Combined application of membrane ultrafiltration, adsorption, and ultrasound irradiation for the removal of pharmaceutical compounds from real wastewater

Secondes M.F.N.[1,3,*], Borea, L.[2], Naddeo V.[2], Ballesteros F.C.[3] And Belgıorno V.[2]

[1]College of Engineering, University of Negros Occidental – Recoletos, Bacolod City, Philippines

[2]Sanitary and Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno, Fisciano 84084 (SA), Italy

[3]Environmental Engineering Program, National Graduate School of Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines

*corresponding author: Mona Freda Secondes

e-mail: msecondes@gmail.com

Abstract The presence of emerging contaminants (ECs) in water resources has raised a great concern in the last decades due to their persistence in the environment and their chronic toxicological and endocrine disrupting effects on terrestrial and aquatic organisms. Thus, advanced treatment methods are necessary for the removal of these contaminants before wastewater reuse or disposal into aquatic ecosystem. In the present study, the hybrid process USAMe®, which combines ultrasound irradiation (US), adsorption (A) and membrane filtration (Me), was investigated for the removal of ECs from real wastewater. Three pharmaceutical compounds - diclofenac (DCF), carbamazepine (CBZ), and amoxicillin (AMX), were chosen for this study to represent highly consumed and frequently detected pharmaceuticals in the aquatic environment. All three pharmaceuticals were spiked into real wastewater 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 results obtained showed improved pharmaceutical removals in the membrane ultrafiltration process whenever an auxiliary treatment was employed. The degree of pharmaceutical removal was achieved in the order: Me<USMe<AMe<USAMe®. The USAMe® process applied to real wastewater successfully removed the target ECs, displaying its potential as an advanced method for wastewater treatment.

Keywords: emerging contaminants, hybrid membrane process, activated carbon, sonication, ultrasound frequency

1. Introduction

Low levels of ECs in bodies of water, even at ng/L to µg/L concentrations, has raised countless concerns because of the ECs persistence, toxicity, and endocrine disrupting effects (Fent *et al*., 2006). The impact is overwhelming, as even the simple interruption of normal body functions, in the course of time, may lead to serious problems like biodiversity loss. Several pharmaceuticals, for instance, are considered endocrine disrupting compounds (EDCs). EDCs alter the growth of organisms, repress its reproduction, thereby causing to population decline (Naidu *et al*., 2016). The anti-epileptic CBZ and anti-inflammatory DCF are just two examples of potential EDCs that are commonly detected in the environment and correspondingly the ECs of highest concentrations in the secondary effluent (Fent *et al*., 2006; Noguera-Oviedo, 2016). Antibiotics, on the other hand, are posing the risk of the development of highly-resistant microbial strains. The occurrence of the most prescribed antibiotic AMX in wastewater and soil is linked to this superbug mutation (Merlin *et al*., 2011). Moreover, the presence of ECs in the environment is even linked to serious human health problems – infertility and cancer (Fent *et al*., 2006; Naidu *et al*., 2016).

With pharmaceuticals and personal care product being a large fraction of these ECs, the domestic wastewater is a hotspot and an access way of the spread of these contaminants into the environment. Removal of ECs by conventional treatment is not satisfactory (Noguera-Oviedo, 2016); thus, advanced treatment methods are necessary before wastewater is reused or disposed of.

Membrane filtration (Me) and adsorption (A) are among the two most commonly used advance treatment processes. Ultrasonic irradiation (US), aside from its destructive effect on ECs through sonication, is also a good auxiliary method which enhances the membrane filtration and adsorption processes (Cai *et al*., 2010; Gai & Kim, 2008; Hamdaoui *et al*., 2003). Several benefits were found when the mentioned methods are combined in a hybrid process (Cai *et al*., 2013; Gai & Kim, 2008; Kim *et al*., 2009). A recent investigation on the simultaneous application of the three methods in a hybrid process called USAMe® resulted to excellent EC removals from synthetic wastewater (Secondes *et al*., 2014a). Thus, further investigation of its potential for the advanced treatment of real wastewater is important.

A major consideration in the treatment of wastewater is the problem brought by the presence of NOM. 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 (Zularisam *et al.*, 2011). In adsorption, NOM competes with the target contaminants for the available adsorbent area, thereby decreasing capacity to adsorb ECs. NOM in wastewater also adds to the total concentration of contaminants that needs to be degraded through sonolysis, which increases the energy requirement for more intense sonication and extended reaction durations.

The present study investigates the performance of the USAMe® process, in terms of EC removal, in treating real wastewater. The possible removal mechanisms in the hybrid process will also be explored.

