaluation of the untreated and treated wastewater using catfish (Heteropneustes fossilis), Chemosphere 146 (2016) 133–144, https://doi.org/10.1016/j.chemosphere.2015.12.004.

[48] E. Eray, V. Boffa, M.K. Jørgensen, G. Magnacca, V.M. Candelario, Enhanced fabrication of silicon carbide membranes for wastewater treatment: from laboratory to industrial scale, J. Membr. Sci. 606 (2020) 118080, https://doi.org/10.1016/j.memsci.2020.118080.

[49] I.V. Carranzo, APHA, AWWA, WEF. “Standard Methods for examination of water and wastewater.,” APHA, AWWA, WEF. “Standard Methods Exam. Water Wastewater.” 5 (2012) 185–186. https://doi.org/10.5209/rev_ANHM.2012.v5.n2.40440.

[50] A. Arias, C.R. Behera, G. Feijoo, G. Sin, M.T. Moreira, Unravelling the environmental and economic impacts of innovative technologies for the enhancement of biogas production and sludge management in wastewater systems, J. Environ. Manage. 270 (2020) 110965, https://doi.org/10.1016/j.jenvman.2020.110965.

[51] D. Giuliano Perez, C.S. Fontanetti, Assessment of the toxic potential of sewage sludge in the midgut of the diplopod Rhinocricus padbergi, Water. Air. Soil Pollut. 218 (1-4) (2011) 437–444, https://doi.org/10.1007/s11270-010-0657-9.

[52] D.J.K. Vojo Deretic, How cells clean house, Sci. Am. 298 (2019) 74–81, https://doi.org/10.1017/CBO9781107415324.004.

[53] P. Krzeminski, M.C. Tomei, P. Karaolia, A. Langenhoff, C.M.R. Almeida, E. Felis, F. Gritten, H.R. Andersen, T. Fernandes, C.M. Manaia, L. Rizzo, D. Fatta-Kassinos,

Performance of secondary wastewater treatment methods for the removal of contaminants of emerging concern implicated in crop uptake and antibiotic resistance spread: a review, Sci. Total Environ. 648 (2019) 1052–1081, https://doi.org/10.1016/j.scitotenv.2018.08.130.
[54] J.H.J.M. van der Graaf, J.H. Roorda, New developments in upgrading waste-water treatment plant effluent using ultrafiltration, Membr. Technol. 2000 (126) (2000) 4–7, https://doi.org/10.1016/S0958-2118(00)80234-7.
[55] A.M. Vajda, L.B. Barber, J.L. Gray, E.M. Lopez, A.M. Bolden, H.L. Schoenfuss, D. O. Norris, Demasculinization of male fish by wastewater treatment plant effluent, Aquat. Toxicol. 103 (3-4) (2011) 213–221, https://doi.org/10.1016/j.aquatox.2011.02.007.
[56] P. Cartagena, M. El Kaddouri, V. Cases, A. Trapote, D. Prats, Reduction of emerging micropollutants, organic matter, nutrients and salinity from real wastewater by combined MBR-NF/RO treatment, Sep. Purif. Technol. 110 (2013) 132–143, https://doi.org/10.1016/j.seppur.2013.03.024.
[57] F.A. El-Gohary, F.A. Nasr, S. El-Hawaary, Performance assessment of a wastewater treatment plant producing effluent for irrigation in Egypt, Environmentalist 18 (1998) 87–93, https://doi.org/10.1023/A:1006618307270.
[58] N. Henning, U. Kunkel, A. Wick, T.A. Ternes, Biotransformation of gabapentin in surface water matrices under different redox conditions and the occurrence of one major TP in the aquatic environment, Water Res. 137 (2018) 290–300, https://doi.org/10.1016/j.watres.2018.01.027.
[59] J.T. Yu, E.J. Bouwer, M. Coelhan, Occurrence and biodegradability studies of selected pharmaceuticals and personal care products in sewage effluent, Agric. Water Manage. 86 (1-2) (2006) 72–80, https://doi.org/10.1016/j.agwat.2006.06.015.
[60] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, Illicit drugs and pharmaceuticals in the environment – Forensic applications of environmental data, Part 2: pharmaceuticals as chemical markers of faecal water contamination, Environ. Pollut. 157 (6) (2009) 1778–1786, https://doi.org/10.1016/j.envpol.2009.02.019.
[61] L. Zhang, P.N. Carvalho, U.E. Bollmann, H. EI-taliawy, H. Brix, K. Bester, Enhanced removal of pharmaceuticals in a biofilter: effects of manipulating co-degradation by carbon feeding, Chemosphere 236 (2019) 124303, https://doi.org/10.1016/j.chemosphere.2019.07.034.
[62] C. Liang, L. Zhang, N.B. Nord, P.N. Carvalho, K. Bester, Dose-dependent effects of acetate on the biodegradation of pharmaceuticals in moving bed biofilm reactors, Water Res. 159 (2019) 302–312, https://doi.org/10.1016/j.watres.2019.04.026.
[63] C.J. Kelly, N. Tumsaroj, C.A. Lajoie, Assessing wastewater metal toxicity with bacterial bioluminescence in a bench-scale wastewater treatment system, Water Res. 38 (2) (2004) 423–431, https://doi.org/10.1016/S0043-1354(03)00432-9.
[64] T.T. Nguyen, H.H. Ngo, W. Guo, Pilot scale study on a new membrane bioreactor hybrid system in municipal wastewater treatment, Bioresour. Technol. 141 (2013) 8–12, https://doi.org/10.1016/j.biortech.2013.03.125.
[65] R. Li, S. Braekevelt, J.L.N. De Carfort, S. Hussain, U.E. Bollmann, K. Bester, Laboratory and pilot evaluation of aquaporin-based forward osmosis membranes for rejection of micropollutants, Water Res. 194 (2021) 116924, https://doi.org/10.1016/j.watres.2021.116924.