Integrating Membrane Bioreactor with Advanced TiO$_2$ Photocatalytic Technology for the Removal of Pharmaceutical Drugs from Recycled Wastewater

M.N. Chong*, G. Laera** and B. Jin***

*CSIRO Land and Water, Ecosciences Precinct, 41 Boggo Road, Dutton Park QLD 4102 Australia (E-mail: *Meng.Chong@csiro.au*)
*Istituto di Ricerca Sulle Acque, Consiglio Nazionale delle Ricerche, Viale De Blasio 5, Bari, 70132, Italy (E-mail: *Giuseppe.Laera@ba.irsa.cnr.it*)
*** School Chemical Engineering, The University of Adelaide, Adelaide 5005, Australia (E-mail: *Bo.Jin@adelaide.edu.au*)

Abstract
The presence of pharmaceutical drugs and residues in wastewaters is of concern due the potential health and environmental risks when the wastewater is recycled as an alternative water source. This study investigated the application of an integrated membrane bioreactor with titanium dioxide photocatalytic technology (MBR-TiO$_2$), as a combined treatment barrier to remove Carbamazepine (CBZ) from pharmaceutical wastewater. A laboratory MBR-TiO$_2$ system was started-up, operated and monitored for its treatment efficiency with respect to CBZ concentration. Prior to the integration, the individual systems of MBR and TiO$_2$ photocatalytic technology were monitored separately, in order to distinguish the synergistic operational effects. Respirometric tests showed that the introduction of CBZ acts as a chemical stressor, influencing the biomass metabolism in the MBR and resulting in reducing sludge yield. Thereafter, the chemical stressor effects were alleviated when the combined MBR-TiO$_2$ system was operated in a 4:1 ratio. A maximum CBZ removal efficiency of 95% was observed, but the treatment efficiency was found to decrease with increasing number of treatment cycles possibly due to fouling by different organic and divalent ions found in wastewater.

Keywords
Integrated systems; membrane bioreactor; advanced oxidation technology; Carbamazepine; pharmaceutical and personal care products; decentralized treatment.

INTRODUCTION

In recent years, the presence of pharmaceutical drugs and their residues in wastewater has attracted attention and concerns worldwide owing to potential public health and environmental risks to the natural ecosystems. The pharmaceutical compounds are usually persistent to environmental degradation processes and can result in serious bioaccumulation problems in the environment that could affect aquatic and terrestrial ecosystems. It has been reported that the pharmaceutical compounds could affect aquatic organisms even when they exist at trace concentrations (Chong *et al*., 2012). Also, the reuse of treated sewage effluent for non-potable end-uses becomes more eminent due to the higher possibility for potential human contacts or ingestion that may cause severe public health risk exposures. In order to minimise this point source of pollution while avoiding direct or indirect discharge into the sewer system, there is a need to provide a better-engineered treatment system to reduce the concentration levels to the risk amenable threshold.

Among the suite of advanced wastewater treatment technologies, integrating membrane bioreactor (MBR) with advanced TiO$_2$ photocatalytic treatment seems to be a promising hybrid technology for the removal of pharmaceutical compounds from recycled wastewater. Previously, it was revealed that only a stand-alone MBR system could not remove few specific pharmaceutical drugs such as Loratidine, Carbamazepine (CBZ) and Hydrochlorothiazide. In particular, the antiepileptic CBZ drug has been found to be very resistant to biological degradation during wastewater treatment, with

a low removal efficiency between negligible and up to 30% (Abegglen *et al.*, 2009; Miao *et al.*, 2005; Miège *et al.*, 2009). Previous studies have revealed that the adsorption of CBZ onto the activated sludge only plays a minor role (Joss *et al.*, 2005; Miao *et al.*, 2005). In general, the removal efficiency of pharmaceutical compounds could be improved with coupling the biological treatment with advanced oxidation technologies (AOTs) such as ozonation, Fenton process and hydrogen peroxide treatments (Klavarioti *et al.*, 2009).

In this instance, the TiO_2 photocatalytic technology offers a number of key coupling advantages among all other AOTs, including: (1) stable and non-toxic photocatalysts; (2) mild operating conditions; (3) complete mineralisation of parent drug compounds or their intermediate by-products without creating secondary pollution and (4) low operating costs (Chong *et al.*, 2010). The resultant highly reactive oxygen species (ROS) formed for organics removal and pathogens inactivation is well documented, but the practical application is still experiencing a series of technical challenges. The post-separation of the spent TiO_2 photocatalysts after wastewater treatment remains as a major obstacle towards the practicality as a wastewater treatment process. A few studies have investigated on the coupling of MBR with TiO_2 photocatalytic technology, but none is a success owing to the problems associated with the recovery and reuse of spent TiO_2 photocatalysts (Gomez *et al.*, 2007; Essam *et al.*, 2007; Qu *et al.*, 2009).