2. Materials and Methods

Three pharmaceutical compounds, DCF, CBZ, and AMX, were chosen for this study to represent highly consumed and frequently detected pharmaceuticals in the aquatic environment (Fent *et al*., 2006; Noguera-Oviedo, 2016). All three pharmaceuticals 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 are pH: 7.6 - 8.3, COD: 25 - 60 mg/L as tested through Open Reflux Method, and a BOD of 1-4 mg/L as tested by OxiTop BOD Measurement Instrumentation. The EC-spiked wastewater served as feed to all tests.

The novel USAMe® process is patented by the Sanitary and Environmental Engineering Division of the University of Salerno. Fig. 1 illustrates the experimental set-up. The membrane unit is Polysulfone fiber with a nominal molecular weight cut-off (MWCO) of 100 kDa and a transfer area of 6.6 cm^2. Cross-flow configuration is employed at a constant flux of 150 L/m^2h. TMP is continuously monitored all throughout the experiments. Cleaned and dried powdered activated carbon (PAC) is used for adsorption. Preparatory and post-experimental procedures, as well as the complete description of the set-up, are discussed in detail in the previous study (Secondes *et al*., 2014a).

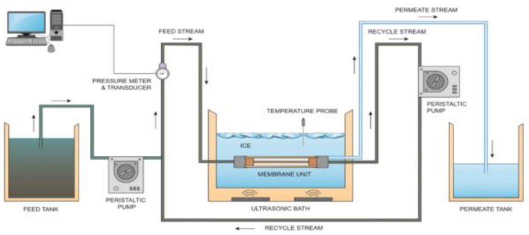

Figure 1. Experimental Set-up (Secondes *et al*., 2014)

A PAC dose of 4.5 g/m^2, falling at the lower end of the doses commonly used in literature (Cai *et al*., 2013; Kim *et al*., 2009), was used. The configuration allows circulation of PAC within the membrane, the mixed stream, and the recirculation lines, thereby producing lower actual concentrations in the membrane at any time.

An Elma ultrasonic bath was used for sonication. It is operated at a specific ultrasound density of 35 W/L and 29 W/L for the frequencies 35kHz and 130kHz, respectively, as measured by the calorimetric method (Mason & Peters, 2002). Continuous irradiation was conducted while maintaining the bath temperature at 25±2 ^oC.

Several experiments employing different combinations of the three treatment methods were conducted to investigate the degree of removal and the removal mechanisms: membrane ultrafiltration alone (Me), ultrafiltration with ultrasound irradiation at 35kHz (USMe35) and 130kHz (USMe130), ultrafiltration with activated carbon adsorption (AMe), and the hybrid USAMe® process at 35 kHz (USAMe®35) and 130 kHz (USAME®130). Permeates were analyzed using LC-MS/MS system, and ecotoxicity was tested with Daphnia magna (ISO 6341:2012).

3. Results and Discussions

3.1 Effect on NOM

In the experiments performed using synthetic wastewater, the TMP remained approximately constant and very low (Secondes, Naddeo, Belgiorno, *et al*., 2014), while fouling was apparent in the membrane filtration employing real wastewater as feed. The TMP profile is presented in Fig. 2. Fouling is attributed to the presence of NOM in wastewater (Zularisam *et al*., 2011).

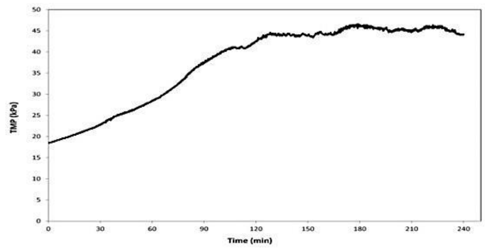

Figure 2. TMP profile of membrane ultrafiltration of wastewater at 150 L/m^2h

On the other hand, membrane filtration using real wastewater results to increasing EC removal with time. This suggests the occurrence of other removal mechanisms which could be attributed to the presence of NOM in WW. Increasing TMP (Fig. 2) could indicate pore blocking that resulted from the deposition and accumulation of low molecular weight colloidal NOM fractions that narrows the pores, thereby providing the steric hindrance making rejection of ECs possible. The contribution of NOM adsorption and pore blocking to the retention of low molecular weight solutes in ultrafilters has also been observed in other studies (Acero *et al*., 2010; De Munari *et al*., 2013). Also, because ECs have some affinity to organic carbon, a fraction of it will bind with NOM and partition to suspended solids, enabling the membrane to reject the ECs as large-sized EC-NOM complexes (Jermann *et al*., 2009). Finally, fouling by NOM leads to the formation of a gel or cake fouling layer that could act as a secondary filter, tighter than the ultrafilter itself, hence retaining ECs and enhancing removal.

