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Removal of contaminants of emerging concern from real wastewater by an innovative hybrid membrane process – UltraSound, Adsorption, and Membrane ultrafiltration (USAMe®)

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ABSTRACT

The low-level presence of emerging contaminants (ECs) in the environment has raised a great concern due to their persistence, chronic toxicological, and endocrine disrupting effects on terrestrial and aquatic organisms. Wastewater treatment plants (WWTPs) have become hotspots for the spread of these contaminants to the environment as conventional processes are not efficient in removing them. Thus, the integration of advanced treatment methods within the chain of WWTPs is very essential. In this study, the innovative hybrid process USAMe® which integrates ultrasound irradiation (US), adsorption (A) and membrane filtration (Me) was investigated for the removal of ECs from secondary effluents. Diclofenac, carbamazepine, and amoxicillin were selected due to their large consumption and frequent presence in the aquatic environment. All three ECs were spiked into real secondary wastewater effluent at two concentrations of 10 ppm and 100 ppb. Membrane ultrafiltration and its combination with US (USMe) or adsorption (AMe) were also studied as control tests. The hybrid combination of all the three methods in the USAMe® processes elevated the EC removals to above 99% as compared to only around 90% in the AMe process. All effluents of the hybrid USAMe® processes gave "No Effect" to D. magna, with immobilization of $\leq$20%. Therefore, results showed that the USAMe® process was efficient in not only removing ECs, but also in generating safe and less toxic treated effluents; thereby displaying its potential as an advanced method for wastewater treatment.

1. Introduction

Low levels of contaminants of emerging concern (CECs), also known as emerging contaminants (ECs) in water bodies, even at ng/L to µg/L concentrations, have raised countless concerns because of the ECs persistence, toxicity, and endocrine disrupting effects [1]. The effects of simple interruption of normal body functions may lead to overwhelming impacts of biodiversity loss in the course of time. Several pharmaceuticals, for instance, which are considered endocrine disrupting compounds (EDCs) alter the growth of organisms and repress their reproduction, thereby resulting to population decline [2]. The anti-epileptic drug carbamazepine (CBZ) and anti-inflammatory drug diclofenac (DCF), are potential EDCs and correspondingly the ECs of highest concentrations in the secondary wastewater effluent [1,3]. Antibiotics on the other hand, like the most prescribed amoxicillin (AMX), are posing the risk of the development of highly-resistant microbial strains as their occurrence in wastewater and soil is linked to a superbug mutation [4]. Moreover, the presence of ECs in the environment is even linked to serious human health problems of infertility and cancer [5,6].

In most wastewater treatment plants (WWTPs), conventional biological treatment is the core step in toxic contaminant removal, nonetheless and due to non-biodegradability of most ECs like CBZ and DCF [7–9]; ECs' concentrations are not significantly altered in conventional biological processes. Several studies have reported the poor removal of CBZ and DCF in WWTPs [10–12]. A systematic assessment to understand ECs degradation in a biological anaerobic-anoxic-aerobic process with MBR by Xue et al., 2010 [13] revealed that CBZ was first removed

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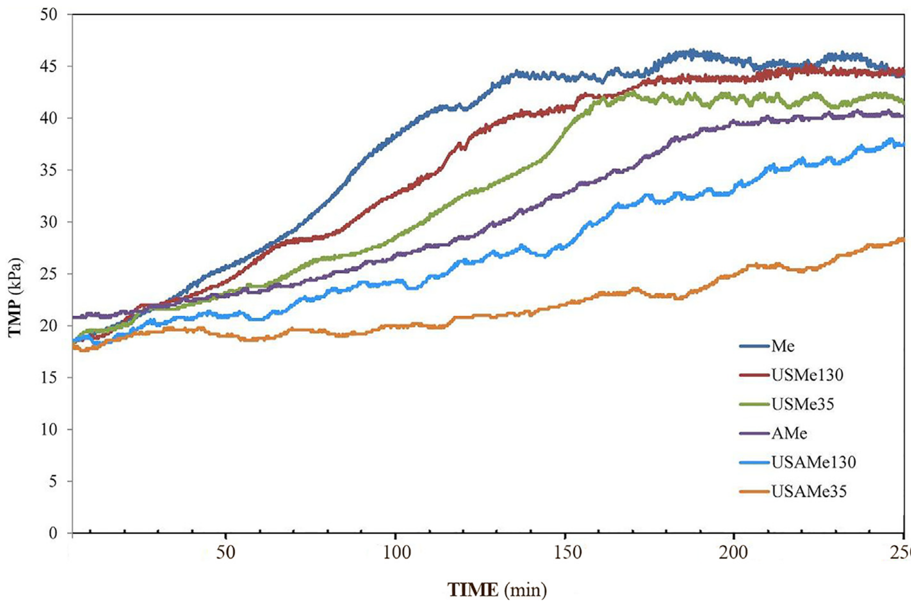

Fig. 1. Flow diagram of each process tested.

in the anaerobic tank and further removed in the anoxic tank. However, the concentration has increased in the aerobic tank and in the MBR, giving a low removal at the end. The same treatment resulted in decreasing DCF concentration until the aerobic tank, but DCF the concentration started to increase in the MBR, also resulting in high DCF concentration in the effluent. This denotes probable transformation, cleavage, and reformation of the parent compound within the biological processes. It was also reported that the major mechanisms of EC_S removal are biodegradation and sorption to sludge, both of which are poor for ECs such as CBZ and DCF as they are the most recalcitrant ECs in conventional activated sludge process [14]. Even with the application of conventional tertiary treatments, CBZ and DCF are still highly detectable in the effluent [15], and report no removals at some point [12,16].

With pharmaceuticals and personal care products being a large fraction of ECs, and considering that the removal of ECs by conventional WWTPs is not satisfactory [17], municipal wastewater becomes a hotspot and an access way of the spread of these ECs into the environment. Thus, the application of effective and advanced treatment methods as post-treatments of the existing biological methods in WWTPs are of great importance prior to discharging them to aquatic environments.

Membrane filtration (Me) and adsorption (A) are among the two most commonly used advanced treatment processes. Ultrasound irradiation (US), aside from its destructive effect on ECs through sonolysis, is also a good auxiliary method which enhances the membrane filtration and adsorption processes [18–20]. Several advantages were reported when the mentioned methods are combined [18,19,21]. A previous investigation on the simultaneous application of the three methods – ultrasound, adsorption, and membrane filtration – in a hybrid process called USAMe® resulted in excellent ECs removals from synthetic wastewater [22]. However, ECs were seldom detected as the only contaminants in wastewater, they were usually present with other contaminants like organic pollutants. The ECs in wastewater are expected to be present together with background organic contaminants in WWTP effluent. This necessitated further study, where the application of this innovative hybrid USAMe® process, as a post-treatment of the biological process in a WWTP, is investigated.

A major consideration in this integration is the problem brought about by the presence of the natural organic matter (NOM). This NOM clogs the pores of the membrane and increases the trans-membrane pressure (TMP), which not only requires more frequent cleaning but also challenges the material integrity of the membrane [23]. In adsorption, NOM competes with the target contaminants for the adsorption sites, thereby lowering adsorption capacity for the target contaminants and requiring greater doses to achieve effective adsorption. Moreover, NOM adds to the total concentration of contaminants in wastewater that needs to be degraded through a more intense sonication and extended reaction durations, which will increase the energy requirement.