The aim of this study was to assess the feasibility of integrating MBR with advanced TiO_2 photocatalytic treatment technology as a combined treatment barrier to remove CBZ from high-strength synthetic pharmaceutical wastewater. A laboratory MBR-TiO_2 prototype system was started-up, operated and monitored for its treatment efficiency with respect to CBZ concentration and other water quality parameters. To improve the post-separation and recovery of spent TiO_2 photocatalysts, a new and proven nanofiber TiO_2 photocatalyst was applied in the integrated system. Prior to this, a lab scale system of MBR and TiO_2 photocatalytic technology was also monitored separately, in order to distinguish the synergistic operational effects. A practical long-term monitoring on the photoactivity of the nanofiber TiO_2 photocatalyst was also performed to ascertain the feasible application of TiO_2 photocatalytic technology as a wastewater treatment process. This laboratory study serves as a feasibility study to conclude with recommendations on the possible application of such integrated systems for small-decentralised wastewater applications for the future sustainable cities.

MATERIAL AND METHODS

Chemicals and catalyst preparation
CBZ (Sigma-Aldrich) was dissolved in water and MBR effluent as received or after dissolution in pure methanol (for preparation of analytical standards and synthetic feed). The nanofiber TiO_2 photocatalysts was obtained by autoclaving a basic suspension of anatase particles (Sigma-Aldrich) at 180°C for 48 h (Zhu *et al.*, 2005). The nanofiber TiO_2 possessed the fibril morphology of the sodium titanate, with diameter in the range of 10-50 nm and length in the range of 1-10 μm. The specific surface area and point of zero charge of the nanofiber TiO_2 photocatalyst were found to be 15.7 m^2/g and 4.6, respectively. All other chemicals were analytical grade.

High-strength synthetic pharmaceutical wastewater feed
The high-strength synthetic pharmaceutical wastewater was prepared by dissolving sodium acetate, methanol, ammonium chloride and potassium hydrogen phosphate in tap water. CBZ was dissolved in methanol prior to mixing with tap water. The obtained synthetic feed contained (mg/L): COD 2500, Carbamazepine 10, total nitrogen 61 and total phosphorus 1.5.

Experimental set-up

The MBR system, as sketched in Fig 1 used for this study was a 4 L column reactor equipped with a Zenon hollow fiber membrane module (filtering surface 0.047 m^2, nominal pore size of 0.1 μm), which was described in detail previously (Laera *et al*., 2011). The membrane module was sunk in the reactor and the permeate solution was extracted at a flux of about 17 L/hm^2, by imposing a negative pressure on the membrane (never exceeding 0.7 bar). The system was controlled by timers that allowed operating it in sequencing batch mode: feeding (30 min), anoxic (30 min), aeration plus filtration (60 min). During the latter phase, the permeated solution was continuously extracted under a constant airflow through the membrane module (5 L/min). This operation allowed to limit fouling and cake formation, and to provide enough dissolved oxygen (DO) for COD removal and nitrification. A submersible pump was continuously run to keep the reactor completely mixed. The described sequencing batch membrane bioreactor was operated with hydraulic retention time of 50 h and sludge retention time of 60 d.

