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Short Communication

An integrated MBR–TiO_2 photocatalysis process for the removal of Carbamazepine from simulated pharmaceutical industrial effluent

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ABSTRACT

This paper aims to demonstrate that integrating biological process and photocatalytic oxidation in a system operated in recycling mode can be a promising technology to treat pharmaceutical wastewater characterized by simultaneous presence of biodegradable and refractory/inhibitory compounds. A lab-scale system integrating a membrane bioreactor (MBR) and a TiO_2 slurry photoreactor was fed on simulated wastewater containing 10 mg/L of the refractory drug Carbamazepine (CBZ). Majority of chemical oxygen demand (COD) was removed by the MBR, while the photocatalytic oxidation was capable to degrade CBZ. CBZ degradation kinetics and its impacts on the biological process were studied. The adoption of a recycling ratio of 4:1 resulted in removal of up to 95% of CBZ. Effluent COD reduction, sludge yield increase and respirometric tests suggested that the oxidation products were mostly biodegradable and not inhibiting the microbial activity. These results evidenced the advantages of the proposed approach for treating pharmaceutical wastewater and similar industrial effluents.

1. Introduction

The degradation of pharmaceuticals and their residues is of particular interest due to the ubiquity of these compounds and to their capacity of affecting aquatic organisms even if they exist at trace concentrations. With increasing water scarcity and reuse practices, the concentration of pharmaceuticals and their residues in the aquatic environment are expected to increase. In this contest, segregation and efficient treatment of the wastewaters deriving from pharmaceutical production is highly desired, in order minimize this point-source of pollution, avoiding direct or indirect discharge of drugs and other production chemicals into the sewer (i.e. after unsuccessful biological treatment in on-site wastewater treatments).

In a recent review on the potential of ozonation and advanced oxidation processes (AOP) for the removal of pharmaceuticals from various aqueous systems, Klavarioti et al. (2009) concluded that the application of AOP for treatment-at-source may be a realistic option only for drinking water plants and for the treatment of pharmaceutical wastewaters. Coupling with biological treatment is the approach usually adopted to treat wastewater containing refractory compounds and to limit the high treatment costs associated with chemical oxidations. The latter can be introduced as either a pre-treatment for toxicity reduction or a post-treatment for final polishing of the wastewater (Klavarioti et al., 2009; Oller et al., 2010). However, pharmaceutical wastewater often contains minor fraction of refractory and/or inhibitory organic compounds in a biodegradable matrix (Mascolo et al., 2010a). For this kind of effluent, the pre-treatment with AOP is not effective due to the lack of selectivity of the hydroxyl radicals, while the post-treatment could leave a number of by-products of unknown harmfulness or otherwise reach an expensive complete mineralization. In this case, a full integration of the biological and chemical processes is proposed, in which the AOP is operated in a recycling stream to the biological treatment (Mascolo et al., 2010b; Oller et al., 2010). The main goal of the chemical oxidation in the integrated process is to increase the biodegradability of refractory/inhibitory compounds, avoiding their complete mineralization.

Among the different AOP, the heterogeneous photocatalysis based on TiO_2 offers key advantages, such as mild reaction conditions and inexpensive/nontoxic/stable catalyst. However, practical application of this technology is hindered by either post-separation issues (in case of slurry reactors) or limited photoactivity (in case of supported catalysts). To overcome these limitations, a new titanium nanofiber has been recently developed for application in slurry reactors, demonstrating satisfactory photocatalytic activity and easy post-separation by settling (Chong et al., 2009; Laera et al., 2011).

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On the other hand, membrane bioreactors (MBRs) have been selected for integration with the photocatalytic oxidation, as this technology offers great operational flexibility and superior performances in removing suspended solids and micropollutants. The absence of suspended solids in the MBR effluent is of particular benefit for the application of UV light, avoiding light shielding and scattering by suspended particles. Moreover, the use of MBR instead of conventional activated sludge systems offers further advantage of higher potential for biomass acclimation and augmentation, especially when operated at high sludge retention time.

In order to investigate the feasibility and potential benefit of an integrated MBR–TiO_2 photocatalysis system, wastewater from the production of the antiepileptic Carbamazepine (CBZ) has been simulated in this study. CBZ is a widely administered drug and has been found to be refractory to biological degradation during wastewater treatment (Joss et al., 2005; Miao et al., 2005). It has been classified as highly persistent with an environmental dissipation half-life greater than 100 d (Benotti and Brownawell, 2009; Loffler et al., 2005). Scarce or no accumulation has been detected in soil and sediments (Loffler et al., 2005; Scheytt et al., 2005; Wu et al., 2009). Therefore, CBZ tends to diffuse and contaminate all compartments of the aquatic environment and its removal is of primary concern.