The current study investigated the performance of the innovative USAMe® process, applied as post treatment of a biological process, in terms of ECs removal. In the present work, USAMe® process was first used on secondary wastewater effluent, from full-scale wastewater treatment plant, as feed for the innovative tertiary treatment. The possible removal mechanisms in the hybrid process were also investigated. It is worth to highlight that the investigation of the hybrid USAMe® process on real wastewater is a key aspect for the scale up of the system.

2. Materials and methods

2.1. Chemicals

Three pharmaceutical compounds, DCF (CAS#15307-79-6), CBZ (CAS#298-46-4), and AMX (CAS#61336-70-7), were chosen for this study to represent highly consumed and frequently detected ECs in the aquatic environment [24]. All three ECs were spiked, at two concentrations of 10 ppm and 100 ppb each, into secondary wastewater effluent taken downstream of the secondary sedimentation tanks of a full-scale wastewater treatment plant in Salerno, Italy. Wastewater characteristics were pH: 7.6–8.3, chemical oxygen demand (COD): 25–60 mg/L as tested through Open Reflux Method, and a biological oxygen demand (BOD) of 1 mg/L to 4 mg/L as tested by OxiTop BOD Measurement Instrumentation. The same EC-spiked wastewater, taken after biological processes of a real wastewater treatment plant, served as feed to all experimental tests that have been performed.

2.2. Experimental setup and operating conditions

The innovative hybrid USAMe® process is patented by the Sanitary and Environmental Engineering Division (SEED) of the University of

Salerno which simultaneously combines membrane ultrafiltration, activated carbon adsorption and ultrasound irradiation. Fig. 1 illustrates the different experimental set-ups also used in a previous study [22].

Several experiments, applying different combinations, were performed to investigate the removal efficiencies, mechanisms and the effect of US and PAC addition on membrane performance, which include (Fig. 1): Membrane ultrafiltration alone (Me), ultrafiltration with ultrasound irradiation at 35 kHz (USMe35) and 130 kHz (USMe130), ultrafiltration with activated carbon adsorption (AMe), and the hybrid USAMe® process at 35 kHz (USAMe®35) and 130 kHz (USAME®130).

A single hollow fiber membrane (A/G Technology Corporation, USA) was used for the experiment enclosed in a glass tube to collect the permeate with an inside-outside flow pattern while the system was immersed in an ultrasonic bath [22]. The membrane material was polysulfone with nominal MWCO of 100 kDa and an effective transfer area of 6.6 cm^2 and a nominal pore size of 0.1 μm [22]. Cross-flow configuration is employed at a constant flux of 150 L/m^2h.

For tests with adsorption (AMe and USAMe), cleaned and dried powdered activated carbon (PAC) of Carlo Erba Reagenti (Italy) is used. The preparatory and post-experimental procedures, together with the complete description of the set-up, were discussed in [22]. A PAC dose of 4.5 g/m^2, falling at the lower end of the doses commonly employed in literature [21,25-27] was used. This is greater than the dose used in the previous studies [22] to deal with the effects of NOM caused by the application as post-treatment of the biological process. The employed cross-flow configuration allows the circulation of the PAC adsorbent within the membrane, the mixed stream, and the recirculation lines, thereby producing lower actual adsorbent concentrations in the membrane at any time.

For ultrasound irradiation, in the USMe and USAMe tests, the membrane unit was immersed in a TI-H-10 Ultrasonic Bath (Elma®, Germany), operated at a specific ultrasonic density of 35 W/L and 29 W/L for the frequencies 35 kHz and 130 kHz, respectively, as measured by the calorimetric method [28]. Continuous irradiation was employed while the bath was filled with 5 L of deionized water and the bath temperature was maintained at 25 ± 2 °C.

2.3. Analysis performed

Permeate quality was analyzed in terms of EC concentrations using LC-MS/MS system where they were analysed in ESI-positive mode using a mobile phase composed of A: 0.1% formic acid in water and B: acetonitrile–water (1:1, v/v) solution with a limit of quantification lower of 1 ng/L. An Inertsil ODS-3 C18 column was used for the separation step. A pH211 microprocessor pHmetre (Hanna Instruments, USA) was used to monitor temperature throughout the process and pH at fixed times. Membrane fouling formation was evaluated monitoring TMP variation over time through a PCE-932 full line pressure meter and a PS100 transducer (PCE Instruments, Italy) connected to a computer for the acquisition of the data. Membrane stability under the effect of acoustic cavitation and the extent of membrane erosion were evaluated by the use of an electron microscope (emission on the field JEOL 7000, scanning electron microscope – SEM). Ecotoxicity was tested with Daphnia magna [29] to ascertain safety disposal in actual applications.

3. Results and discussions

3.1. Effect of NOM on membrane filtration

In the experiments performed using synthetic wastewater, the TMP remained approximately constant and very low [22]. In this study where the membrane process was applied as a post treatment of a biological process, test results showed that membrane fouling has increased over time in the membrane filtration employing real secondary wastewater effluent as feed, as evidenced by the TMP profile over time presented in Fig. 2. Membrane fouling is attributed to the presence of

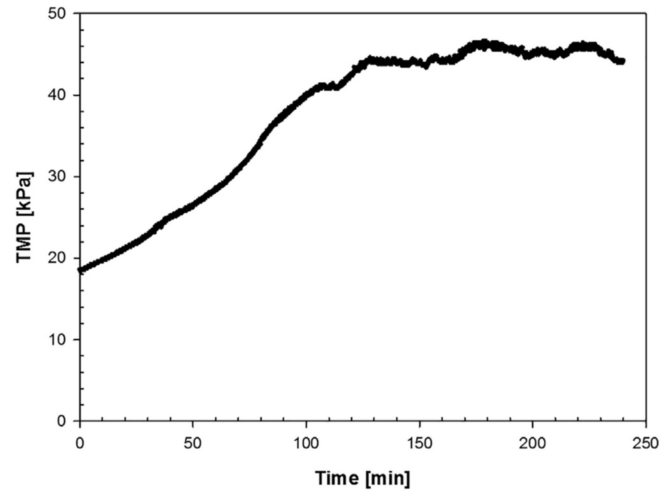

Fig. 2. Trans-membrane pressure (TMP) variation over time using secondary real wastewater effluent by different membrane processes at 150 L/m^2h (Membrane ultrafiltration alone (Me), ultrafiltration with ultrasound irradiation at 35 kHz (USMe35) and 130 kHz (USMe130), ultrafiltration with activated carbon adsorption (AMe), and the hybrid USAMe® process at 35 kHz (USAMe®35) and 130 kHz (USAMe®130)).

the background NOM in wastewater [23,30]. In a constant flux operation, Darcy's law states that the TMP increases as resistance develops [31]. As filtration progresses and fouling grows, greater TMP is necessary in order to maintain the desired output flux. After 120 min, the slope rapidly changed. At around 180 min, the highest TMP value equal to around 45 kPa was reached and the TMP remained around this level until the end of the experiment. The increase in the resistance could be due to concentration polarization caused by the accumulation of NOM particles adjacent to the membrane surface [21,32]. Such accumulation could result in pore blockage through which NOM particles could diffuse through the membrane pores leading to flux decline [33–35].