A stainless steel annular slurry photoreactor (ASP) was equipped with an axial quartz tube, holding an 8 W UVA lamp peaked at 360 nm and with nominal UV output of 1 W (NEC FL8BLB). Aeration from the bottom of the conical-shaped base of the reactor ensured optimal mixing of the catalyst slurry and oxygen transfer during the photocatalytic reaction. The adopted catalyst showed good settling properties (Chong et al., 2009) and allowed for an easy separation of the treated wastewater. Based on this property, the ASP was operated in sequencing batch mode: filling (30 min), reaction (6 h), settling (1 h), discharge (1 h). The reactor working volume was 4 L, while the exchange volume was fixed at 3.2 L in order to treat the MBR effluent in 3 cycles per day. Effluent and buffer tank completed the integrated system, allowing to match the operations of MBR and ASP according to the adopted recycling ratio of 4:1.
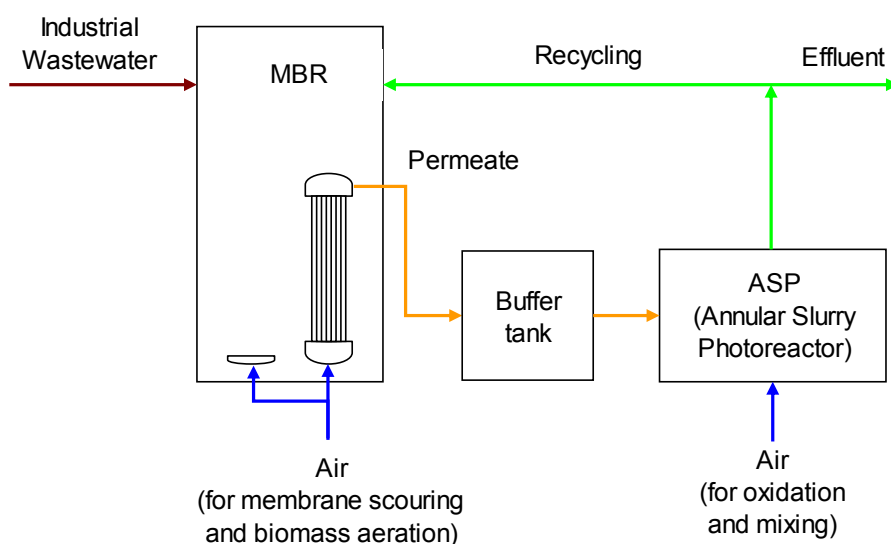

Figure 1. Schematic diagram of the lab-scale MBR-ASP system

Chemical analysis

High performance size exclusion chromatography (HPSEC) and UV detection were used to investigate the changes in the apparent molecular weight (AMW) profile. The samples were analysed using a coupling method reported by Liu *et al*. (2008).

CBZ concentration was measured using an HPLC (Varian Pro-Star) equipped with C-18 column (Microsorb-MW 100-5, 4.6 x 150 mm, 5 µm) and UV detector (254nm). The mobile phase was methanol 60% plus ammonium acetate (10mM) and acetic acid (5mM) and the adopted flow rate was 1 mL/min. Sample pre-treatment consisted of centrifugation at 13400 rpm for catalyst removal and filtration on 0.2 µm filter.

Respirometric tests were performed after aerating the sludge samples overnight to obtain endogenous respiration conditions. The oxygen uptake rate (OUR) was measured in a closed respirometric vessel with a volume of 133 mL equipped with DO probe, magnetic stirrer and temperature control system ($20 \pm 1°C$).

Chemical oxygen demand (COD), total nitrogen (TN), ammonium nitrogen (N-NH$_4$) and total phosphorus (TP) were measured using measurement kits (Hach, United States), comprising digestion solutions, digestion chamber (Hach DRB 200) and colorimeter (Hach DR890). Nitrite, nitrate and orthophosphate were measured by ion chromatography, using an HPLC (Varian ProStar) equipped with anionic column (Ionospher 5A, 4.6 x 250 mm, 5 µm) and refractory index detector (Varian 390 RI). Potassium phthalate 4mM in water was used as mobile phase at 1.5 mL/min. Total and volatile suspended solids were measured according to standard wastewater methods.

RESULTS AND DISCUSSION

Multiple tests for CBZ biodegradability/toxicity probing in integrated system
The primary reason for the integration of MBR with TiO$_2$ photocatalytic technology is to enhance the biodegradability of CBZ for subsequent treatment. In this instance, the TiO$_2$ photocatalytic technology can be integrated as pre- or post- MBR treatment. The dissimilarity between the process integration positioning is such that, (1) pre-MBR integration will enhance biodegradability of CBZ and toxicity reduction and (2) post-MBR integration will treat the un-degraded CBZ. However, in this study, a post-MBR integration with recycling stream (4:1 ratio) was operated in order to enhance the biodegradability and performance for CBZ removal.