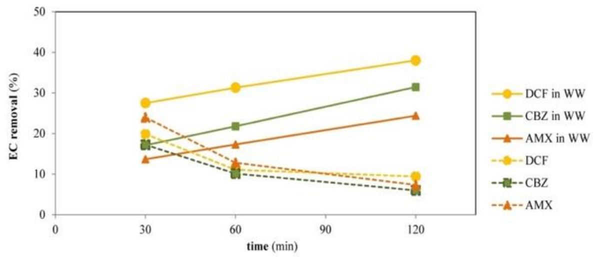

Figure 3. Removal of ECs by membrane ultrafiltration at 150 L/m^{2}h in synthetic (broken lines) and real (solid lines) wastewater at 10 ppm EC concentrations

3.2 EC removals by different membrane processes

The results of the tests performed with real WW are summarized in Fig. 4. For all ECs, it is evident that the hybrid USAMe® processes resulted to almost complete EC removals within the duration of the experiments. This is followed by the AMe process, registering slightly lower but still outstanding performance as it pulled up the removals to above 90% from only around 30% in the Me process. The enhancement effect of ultrasound in the USMe process was quite low, improving EC removals by only 5-10% for AMX to 20-30% for DCF and CBZ. No synergy between the methods was observed, as the improvement brought by US and AC application to the membrane in the USAMe® process was even short of the additive separate effects of USMe and AMe processes, except for AMX which was nearly additive. Nevertheless, elevating the removals from around 90% in the AMe to above 99% in the USAMe® processes is a valuable improvement since the removal of a compound at the remaining lower concentrations are typically more difficult due to the dependence of reaction rate or mass transfer on concentration.

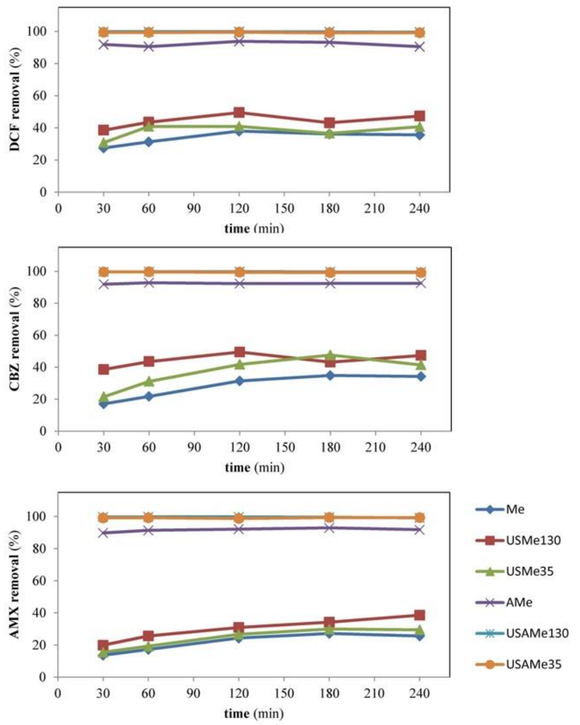

Figure 4. Removal of ECs from wastewater by different membrane processes at 150 L/m2h

3.3 Effect of auxiliary methods

Though the use US did not significantly enhance EC removal in the membrane for USME processes, the performance is better with 130 kHz. This could be attributed mainly to two reasons, the more effective sonolytic degradation and the aid of fouling layer maintained in the membrane. A higher frequency US, shorter cavitation cycles releases smaller cavitation bubbles, generating lesser energies upon collapse and ejecting more hydroxyl radicals out of the bubble (Mason and Peters, 2002). The milder forces that are less effective in dislodging particles away from the membrane surface, thus maintaining the fouling layer developed and providing a greater chance for ECs rejection by interaction with NOM in the fouling layer. More hydroxyl radicals generated means greater oxidation capacity for the more effective degradation of ECs (Cai *et al*., 2010; Mason & Peters, 2002).

On the other hand, the use of PAC in the AMe considerably pulled up the EC removals, suggesting that adsorption is a major contributing mechanism in the removal of pharmaceutical in the hybrid process (Gai & Kim, 2008; Kim *et al*., 2009). The PAC is mainly responsible for adsorption 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 hinders ECs from reaching the membrane, resulting to improved and stable EC removals. This layer further protects the membrane from fouling as NOM adsorbs onto PAC before the feed reaches the membrane. However, NOM competes against ECs with the PAC adsorption sites, requiring higher adsorbent doses.