Membrane performance is improved in following ascending order: USME < AMe < USAMe, with performance under 35 kHz better than 130 kHz in cases where US was employed. The addition of PAC lowered fouling by adsorption of small-sized NOM fraction thus preventing them from entering the membrane pores (Fig. 2). The effect of PAC on fouling abatement was superior over US. As shown in Fig. 2, membrane fouling rate in USMe process was higher than that of AMe process since a more porous layer NOM-PAC aggregate is more permeable than the NOM gel layer most likely formed in the absence of PAC. For USMe processes, fouling rate was lower in 35 kHz than in 130 kHz. This confirms the superior cleaning capacity of US at lower frequencies which lessens both internal and external fouling due to the cavitation effects. The enhancement effect of PAC and US in the USAMe process is additive with a ΔTMP reductions equal to 68% and 90% in USAMe130 and USAMe35, respectively (Fig. 2). Therefore, adsorption and ultrasound perform their specific actions in the hybrid process. Small PAC particles were produced from the destruction of PAC upon ultrasonic action. The result shows the capacity of low-frequency US to effectively knocking off particles from the membrane surface, which is even made easier by the presence of PAC particles of greater back-transport velocity. US serves to extend filtration time by maintaining lower TMP values, which could be attributed to its mechanical and acoustic forces that continuously clean the membrane and aid adsorption through several mechanisms [18].

Fig. 3 shows the SEM images at the start and the end of the USAMe35 filtration test. It can be seen the pores are homogeneously distributed over the whole investigated membrane surface and the membrane shows its typical spongy structure. After the application of US, the outer membrane surface remained intact and no damage to the fibers was found. Same results were found for the other experimental

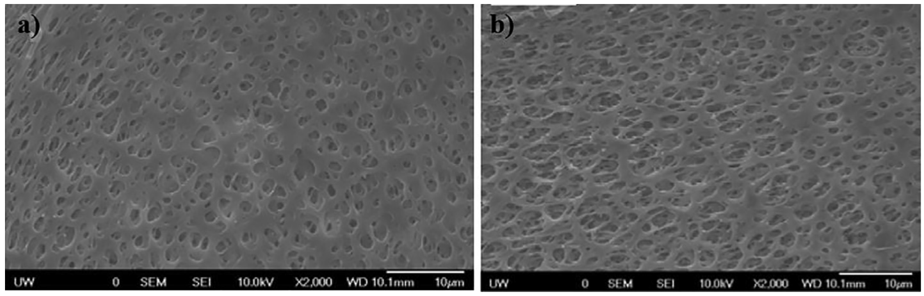

Fig. 3. SEM images of the external membrane surface for the USAMe35 test a) at the start of the experiment and b) at the end of experiment (2000X Magnification; permeate flow 150 L / (m^2h); US 35 kHz).

tests.

3.2. ECs removal by membrane filtration applied as post-treatment of the biological process

While membrane filtration of synthetic wastewater results to very poor and decreasing EC removal over time [22], the use of membrane filtration as post-treatment of biological process, that is, using the secondary wastewater effluent as feed to the membrane, resulted in increasing EC removal over time (Fig. 4). This suggests the occurrence of other removal mechanisms, which may be attributed to the presence of NOM in wastewater. Increasing TMP (Fig. 2) could indicate pore blocking that resulted from the deposition and accumulation of low molecular weight colloidal NOM fractions that narrow the pores, thereby providing the steric hindrance which made the rejection of ECs possible. Other studies have also observed the contribution of NOM adsorption and pore blocking to the retention of low molecular weight solutes in ultrafilters [36,37]. Moreover, because ECs have some affinity to organic carbon, a fraction of them will bind with NOM and partition to suspended solids, enabling the membrane to reject the ECs as large-sized EC-NOM complexes [38]. Finally, the gel or cake fouling layer formed by NOM acts as a secondary filter, which is tighter than the ultrafilter itself, thus retaining ECs and enhancing contaminant removal in the loose membrane.

3.3. ECs removal in AMe process applied as post treatment of the biological process

The application of this innovative hybrid process as tertiary treatment, which has been tested through the use of real secondary wastewater effluent in this study, introduced the presence of an additional adsorbate that is the NOM. A quick comparison of the effect of NOM to ECs removal in the AMe process is displayed in Fig. 5. In this figure the results of the AMe experiments of the previous study [22], characterized by the use of synthetic wastewater as feed at an adsorbent dose of 1.5 g/m^2, is graphed together with the results of this study.

Despite the higher PAC dose used in present work, ECs removals were still lower in the presence of the NOM. Indeed, the average EC removals were found equal to 92,03 ± 1,50%, 92,43 ± 0,35%, 91,65 ± 1,17% for DCF, CBZ and AMX, respectively, in real wastewater and 99,08 ± 0,34%, 99,15 ± 0,64%, 98,94 ± 0,62% for DCF, CBZ and AMX, respectively, in synthetic wastewater.

This confirms the considerable detrimental effect of NOM to ECs adsorption onto PAC, the main removal mechanism in the AMe process. In adsorption, the presence of NOM may reduce diffusivities and increase internal resistance while it competes with the target contaminants for the available adsorbent area [39–41]. This may decrease the affinity of the contaminant to the adsorbent as well as lower the adsorption capacity for ECs [38]. Once the available adsorbent sites were saturated, EC removals kept stable and did not shown an increase over time.

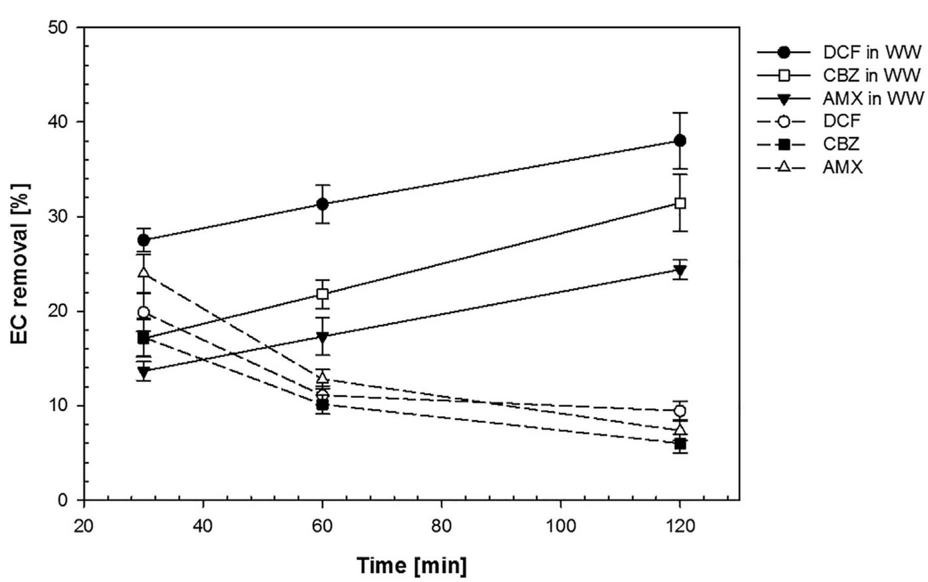

Fig. 4. Removal of ECs by membrane ultrafiltration at 150 L/m^2h in synthetic (broken lines) [22] and real secondary wastewater (WW) (solid lines) at 10 ppm initial EC concentrations.