Results showed that the biodegradability of CBZ increased with the integrated system. Fig. 2 shows the result from HPSEC to account for the changes in apparent molecular weight (AMW) fractions during the CBZ degradation in the synthetic effluents. From Fig. 2, it was observed that the initial AMW peak at 100kDa was disappeared after 30 min of reaction time and a subsequent peak appeared at the AMW of 750 Da (Chong *et al.*, 2012). The UV$_{260}$ absorbance intensity peaks were weaken from thereof, at 1 h reaction time up to 4 h. The initial shift in AMW peaks indicated the TiO$_2$ photocatalytic treatment resulted in the formation of smaller organic degradation by-products. Fig. 3 shows the chromatographic analysis of the samples collected during the operation of the integrated system. Data shown in Fig. 3 further indicate that the parent CBZ peak (i.e., retention time 4.8 min) disappeared and resulted in the formation of more hydrophilic compounds at lower retention time with negligible amounts of hydrophobic compounds. Therefore, an increase in biodegradability can be expected.
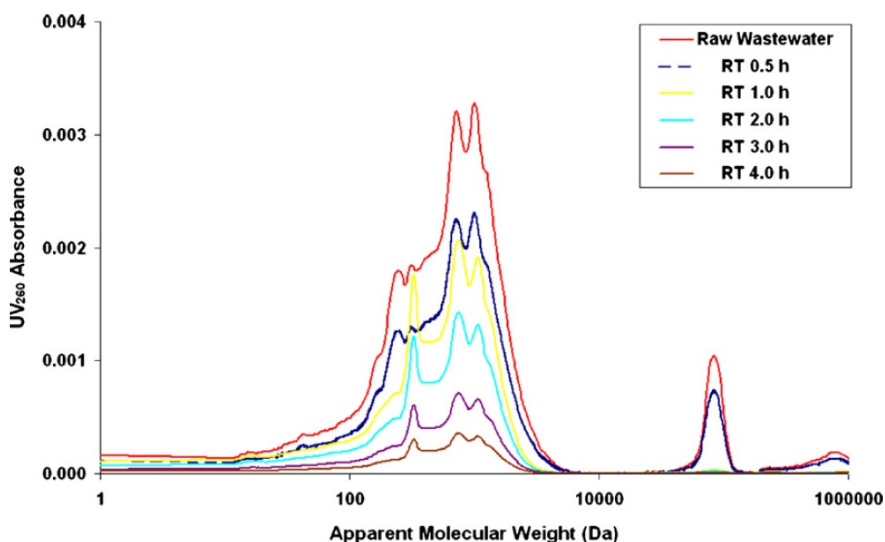
Figure 2.   HPSEC chromatograms at different reaction times during the photocatalytic degradation of CBZ in MBR effluent
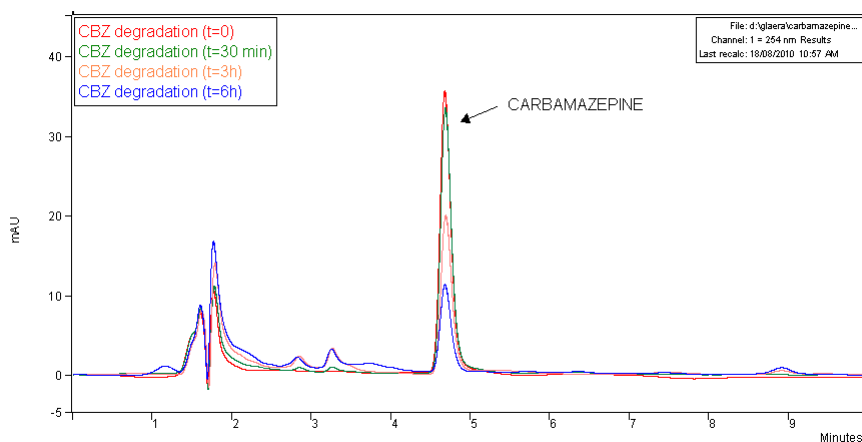

Figure 3.   HPLC chromatograms at different reaction times (0, 30 min, 3 and 6 hours, respectively) during the degradation of CBZ in effluent from the MBR treatment of simulated pharmaceutical wastewater.

In relation to this, the respirometric tests were conducted in order to better investigate the CBZ biodegradability and the possible occurrence of inhibiting and toxic degradation by-products. The endogenous and maximum oxygen uptake rate (OUR) were measured for un-acclimated sludge mixed with either treated (i.e., with possible degradation by-products) and or untreated CBZ in synthetic pharmaceutical effluent. Fig. 4 shows that the endogenous respiration rate increased significantly in the presence of untreated CBZ in the synthetic effluent, while the maximum OUR remains comparable with that of the control test. Meanwhile, the removal of CBZ was found to be negligible during respirometric testing, confirming the refractory character of this compound. These findings are particularly interesting, as the significant increase in the endogenous respiration rate may be related to the presence of sub-lethal concentration of chemical stressor. This is in agreement with Ray and Peters (2008), whereby they had demonstrated that an excess of carbon and energy was required in the presence of stressing conditions for the biomass, beyond the amounts needed for normal cell maintenance and decay. Therefore, the presence of untreated CBZ compounds in a relatively high concentration can be considered as a chemical stressor influencing the biomass metabolism. On the other hand, the above chemical stressor effects were almost completely removed after the treatment with UV/TiO$_2$. Furthermore, no significant variations were observed for