3.4 Removal mechanisms in the USAMe® process

Fig. 4 shows that among the membrane processes investigated, the USAMe® processes resulted to the greatest and most stable removal. PAC or US separately applied to the membrane were unable to pull up removals to near completion, but the USAMe® processes reached not only such high degrees of removal but also maintained excellent performance within the duration of the experiment. The graph even has a gentle slope, suggesting that if removal continues in this trend, excellent removals could be maintained for extended periods.

The enhancement of removal in the USAMe® process 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 US (Secondes *et al*., 2014b). The enhancement was due to an increase in adsorption capacity and/or kinetic rate constant, as also observed by other studies with an improvement of both liquid mass transfer and intra-particle diffusion (Hamdaoui *et al*., 2003; Landi *et al*., 2010). 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 (Muthukumaran *et al*., 2005). 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. US also facilitates the gathering of small particles into agglomerates like the formation of the PAC-NOM-ECs aggregates, thereby increasing rejection and also reducing TMP (Muthukumaran *et al*., 2005).

3.5 Factors affecting USAMe® performance

The differences in enhancements between processes with and without ultrasound are very small, implying that ultrasound alone did not play a significant role in the removal of pharmaceuticals. However, in the absence of ultrasound, TMP values easily increase, requiring frequent cleaning of the membrane. NOM present in real wastewater clogs the pores of the ultrafilter causing TMP values to rise. In the case of AMe process, early TMP rise requires not only cleaning but also replacement of the spent adsorbent, thus contributing to the economic cost. Ultrasound serves to extend filtration time by maintaining lower TMP values, which could be attributed to its mechanical and acoustic forces that continuously cleans the membrane (Cai *et al*., 2010) and aids adsorption through several mechanisms (Hamdaoui *et al*., 2003). US makes it 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.

The degree of removal in the presence of ultrasound is slightly affected by ultrasonic frequency. In the USAMe® process, the mechanical strength of ultrasound affects the integrity and adsorption capacity of the PAC layer next to the membrane which contributes much to the pharmaceutical removal, as adsorption is the main mechanism of EC rejection in USAMe®. It is interesting to note that higher frequency ultrasound results to better performance of the USAMe® process in the treatment of real wastewater, which is opposite the trend observed in the previous study with synthetic wastewater (Secondes *et al*., 2014a).

3.6 Performance at low EC concentrations

Nearly complete removals were observed at 10 ppm pharmaceutical concentrations. In the case of ppb levels, EC removals were somewhat lower (60-70% for USAMe®). This is reasonable based on the idea that concentration gradient serves as the primary driving force for mass transfer (Clark, 2009). Nevertheless, 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 pharmaceutical levels could be used to approximate the trends and behavior observable at lower pharmaceutical levels requiring tedious and complicated analytical tests.

3.7 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 $\leq 20\%$. On the average, USMe effluents gave little to no immobilization to daphnids, which may be attributed to the unknown toxicity of some sonolytic degradation products. Nevertheless, the results still qualify within the "No Effect" toxicity level, hence indicating the production of safe effluents.

4. Conclusions

The simultaneous application of ultrasound, adsorption, and membrane filtration minimized the unfavorable effects of NOM observed in the individual methods, resulting into nearly complete EC removal in the hybrid USAMe® process. USAMe® exhibited capability in removing emerging contaminants from secondary WW even at very low environmental concentrations. Efficiency trends among the membrane processes are the same in both feeds containing ppm and ppb EC levels, suggesting that investigations employing ppm concentrations could be used to predict behaviors and trends under lower EC concentrations. The toxicity test results exhibit the reuse potential of the treated effluent. Nonetheless, the results and analyses obtained from this study could be further enhanced through experiments on the treatment of 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 US application for efficiency and economy purposes also need to be explored.

Acknowledgements

The research work was cooperatively supported by the CHED Faculty Development Program, the Sanitary and Environmental Engineering Division of the University of Salerno, the University of the Philippines – Diliman, and the University of Negros Occidental – Recoletos.

References

Acero, J. L., Benitez, F. J., Leal, A. I., Real, F. J., & Teva, F. (2010). Membrane filtration technologies applied to municipal secondary effluents for potential reuse. *Journal of Hazardous Materials*, *177*(1–3), 390–398.

Binh, C. T. T., Heuer, H., Gomes, N. C. M., Kotzerke, A., Fulle, M., Wilke, B.M., Smalla, K. (2007). Short-term effects of amoxicillin on bacterial communities in manured soil. *FEMS Microbiology Ecology*, *62*(3), 290–302.