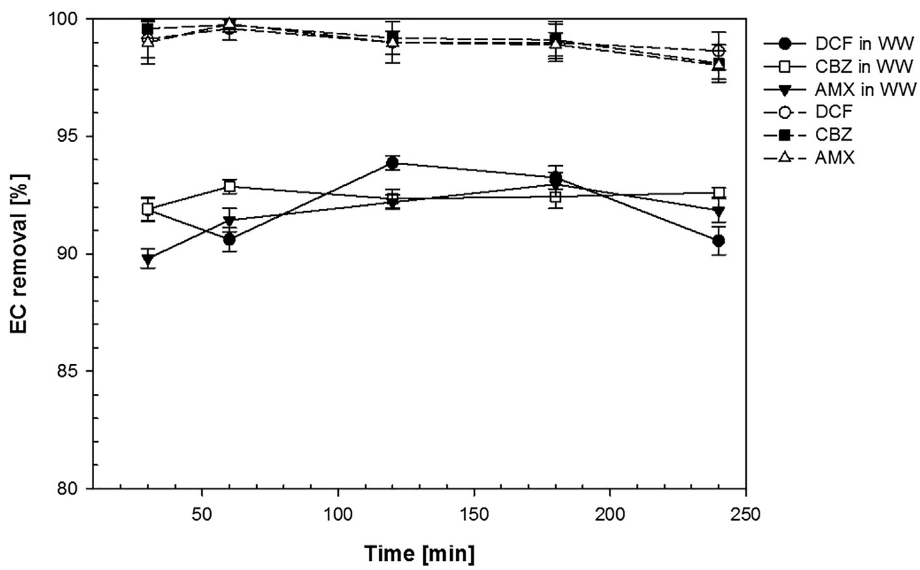

Fig. 5. Removal of ECs by ultrafiltration with activated carbon adsorption (AMe) process at 150 L/m^2h from synthetic wastewater (broken lines) [22] and real secondary wastewater (WW) (solid lines) at 10 ppm initial EC concentrations.

3.4. Comparison of ECs removals by different membrane processes

EC removals by different membrane processes are shown in Fig. 6. The hybrid USAMe® processes resulted in almost complete removals for all three ECs all throughout the duration of the experiments. The AMe process follows at above 90% removal - showing the significant enhancement effect of adsorbent addition as it pulled up the 30% removal in the membrane alone. On the other hand, the enhancement effect of ultrasound in the USMe process was quite low at only around 5–10% improvement for AMX and 20–30% improvement for DCF and CBZ. There was no synergy observed among the methods, as the improvement in removal in the hybrid USAMe® process was only nearly additive for AMX and even short of the additive for the other ECs when ultrasound and adsorption are used separately with the membrane. Nevertheless, the hybrid combination of all three methods in the USAMe® processes which elevated the removals to above 99% as compared to only around 90% in the AMe process is a very significant improvement. The value is seen in the inherent difficulty in removing a contaminant at the remaining lower concentrations due to the dependence of mass transfer and reaction rate on concentration.

3.5. Effect of the advanced methods on EC removal

The use of ultrasound did not significantly enhance EC removal in the USMe processes, but the experiments conducted at different US frequencies showed that the performance was better with 130 kHz than that at 35 kHz (Fig. 6). This could be attributed mainly to two reasons:1) the more effective sonolytic degradation, and 2) the aid of the fouling layer maintained in the membrane at 130 kHz. At this higher frequency of US, shorter cavitation cycles release smaller cavitation bubbles, generating lesser energies upon collapse but ejecting more hydroxyl radicals out of the bubble [28]. The greater amount of hydroxyl radicals generated means higher oxidation capacity for a more effective degradation of ECs [18,28,49]. In addition, these milder forces are less effective in dislodging particles away from the membrane surface, thus maintaining the structure of the developed fouling layer. This layer could provide a greater chance for ECs rejection through interaction and aggregation with NOM, thus increasing EC removal.

On the other hand, the use of PAC in the AMe substantially pulled up the EC removals, suggesting that adsorption is a major contributing mechanism in the removal of pharmaceutical in the hybrid process [19,21]. In this case, the PAC is mainly responsible for adsorption and removal of ECs, and the function of the membrane is somehow reduced to retaining the PAC particles by steric hindrance. The carbon layer itself acts as a secondary membrane which retains ECs and deters it from reaching the membrane, resulting to improved and stable EC removals. This PAC layer further protects the membrane from fouling as NOM also adsorbs onto PAC before the feed reaches the membrane. Some enlargement in PAC particles caused by the adsorbed NOM was observed in other studies, and this enlargement is believed to further aid in filtration [19]. However, NOM competes against ECs with the PAC adsorption sites, requiring higher adsorbent doses. This is the challenge of integration of an adsorption process after the biological process.

3.6. Removal mechanisms in the USAMe® process

Fig. 6 shows that among the membrane processes investigated, the USAMe® processes resulted to the greatest and most stable removals. The PAC or US, when separately applied to the membrane and used after biological treatment, were unable to pull up removals to near completion. The USAMe® processes not only reached such high degrees of removal but also maintained excellent steady performance within the duration of the experiment. The graph even has a gentle slope, suggesting that while removal continues in this trend, excellent removals could be maintained for extended periods of operation.

The enhancement of removal in the USAMe® processes is a result of interlinked and collective effects obtained from each method employed. Ultrasound irradiation, while degrading ECs by sonolytic action, also aids in the adsorption of ECs onto PAC. This was observed in a previous study on adsorption in the presence of ultrasound [42]. The enhancement was due to an increase in adsorption capacity and/or kinetic rate constant, similar to what was observed by other studies with an improvement of both liquid mass transfer and intra-particle diffusion in sonication-adsorption combinations [20,43,44]. While US aids adsorption, PAC aids cavitation as well. Small particles of carbon, having internal crevices and large active surface area, provide additional nuclei or venue where bubbles may form and grow [45,46]. With a greater number of cavitation bubbles, cavitational effects are also improved. More effective cavitation will consequently aid in adsorption and result to better EC degradation, and these bi-directional benefits continue in the hybrid process. US also facilitates the gathering of small particles into agglomerates [47] like the formation of the PAC-NOM-ECs aggregates, thereby increasing the rejection of contaminants while also