the maximum OUR, suggesting that no inhibitory by-products were formed during the photocatalytic treatment.
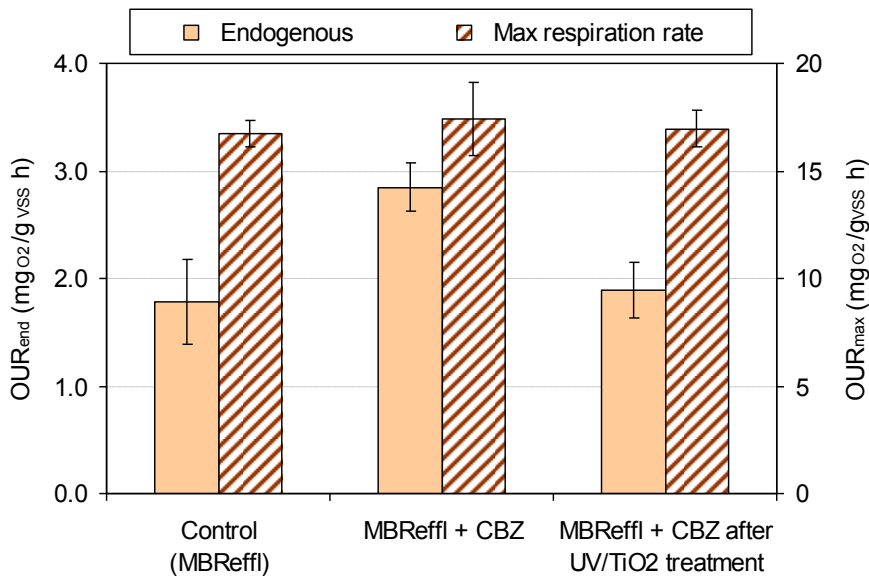

Figure 4. Respirometric tests with un-acclimated sludge.

Performance of integrated MBR-TiO$_2$ system
The MBR was inoculated with biomass from a municipal wastewater treatment plant, and was immediately fed on simulated pharmaceutical wastewater. In order to evidence the effect of integrating the photocatalytic process in the recycle stream of a biological treatment, the lab-scale MBR-TiO$_2$ system was initially run without UV lamp and catalyst slurry (i.e. with the MBR alone). After a short acclimation period the biomass in the MBR system reached the steady state conditions, both in term of biomass growth (1.8±0.2 g$_{VSS}$/L) and removal rates (98.1±1.3% for COD and no removal for CBZ). Once the UV/TiO$_2$ system was turned on, the biomass reached a new and higher steady concentration (2.8±0.3 g$_{VSS}$/L). This can be directly related to the decreased CBZ concentration in the recycled stream with consequent reduction in the biological tank.

Respirometric tests on the acclimated biomass confirmed a biomass profile, which was found for the un-acclimated sludge, i.e. the reduction of CBZ concentration resulted in reducing endogenous respiration rate and no significant variations in the maximum respiration rate. Therefore, also with acclimated biomass the chemical stress due to the presence of CBZ was strongly reduced. As a consequence of the reduced chemical stress, part of the substrate was no more diverted to cell maintenance functions and was available for the biomass growth. The latter can be expressed in terms of observed biomass yield (Y_{obs}), which is defined as the ratio between produced biomass and removed substrate and is related to maximum yield (Y_{max}), endogenous decay (b) and sludge age (SRT) through the following equation:

$$\frac{1}{Y_{obs}} = \frac{1}{Y_{max}} + \frac{b \cdot SRT}{Y_{max}}$$

(1)

In case of stressor for the biomass, the equivalent substrate and/or energy spilling will turn in increased endogenous decay with consequent reduction of the observed yield, as it can be evidenced by re-arranging the previous equation into Equation 2, as follows:

$$\frac{Y_{obs2}}{Y_{obs1}} = \frac{b_1 \cdot SRT + 1}{b_2 \cdot SRT + 1} \tag{2}$$