Cai, M., Zhao, S., & Liang, H. (2010). Mechanisms for the enhancement of ultrafiltration and membrane cleaning by different ultrasonic frequencies. *Desalination*, *263*(1–3), 133–138.

Cai, Z., Wee, C., & Benjamin, M. M. (2013). Fouling mechanisms in low-pressure membrane filtration in the presence of an adsorbent cake layer. *Journal of Membrane Science*, *433*, 32–38.

Clark, M. M. (2009). *Transport Modeling for Environmental Engineers and Scientists*. John Wiley & Sons.

De Munari, A., Semiao, A. J. C., & Antizar-Ladislao, B. (2013). Retention of pesticide Endosulfan by nanofiltration: Influence of organic matter–pesticide complexation and solute–membrane interactions. *Water Research*, *47*(10), 3484–3496. https://doi.org/10.1016/j.watres.2013.03.055

Fent, K., Weston, A. A., & Caminada, D. (2006). Ecotoxicology of human pharmaceuticals. *Aquatic Toxicology*, *76*(2), 122–159.

Gai, X.-J., & Kim, H.-S. (2008). The role of powdered activated carbon in enhancing the performance of membrane systems for water treatment. *Desalination*, *225*(1), 288–300. https://doi.org/10.1016/j.desal.2007.07.009

Hamdaoui, O., Naffrechoux, E., Tifouti, L., & Pétrier, C. (2003). Effects of ultrasound on adsorption–desorption of p-chlorophenol on granular activated carbon. *Ultrasonics Sonochemistry*, *10*(2), 109–114.

ISO 6341:2012 - Water quality -- Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea) -- Acute toxicity test. (n.d.). Retrieved March 19, 2017, from https://www.iso.org/standard/54614.html

Jermann, D., Pronk, W., Boller, M., & Schäfer, A. I. (2009). The role of NOM fouling for the retention of estradiol and ibuprofen during ultrafiltration. *Journal of Membrane Science*, *329*(1–2), 75–84.

Kim, K.-Y., Kim, H.-S., Kim, J., Nam, J.-W., Kim, J.-M., & Son, S. (2009). A hybrid microfiltration–granular activated carbon system for water purification and wastewater reclamation/reuse. *Desalination*, *243*(1), 132–144. https://doi.org/10.1016/j.desal.2008.04.020

Landi, M., Naddeo, V., & Belgiorno, V. (2010). Influence of ultrasound on phenol removal by adsorption on granular activated carbon. *Desalination and Water Treatment*, *23*(1–3), 181–186.

Mason, T. J., & Peters, D. (2002). *Practical Sonochemistry, Second Edition: Power Ultrasound Uses and Applications* (2 edition). Cambridge: Woodhead Publishing.

Merlin, C., Bonot, S., Courtois, S., & Block, J.-C. (2011). Persistence and dissemination of the multiple-antibiotic-resistance plasmid pB10 in the microbial communities of wastewater sludge microcosms. *Water Research*, *45*(9), 2897–2905.

Muthukumaran, S., Kentish, S. E., Ashokkumar, M., & Stevens, G. W. (2005). Mechanisms for the ultrasonic enhancement of dairy whey ultrafiltration. *Journal of Membrane Science*, *258*(1–2), 106–114. https://doi.org/10.1016/j.memsci.2005.03.001

Naidu, R., Espana, A., Liu, Y., Jit, J. (2016). Emerging Contaminants in the environment: Risk-based analysis for better management. *Chemosphere, 154*,350-357

Noguera-Oviedo, K., & Aga, D. S. (2016). Lessons learned from more than two decades of research on emerging contaminants in the environment. *Journal of Hazardous Materials*, *316*, 242–251.

Secondes, M. F. N., Naddeo, V., Ballesteros Jr., F., & Belgiorno, V. (2014b). Adsorption of emerging contaminants enhanced by ultrasound irradiation. *Sustainable Environment Research*, *24*(5), 349–355.

Secondes, M. F. N., Naddeo, V., Belgiorno, V., & Ballesteros Jr., F. (2014a). Removal of emerging contaminants by simultaneous application of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation. *Journal of Hazardous Materials*, *264*, 342–349.

Zularisam, A. W., Ahmad, A., Sakinah, M., Ismail, A. F., & Matsuura, T. (2011). Role of natural organic matter (NOM), colloidal particles, and solution chemistry on ultrafiltration performance. *Separation and Purification Technology*, *78*(2), 189–200.