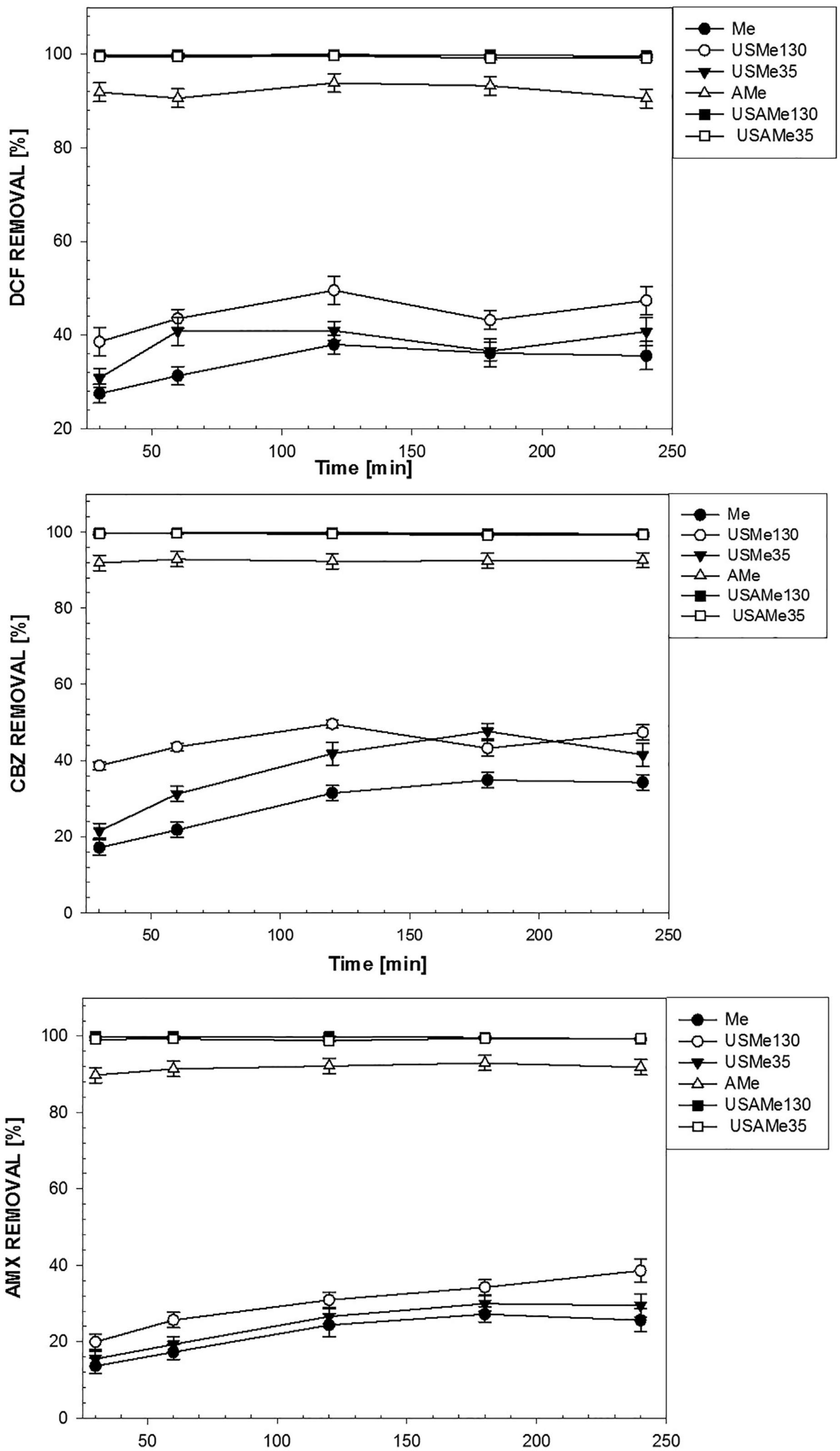

Fig. 6. Removal of ECs from real secondary wastewater (WW) by different membrane processes at 150 L/m^2h (Membrane ultrafiltration alone (Me), ultrafiltration with ultrasound irradiation at 35 kHz (USMe35) and 130 kHz (USMe130), ultrafiltration with activated carbon adsorption (AMe), and the hybrid USAMe® process at 35 kHz (USAMe®35) and 130 kHz (USAMe®130)).

Table 1
Percentage enhancement in hybrid processes based on EC removal capacity of an ultrafilter (Me process) without any auxiliary method.

Target EC	USMe35	USMe130	AMe	USAMe35	USAMe130
DCF	108	128	253	271	272
CBZ	130	139	276	296	297
AMX	111	134	359	385	387

reducing TMP build-up [46]. This is evidenced by observed stable mild TMPs and constant effluent production in the USAMe® experiments, indicating effective control of fouling in the membrane.

3.7. Analysis of enhancements

To determine the contribution of each auxiliary method to membrane performance, the average percentage enhancements in relation to EC removal in the Me process are computed based on Eq. (1).

$$\%Enhancement = \frac{Removal_{Hybrid}}{Removal_{Me}} \times 100\% \tag{1}$$

where the removal used in the equation is the average of values in the last two hours of each process. Results are presented in Table 1.

The enhancements in the USMe processes are very small compared to that of the AMe process. Moreover, the difference in enhancements between the AMe and the USAMe® processes are also very small. This confirms that PAC adsorption is the major mechanism of EC removal in the USAMe process.

3.8. Factors affecting USAMe® performance

The enhancements with ultrasound are very small, implying that ultrasound did not significantly contribute to the removal of ECs. However, in the absence of ultrasound, TMP values easily increase (Fig. 2), requiring frequent cleaning of the membrane. This is one major concern when a membrane process is applied after a biological process. NOM present in secondary wastewater effluent clogs the pores of the ultrafilter causing TMP values to rise. The employment of ultrasound and its membrane cleaning ability [18], therefore, is critical in maintaining a good productivity in a membrane process after a biological process.

The use of PAC results to outstanding EC removals, which suggests the major role of adsorption in EC retention. However, it is also observed that the AMe process results to early TMP rise which requires not only cleaning but also replacement of the spent adsorbent, thus contributing to the economic cost. It is ultrasound that serves to extend the filtration time by maintaining lower TMP values. This is attributed to its mechanical and acoustic forces that continuously clean the membrane [18]. Removals in the AMe process are also lower than that of the USAMe® processes. It is again ultrasound that aid adsorption through several mechanisms [20]. US makes possible to conduct the USAMe® process at milder TMPs while sustaining effective EC removals, thus is a major factor for continuous performance and better productivity, and a necessity when this innovative hybrid membrane process is after a biological process.

The degree of removal in the presence of ultrasound is slightly affected by ultrasonic frequency. Fig. 7 shows a clearer comparison of the USAMe® processes at different frequencies, where USAMe®130 gave better EC removals than USAMe®35. Noting that adsorption is the main removal mechanism in the USAMe® process, the mechanical strength of ultrasound affects the integrity and adsorption capacity of the PAC-NOM layer next to the membrane which contributes much to the EC removal. It is interesting to note that higher frequency ultrasound results to better performance of the USAMe® process as a post-treatment of a biological process, which is opposite to the trend observed in the previous study with synthetic wastewater as feed [22]. Though the differences are only nearly 0.5%, this still indicates that the PAC-NOM fouling layer next to the membrane has a positive effect on EC removal, and therefore must be maintained. Thus, any action detrimental to this layer, such as the stronger cavitational forces at lower US frequencies, could make the layer thinner and easily detached from the surface, hence diminish its capacity to retain ECs.

3.9. Performance at low EC concentrations

Nearly complete removals were observed at 10 ppm pharmaceutical concentrations. In the case of ppb levels, Fig. 8 shows that EC removals were lower for USAMe® (i.e. 60–70%) This is reasonable based on the idea that concentration gradient serves as the primary driving force for mass transfer [48]. Nevertheless, the USAMe® process practically doubled the removal in the membrane (25–40%) even at ppb levels, and the trend in removal (Me < USMe < AMe < USAMe®) is exactly the same to that of the ppm levels. Thus, the results of simple and quick tests conducted at higher EC levels could be used to approximate the trends and behavior observable at lower pharmaceutical levels requiring tedious and complicated analytical tests. The results of the ppb test further indicate the potential of the USAMe® process after biological process, where secondary wastewater effluent usually contains low environmental concentrations of ppb to ppt levels.