As it can be noticed from the equations above, the interdependence of endogenous decay and sludge yield is modulated by the sludge age. However, for high *SRT* the equation can be simplified as Equation 3.

$$\frac{Y_{obs2}}{Y_{obs1}} \cong \frac{b_1}{b_2} \cong \frac{1}{b_2/b_1} \tag{3}$$

Considering that the endogenous decay is directly related to the endogenous OUR, the above equations can be easily verified: as shown in Fig 5. The endogenous respiration in presence of CBZ was about 150% of that was measured in the wastewater with treated or no CBZ. Hence, a reduction of biomass yield of about 67% could be predicted according to the Equation 3. This is in agreement with the experimental variations of 69 and 72%, which were found respectively with reference to the observed yield with treated CBZ (i.e. after the introduction of the photocatalytic process) or no CBZ (i.e. in a further test without CBZ in the MBR feed). As the same OUR ratio was found for un-acclimated biomass, this simple method and approach can be proposed as a predictive tool to estimate the effect of the chemical stressors on the biomass growth in different applications.
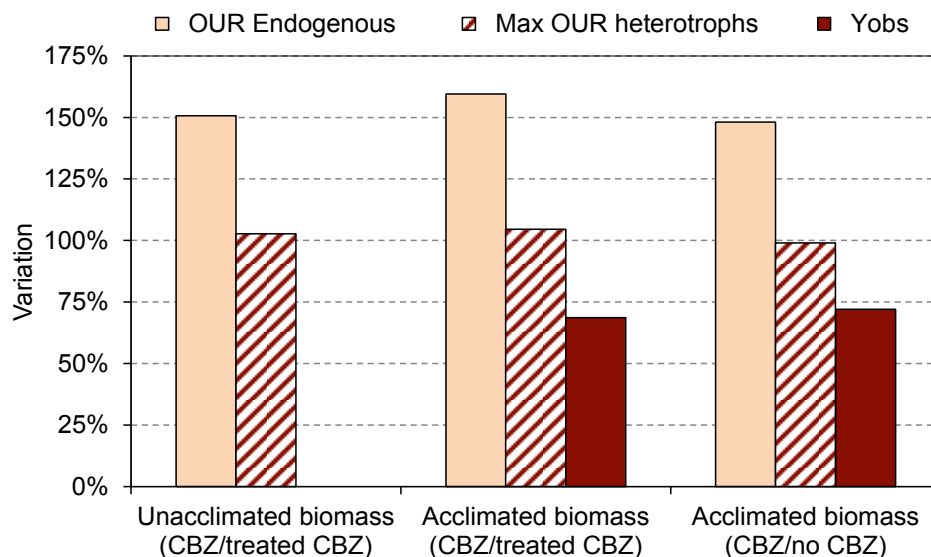

Figure 5.　Variations of respiration rates and observed yields for MBR biomass un-acclimated or acclimated to CBZ.

As a consequence of the removed stressor effect and the inferred increased biodegradability, the oxidation products formed during the photocatalytic degradation of CBZ should be removed by the

MBR biomass after recycling 80% of the effluent. Considering that a maximum removal of COD associated with the CBZ by the integrated system is about 20 mg/L (Laera *et al*., 2011a). The average reduction of about 17 mg/L of COD in the effluent after the photocatalytic process is perfectly in agreement with the hypothesis of a complete biodegradation of the oxidation products.

Long-term monitoring on nanofiber TiO$_2$ photoactivity
In order to promote the applicability of this integrated system, in particular the post-separation and development of TiO$_2$ photocatalytic technology, a long term monitoring on the photoactivity of nanofiber TiO$_2$ photocatalysts was carried out. For this, the integrated system was filled with the same batch of nanofiber TiO$_2$ photocatalyst and operated for up to a total of 80 treatment cycles. The post-separation and recovery of catalyst particles was almost complete with only less than 3‰ loss of fine particles after each treatment cycle. In this instance, the lost catalyst particles were replenished on a weekly basis to keep to the optimal concentration of 0.5 g/L (Laera *et al*. 2011a).

Fig. 6 shows that during the preliminary operation of the TiO$_2$ photocatalytic system, a maximum 95% removal rate of CBZ was reached after a few days of operation. However, the CBZ removal from the sequencing operation started to deteriorate after 2 weeks of operation. Direct monitoring of the catalytic activity was done by sampling the slurry photo-reactor at regular intervals. As shown in Fig 7, the degradation kinetics followed the pseudo-first order linearization of the Langmuir-Hinshelwood model. After a few cycles of operation, the apparent constant rate stabilized at around 87% of the initial value (0.2 h^{-1}). This finding was in a good agreement with previous results obtained with CBZ in municipal MBR effluent (Laera *et al*., 2011b), which were related to the effluent content of organic matter and divalent ions. However, the catalytic activity started to decrease just before cycle 45. The k_{app} at the end of the experimental run was found to be about 33% of the initial value. As observed in terms of effluent CBZ, a decline in the L-H apparent rate constant started after about 2 weeks of operation and the reaction rate at the end of the test was about 33% of the initial value. A preliminary attempt was made to treat the spent TiO$_2$ catalysts in deionised water. This showed that reversible organic fouling could be induced resulting in a progressive recovery of photocatalytic activity. Further studies are required to quantify the surface foulants' kinetics from different organic and divalent ions potentially found in wastewater.
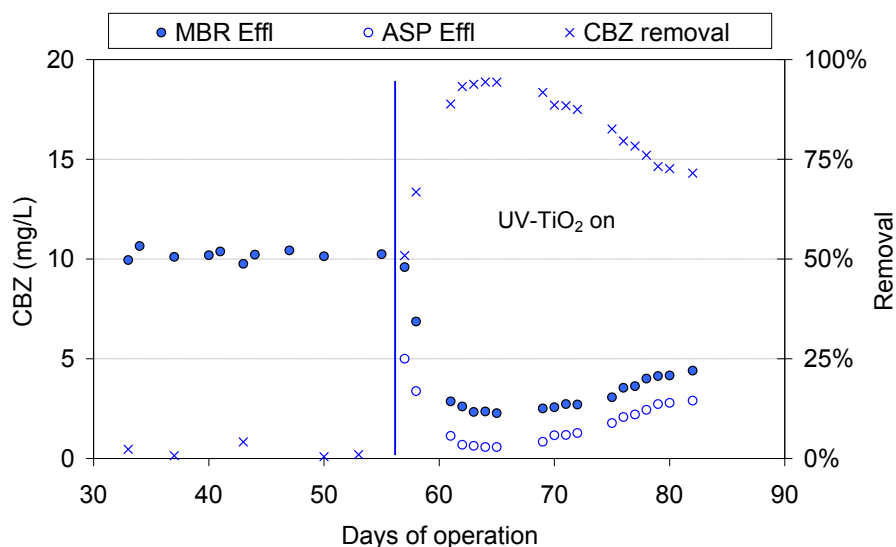

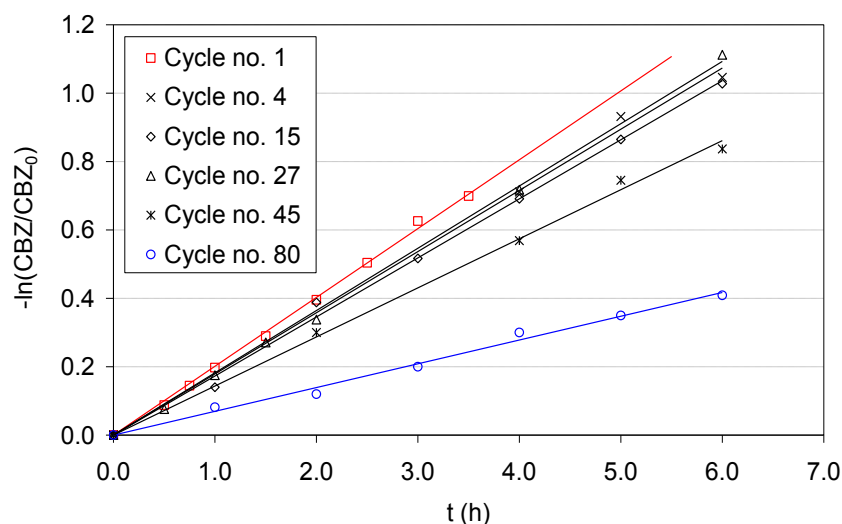**Figure 6**. Effluent Carbamazepine concentration and removal.

Figure 7. Monitoring the nanofiber catalytic activity in the sequencing batch slurry photoreactor.