3.10. Toxicity

Both the raw and spiked WW feed samples, as well as the effluents from AMe process, were negative to toxicity tests. All effluents of the hybrid USAMe® processes gave “No Effect” to D. magna, with immobilization of $\leq 20\%$. A common factor for effluents causing 10–20% immobilization was ultrasonic irradiation under 130 kHz. When compared to the other frequency used, 130 kHz ultrasound irradiation results to greater EC degradation, hence more transformation products are formed. Therefore, the slight immobilization of daphnids can be attributed to the unknown toxicity of some of these products. Nevertheless, the results still qualify within the “No Effect” toxicity level, hence indicating the production of safe effluents.

4. Conclusions

One major challenge of the integration of tertiary treatment processes after a biological process for the removal of ECs is the additional contaminant NOM that have to be dealt with. In the case of membrane processes as post-treatment of the biological process, NOM causes fouling in the membrane, thus affecting productivity and limiting the applicability of the membrane. In adsorption, NOM also competes with ECs for adsorption sites, lowering the adsorption capacity for the target contaminants and thereby increasing the required adsorption dose. An innovative hybrid membrane process called USAMe®- the simultaneous application of ultrasound, adsorption, and membrane filtration - minimized the unfavorable effects of NOM observed in the individual methods, resulting into nearly complete and stable EC removal in the hybrid USAMe® process following a biological process. Its excellent contaminant removal for both EC and NOM and its continuous cleaning action resulting to higher productivity makes USAMe® an ideal advanced treatment applied after biological process. Moreover, USAMe® exhibited a capability in removing emerging contaminants from secondary wastewater even at low environmental concentrations, further verifying its potential as post-treatment of biological processes whose effluent usually contain ppb to ppt EC levels. In addition, safety and reuse potential of the treated effluent is exhibited by the negative toxicity test results, ensuring environmental protection of an actual USAMe® application.

Nonetheless, the results and analyses obtained from this study could be further enhanced through experiments on the treatment of

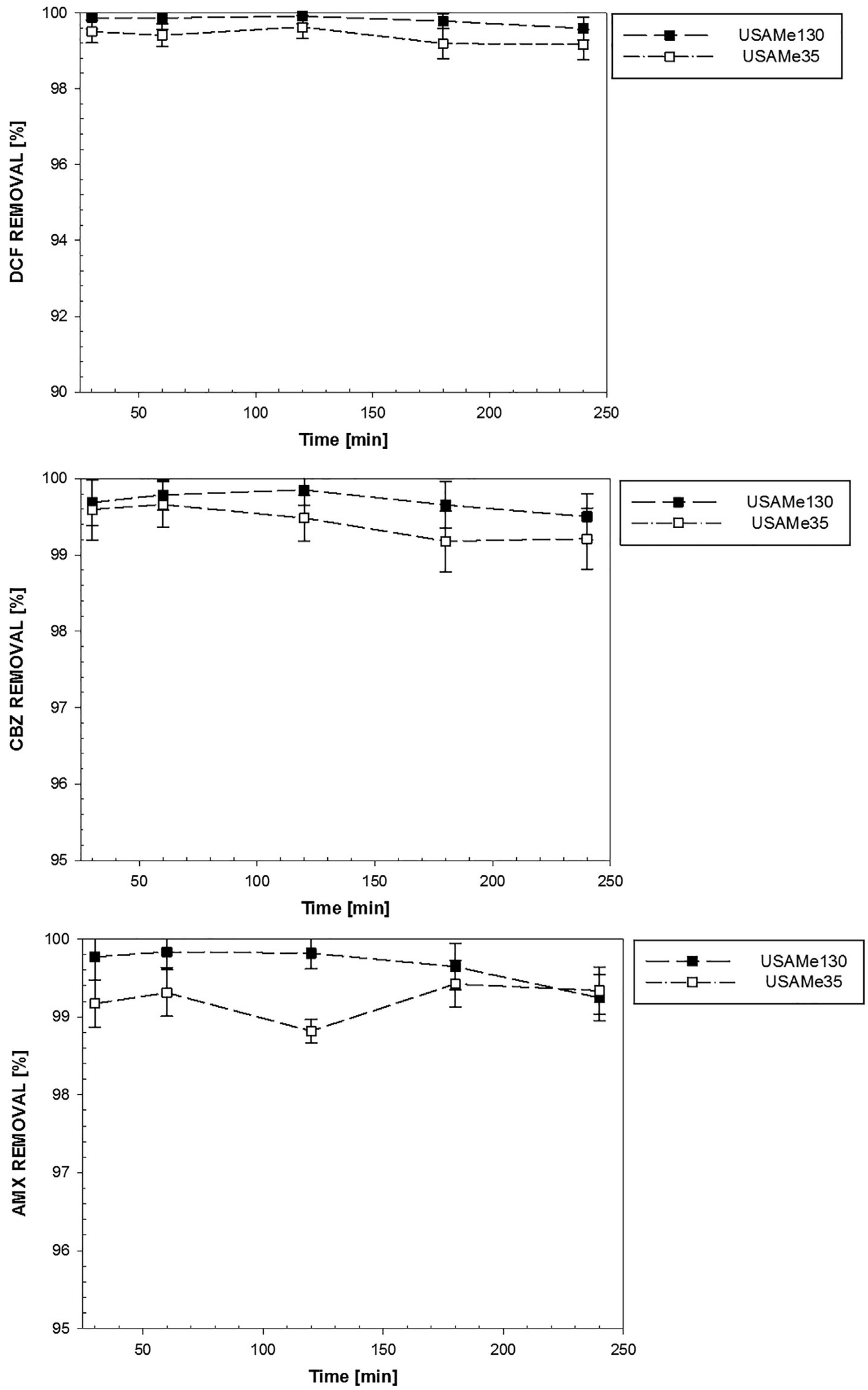

Fig. 7. Removal of ECs from real secondary wastewater in the hybrid USAMe process at 150 L/m^2h and 4.5 g/m^2 PAC dose.

wastewater containing ng/L environmental EC concentrations as well as a deeper investigation of intermediates and transformation products. Design improvements, alternative membrane materials, as well as modes of ultrasound application for efficiency and economy purposes also need to be explored. The proper application as post-treatment of biological process, whether within or after the secondary sedimentation tanks, is also an important matter for investigation.

Author contributions

V.N. and V.B. developed the research idea and planned the research activities, M.F.S. carried out the research activities, V.N., L. B., S.W.H. and F.C.B. analysed the data and prepared the manuscript, V.N., V.B. and F.C.B. reviewed the final draft of the manuscript. Research activities were conducted at Sanitary Environmental Engineering Division under the direction and budget of V.N.

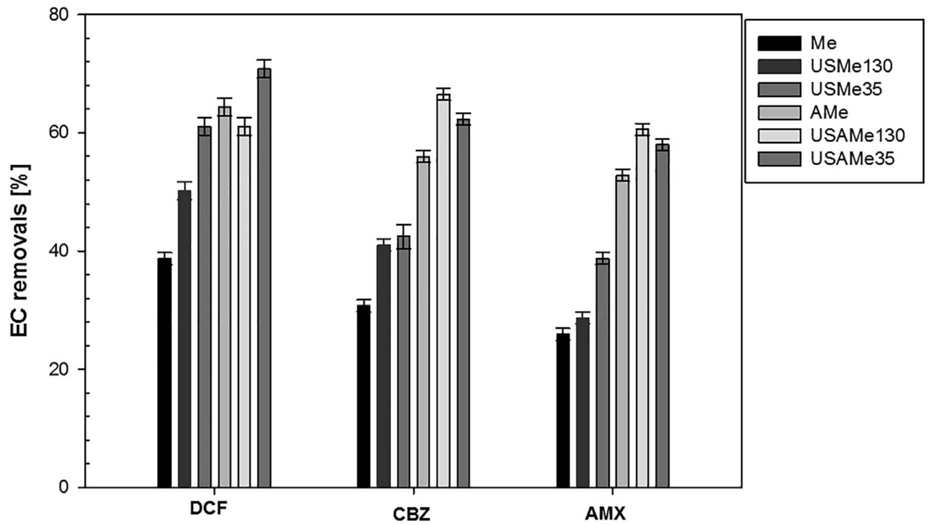

Fig. 8. Removal of ECs after 240 min by the different membrane processes tested at 150 L/m^{2}h where real secondary effluent was spiked with ECs at a concentration of 100 ppb.

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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References

[1] K. Fent, A.A. Weston, D. Caminada, Ecotoxicology of human pharmaceuticals, Aquat. Toxicol. 76 (2006) 122–159, https://doi.org/10.1016/j.aquatox.2005.09.009.
[2] V. Naidoo, K. Wolter, R. Cuthbert, N. Duncan, Veterinary diclofenac threatens Africa's endangered vulture species, Regul. Toxicol. Pharmacol. 53 (2009) 205–208, https://doi.org/10.1016/j.yrtph.2009.01.010.
[3] K. Noguera-Oviedo, D.S. Aga, Lessons learned from more than two decades of research on emerging contaminants in the environment, J. Hazard Mater. 316 (2016) 242–251, https://doi.org/10.1016/j.jhazmat.2016.04.058.
[4] C. Merlin, S. Bonot, S. Courtois, J.-C. Block, Persistence and dissemination of the multiple-antibiotic-resistance plasmid pB10 in the microbial communities of wastewater sludge microcosms, Water Res. 45 (2011) 2897–2905, https://doi.org/10.1016/j.watres.2011.03.002.
[5] P.A. Fowler, M. Bellingham, K.D. Sinclair, N.P. Evans, P. Pocar, B. Fischer, K. Schaedlich, J.-S. Schmidt, M.R. Amezaga, S. Bhattacharya, S.M. Rhind, P.J. O'Shaughnessy, Impact of endocrine-disrupting compounds (EDCs) on female reproductive health, Mol. Cell. Endocrinol. 355 (2012) 231–239, https://doi.org/10.1016/j.mce.2011.10.021.
[6] J.K. Hess-Wilson, K.E. Knudsen, Endocrine disrupting compounds and prostate cancer, Cancer Lett. 241 (2006) 1–12, https://doi.org/10.1016/j.canlet.2005.10.006.
[7] A. Joss, S. Zabczynski, A. Göbel, B. Hoffmann, D. Löffler, C.S. McArdell, T.A. Ternes, A. Thomsen, H. Siegrist, Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme, Water Res. 40 (2006) 1686–1696, https://doi.org/10.1016/j.watres.2006.02.014.
[8] K. Stamatelatou, C. Frouda, M.S. Fountoulakis, P. Drillia, M. Kornaros, G. Lyberatos, Pharmaceuticals and health care products in wastewater effluents: The example of carbamazepine, in: Water Sci. Technol. Water Supply, IWA Publishing, 2003: pp. 131–137. http://www.scopus.com/inward/record.url?eid=2-s2.0-0041381159&partnerID=40&md5=34dcdad0942378fa83101ebb8bb9e189.
[9] K. Kimura, S. Toshima, G. Amy, Y. Watanabe, Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes, J. Membr. Sci. 245 (2004) 71–78, https://doi.org/10.1016/j.memsci.2004.07.018.
[10] A. Jelic, M. Gros, A. Ginebreda, R. Cespedes-Sánchez, F. Ventura, M. Petrovic, D. Barcelo, Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment, Water Res. 45 (2011) 1165–1176, https://doi.org/10.1016/j.watres.2010.11.010.
[11] H. Schaar, M. Clara, O. Gans, N. Kreuzinger, Micropollutant removal during biological wastewater treatment and a subsequent ozonation step, Environ. Pollut. 158 (2010) 1399–1404, https://doi.org/10.1016/j.envpol.2009.12.038.
[12] Y. Zhang, S.-U. Geißen, C. Gal, Carbamazepine and diclofenac: Removal in wastewater treatment plants and occurrence in water bodies, Chemosphere 73 (2008) 1151–1161, https://doi.org/10.1016/j.chemosphere.2008.07.086.
[13] W. Xue, C. Wu, K. Xiao, X. Huang, H. Zhou, H. Tsuno, H. Tanaka, Elimination and fate of selected micro-organic pollutants in a full-scale anaerobic/anoxic/aerobic process combined with membrane bioreactor for municipal wastewater reclamation, Water Res. 44 (2010) 5999–6010, https://doi.org/10.1016/j.watres.2010.07.052.
[14] V. Matamoros, V. Salvadó, Evaluation of a coagulation/flocculation-lamellar clarifier and filtration-UV-chlorination reactor for removing emerging contaminants at full-scale wastewater treatment plants in Spain, J. Environ. Manage. 117 (2013) 96–102, https://doi.org/10.1016/j.jenvman.2012.12.021.
[15] D. Fatta-Kassinos, E. Hapeshi, A. Achilleos, S. Meric, M. Gros, M. Petrovic, D. Barcelo, Existence of pharmaceutical compounds in tertiary treated urban wastewater that is utilized for reuse applications, Water Resour. Manag. 25 (2010) 1183–1193, https://doi.org/10.1007/s11269-010-9646-4.
[16] P. Verlicchi, E. Zambello, How efficient are constructed wetlands in removing pharmaceuticals from untreated and treated urban wastewaters? A review, Sci. Total Environ. 470–471 (2014) 1281–1306, https://doi.org/10.1016/j.scitotenv.2013.10.085.
[17] M. Petrović, S. Gonzalez, D. Barceló, Analysis and removal of emerging contaminants in wastewater and drinking water, TrAC Trends Anal. Chem. 22 (2003) 685–696, https://doi.org/10.1016/S0165-9936(03)01105-1.
[18] M. Cai, S. Zhao, H. Liang, Mechanisms for the enhancement of ultrafiltration and membrane cleaning by different ultrasonic frequencies, Desalination 263 (2010) 133–138, https://doi.org/10.1016/j.desal.2010.06.049.
[19] X.-J. Gai, H.-S. Kim, The role of powdered activated carbon in enhancing the performance of membrane systems for water treatment, Desalination 225 (2008) 288–300, https://doi.org/10.1016/j.desal.2007.07.009.
[20] O. Hamdaoui, E. Naffrechoux, L. Tifouti, C. Pétrier, Effects of ultrasound on adsorption–desorption of p-chlorophenol on granular activated carbon, Ultrason. Sonochem. 10 (2003) 109–114, https://doi.org/10.1016/S1350-4177(02)00137-2.
[21] K.-Y. Kim, H.-S. Kim, J. Kim, J.-W. Nam, J.-M. Kim, S. Son, A hybrid microfiltration–granular activated carbon system for water purification and wastewater reclamation/reuse, Desalination 243 (2009) 132–144, https://doi.org/10.1016/j.desal.2008.04.020.
[22] M.F.N. Secondes, V. Naddeo, V. Belgiorno, F. Ballesteros Jr., Removal of emerging contaminants by simultaneous application of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation, J. Hazard. Mater. 264 (2014) 342–349, https://doi.org/10.1016/j.jhazmat.2013.11.039.
[23] A.W. Zularisam, A. Ahmad, M. Sakinah, A.F. Ismail, T. Matsuura, Role of natural organic matter (NOM), colloidal particles, and solution chemistry on ultrafiltration performance, Sep. Purif. Technol. 78 (2011) 189–200, https://doi.org/10.1016/j.seppur.2011.02.001.
[24] S. Ortiz de García, G. Pinto Pinto, P. García Encina, R. Irusta Mata, Consumption and occurrence of pharmaceutical and personal care products in the aquatic