CONCLUSION

This study has shown a high CBZ removal efficiency of 95% from the integration of advanced TiO_2 photocatalytic treatment technology with MBR operation. The high treatment efficiency of the integrated system also resulted in a high biodegradability of CBZ, where smaller and more hydrophilic molecules were formed. The removal of CBZ also resulted in removal of the chemical stressor effect associated with this pharmaceutical compound. Continuous monitoring on the sequential operation of the system revealed that the mixed fouling effect from the organic matter and divalent ions is of reversible nature and should be studied in the near future. In overall, this study showed that the integrated system, which performed a high CBZ removal efficiency (ca. 75-95%) over 80 treatment cycles, is viable for decentralised applications to minimise the potential health and environmental risks from wastewater containing pharmaceutical compounds. However, further detailed life cycle analysis of this process needs to be conducted to promote the application of such integrated system in the future. The study only constitutes the first step towards the implementation of such an integrated system for decentralised wastewater treatment applications.

ACKNOWLEDGEMENT

REFERENCES

Abegglen, C., Joss, A., McArdell, C.S., Fink, G., Schlusener, M.P., Ternes, T.A., Siegrist, H. 2009 The fate of selected micropollutants in a single-house MBR. *Water Res.* **43**, 2036 – 2046.

Chong, M.N., Jin, B., Zhu, H.Y., Chow, C.W.K., Saint, C. 2009 Application of H-titanate nanofibers for degradation of Congo Red in an annular slurry photoreactor. *Chem. Eng. J.* **150**, 49-54.

Chong, M.N., Jin, B., Chow, C.W.K., Saint, C. 2010 Recent developments in photocatalytic water treatment: a review. *Water Res.* **44**, 2997-3027.

Chong, M.N. and Jin, B. 2012 Photocatalytic treatment of high concentration Carbamazepine in synthetic hospital wastewater. *J. Haz. Mater.* **199-200**, 135-142.

Essam, T., Amino, M.A., Ei, T.O., Mattiasson, B., Guieysse, B. 2007 Sequential photochemical-biological degradation of chlorophenols. *Chemosphere*, **66**, 2001-2209.

Gomez, C., Rodriguez, J., Freer, J., Lizama, C., Zaror, C., Mansilla, H.D. 2007 Coupling of photocatalytic and biological reactors to remove EDTA-Fe from aqueous solution. *Environ. Technol.* **28**, 123-127.

Joss, A., Keller, E., Alder, A.C., Gobel, A., McArdell, C.S., Ternes, T.A., Siegrist, H. 2005 Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Res.* **39**, 3139–3152.

Klavarioti, M., Mantzavinos, D., Kassinos, D. 2009 Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ. Int.* **35**, 402–417.

Laera, G., Chong, M.N., Jin, B., Lopez, A. 2011 (a) Integrated MBR-TiO$_2$ Photocatalysis Process for the Removal of Carbamazepine from Simulated Pharmaceutical Industrial Effluent. *Biores. Technol.* **102**, 7012-7015.

Laera, G., Jin, B., Lopez, A. 2011 (b) Photocatalytic activity of TiO$_2$ nanofibers in simulated and real municipal effluents. *Catal. Today* **161**, 147-152.

Liu, S., Lim, M., Fabris, R., Chow, C., Drikas, M., Amal, R. 2008 TiO$_2$ photocatalysis of natural organic matter in surface water: impact on trihalomethanes and haloacetic acid formation potential. *Environ. Sci. Technol.* **42** 6218–6223.

Miao, X.-S., Yang, J.-J., Metcalfe, C.D. 2005 Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant. *Environ. Sci. Technol.* **39**, 7469–7475.

Miège, C., Choubert, J.M., Ribeiro, L., Eusèbe, M., Coquery, M. 2009 Fate of pharmaceuticals and personal care products in wastewater treatment plants – Conception of a database and first results. *Environ. Poll.* **157**, 1721–1726.

Ray, S., Peters, C.A., 2008 Changes in microbiological metabolism under chemical stress. *Chemosphere* **71**, 474–483.

Qu, Y.Y., Yang, Q., Zhou, J.T., Gou, M., Xing, L.L., Ma, F. 2009 Combined MBR with photocatalysis/ozonation for bromoamine acid removal. *App. Biochem Biotechnol.* **159**, 664-672.

Zhu, H.Y., Lan, Y., Gao, X.P., Ringer, S.P., Zheng, Z.F., Song, D.Y., Zhao, J.C. 2005 Phase transition between nanostructures of titanate and titanium dioxides via simple wet-chemical reactions. *J. Am. Chem. Soc.* **127**, 18, 6730-6736.