environment in Spain, Sci. Total Environ. 444 (2013) 451–465, https://doi.org/10.1016/j.scitotenv.2012.11.057.
[25] Z. Cai, C. Wee, M.M. Benjamin, Fouling mechanisms in low-pressure membrane filtration in the presence of an adsorbent cake layer, J. Membr. Sci. 433 (2013) 32–38, https://doi.org/10.1016/j.memsci.2013.01.007.
[26] J. Kim, Z. Cai, M.M. Benjamin, NOM fouling mechanisms in a hybrid adsorption/membrane system, J. Membr. Sci. 349 (2010) 35–43, https://doi.org/10.1016/j.memsci.2009.11.017.
[27] Y. Li, X. Zhang, W. Zhang, J. Wang, C. Chen, Effect of powdered activated carbon on immersed hollow fiber ultrafiltration membrane fouling caused by particles and natural organic matter, Desalination. 278 (2011) 443–446, https://doi.org/10.1016/j.desal.2011.05.050.
[28] T.J. Mason, D. Peters, Practical Sonochemistry, Second Edition: Power Ultrasound Uses and Applications, 2 edition, Woodhead Publishing, Cambridge, 2002.
[29] ISO 6341:2012 – Water quality – Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea) – Acute toxicity test, (n.d.). https://www.iso.org/standard/54614.html (accessed March 19, 2017).
[30] F. Xiao, P. Xiao, W.J. Zhang, D.S. Wang, Identification of key factors affecting the organic fouling on low-pressure ultrafiltration membranes, J. Membr. Sci. 447 (2013) 144–152, https://doi.org/10.1016/j.memsci.2013.07.040.
[31] J.C. Crittenden, R.R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, MWH's Water Treatment: Principles and Design, 3 ed., John Wiley & Sons, Hoboken, N.J., 2012.
[32] J. Kim, W. Shi, Y. Yuan, M.M. Benjamin, A serial filtration investigation of membrane fouling by natural organic matter, J. Membr. Sci. 294 (2007) 115–126, https://doi.org/10.1016/j.memsci.2007.02.020.
[33] S. Lee, J. Cho, Comparison of ceramic and polymeric membranes for natural organic matter (NOM) removal, Desalination 160 (2004) 223–232, https://doi.org/10.1016/S0011-9164(04)90025-2.
[34] M. Schulz, A. Soltani, X. Zheng, M. Ernst, Effect of inorganic colloidal water constituents on combined low-pressure membrane fouling with natural organic matter (NOM), J. Membr. Sci. 507 (2016) 154–164, https://doi.org/10.1016/j.memsci.2016.02.008.
[35] M.Z. Yunos, Z. Harun, H. Basri, A.F. Ismail, Studies on fouling by natural organic matter (NOM) on polysulfone membranes: Effect of polyethylene glycol (PEG), Desalination 333 (2014) 36–44, https://doi.org/10.1016/j.desal.2013.11.019.
[36] J.L. Acero, F.J. Benitez, A.I. Leal, F.J. Real, F. Teva, Membrane filtration technologies applied to municipal secondary effluents for potential reuse, J. Hazard. Mater. 177 (2010) 390–398, https://doi.org/10.1016/j.jhazmat.2009.12.045.
[37] A. De Munari, A.J.C. Semiao, B. Antizar-Ladislao, Retention of pesticide Endosulfan by nanofiltration: influence of organic matter–pesticide complexation and solute–membrane interactions, Water Res. 47 (2013) 3484–3496, https://doi.org/10.1016/j.watres.2013.03.055.
[38] D. Jermann, W. Pronk, M. Boller, A.I. Schäfer, The role of NOM fouling for the retention of estradiol and ibuprofen during ultrafiltration, J. Membr. Sci. 329 (2009) 75–84, https://doi.org/10.1016/j.memsci.2008.12.016.
[39] J. Hu, A. Martin, R. Shang, W. Siegers, E. Cornelissen, B. Heijman, L. Rietveld, Anionic exchange for NOM removal and the effects on micropollutant adsorption competition on activated carbon, Sep. Purif. Technol. 129 (2014) 25–31, https://doi.org/10.1016/j.seppur.2014.03.019.
[40] Y. Matsui, T. Yoshida, S. Nakao, D.R.U. Knappe, T. Matsushita, Characteristics of competitive adsorption between 2-methylisoborneol and natural organic matter on superfine and conventionally sized powdered activated carbons, Water Res. 46 (2012) 4741–4749, https://doi.org/10.1016/j.watres.2012.06.002.
[41] A. Murray, B. Örmeci, Competitive effects of humic acid and wastewater on adsorption of Methylene Blue dye by activated carbon and non-imprinted polymers, J. Environ. Sci. (2017), https://doi.org/10.1016/j.jes.2017.04.029.
[42] M.F.N. Secondes, V. Naddeo, F. Ballesteros Jr., V. Belgiorno, Adsorption of emerging contaminants enhanced by ultrasound irradiation, Sustain. Environ. Res. 24 (2014) 349–355.
[43] R.-S. Juang, S.-H. Lin, C.-H. Cheng, Liquid-phase adsorption and desorption of phenol onto activated carbons with ultrasound, Ultrason. Sonochem. 13 (2006) 251–260, https://doi.org/10.1016/j.ultsonch.2005.05.001.
[44] M. Landi, V. Naddeo, V. Belgiorno, Influence of ultrasound on phenol removal by adsorption on granular activated carbon, Desalination Water Treat. 23 (2010) 181–186, https://doi.org/10.5004/dwt.2010.1992.
[45] S.N. Katekhaye, P.R. Gogate, Intensification of cavitational activity in sonochemical reactors using different additives: efficacy assessment using a model reaction, Chem. Eng. Process. Process Intensif. 50 (2011) 95–103, https://doi.org/10.1016/j.cep.2010.12.002.
[46] S. Muthukumaran, S.E. Kentish, M. Ashokkumar, G.W. Stevens, Mechanisms for the ultrasonic enhancement of dairy whey ultrafiltration, J. Membr. Sci. 258 (2005) 106–114, https://doi.org/10.1016/j.memsci.2005.03.001.
[47] F. Saravia, F.H. Frimmel, Role of NOM in the performance of adsorption-membrane hybrid systems applied for the removal of pharmaceuticals, Desalination. 224 (2008) 168–171, https://doi.org/10.1016/j.desal.2007.02.089.
[48] M.M. Clark, Transport Modeling for Environmental Engineers and Scientists, John Wiley & Sons, 2009.
[49] Vincenzo Naddeo, Degradation of Antibiotics in Wastewater during Sonolysis, Ozonation, and Their Simultaneous Application: Operating Conditions Effects and Processes Evaluation, Int. J. Photoenergy (2012), https://doi.org/10.1155/2012/624270.