Previous studies on the identification of CBZ oxidation products formed during drinking water treatments showed that most of the degradation pathways pass through the formation of various aldehydes, ketones and hydroxylated intermediates (Hu et al., 2009). Kosjek et al. (2009) and Vogna et al. (2004) also reported the formation of Acridine (known as human carcinogen), which was found to be almost completely biodegradable in lab-scale activated sludge treatments. These evidences suggest that the operation of an integrated system can offer the additional advantage typical of a multiple barrier approach, as most of the oxidation products are recycled back to the biological system.

The main objective of this study was to assess the feasibility and advantages of the integrated approach for the treatment of industrial wastewater. To this aim, a fully automated MBR–TiO_2 integrated system was set-up after preliminary tests. Start-up of the system without UV light and catalyst (i.e. MBR process plus effluent recycling only) was performed in order to evidence the improvements achieved with the following integration of the two processes.

2. Methods

2.1. Chemicals and catalyst preparation

CBZ (Sigma–Aldrich) was dissolved in water, MBR effluent or methanol (for preparation of analytical standards and synthetic feed) as received.

The adopted photocatalyst was prepared by hydrothermal reaction in the laboratory of the School of Physical and Chemical Sciences of the Queensland University of Technology (Brisbane, QLD 4001, Australia), according to the procedure described elsewhere (Zhu et al., 2005). The obtained anatase nanofibers had diameter in the range of 10–50 nm and length in the range of 1–10 μm. The synthesized catalyst was characterized by specific surface area of 15.7 m^2/g, pH_{zpc} of 4.6 and good settling properties (Chong et al., 2009).

2.2. Simulated wastewater

According to recent patents for CBZ production (Eckardt and Jansch, 2006; Palitzsch et al., 1993; Vyas et al., 2001), the final purification step usually involves the precipitation of raw CBZ by addition of water to the reaction mix, followed by washing and re-crystallization. Therefore, CBZ concentration in the collected wastewater is expected to be in the range of the compound solubility (17.7 mg/L). Moreover, as the final reaction step is usually done in alcohol and/or acetic acid a considerable amount of readily biodegradable COD will be also present.

The simulated pharmaceutical wastewater was obtained by dissolving sodium acetate, methanol, ammonium chloride and potassium hydrogen phosphate in tap water. CBZ was dissolved in methanol prior to mix with tap water. The obtained synthetic feed contained (mg/L): COD 2500, CBZ 10, total nitrogen 61.2, and total phosphorus 1.5.

2.3. Experimental set-up

An MBR equipped with a Zenon hollow fiber submerged membrane module (filtering surface 0.047 m^2, nominal pore size of 0.1 μm) has been used for this study. The MBR was operated in sequencing batch mode: feeding/mixing (30 min), anoxic/mixing (30 min), aeration/filtration (60 min). During the latter phase, permeate was continuously extracted at about 17 L/m^2/h and air was pumped through the membrane module in order to limit membrane fouling and provide oxygen for COD removal and nitrification (dissolved oxygen > 2 mg/L at the end of the phase). The MBR was inoculated with biomass from the local sewage treatment plant and operated at room temperature (25 ± 2 °C), hydraulic retention time of 50 h and sludge retention time of 60 days.

A 4 L annular slurry photoreactor (ASP) equipped with an axial quartz tube was adopted, as fully described elsewhere (Chong et al., 2009). For this study, an 8 W UVA lamp peaked at 360 nm (NEC FL8BLB, 1 W nominal UV output) was inserted in the quartz tube. The ASP was operated in sequencing batch mode: filling (30 min), reaction (6 h with UV and aeration), settling (1 h), and discharge (30 min). Effluent and buffer tank completed the integrated system, allowing to match the operations of MBR and ASP according to a recycling ratio of 4:1.

2.4. Analysis

CBZ concentration was measured by HPLC, with standard C-18 column, UV detector (254 nm), and mobile phase containing methanol 60%, ammonium acetate 10 mM and acetic acid 5 mM. Sample pre-treatment consisted of centrifugation at 13400 rpm for catalyst removal and filtration on 0.2 μm filter. Chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) were measured on fresh samples, without pretreatment and using commercial test kits (Hach, United States). Nitrite, nitrate and orthophosphate were measured by HPLC, with anionic column, refractory index detector and potassium phthalate 4 mM in water as mobile phase. Total and volatile suspended solids were measured according to standard methods. Respirometry 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 (volume 133 mL), equipped with dissolved oxygen probe, magnetic stirrer and temperature control system (20 ± 1 °C).

3. Results and discussion

3.1. Preliminary studies

Initial investigations were mainly focused at optimizing the photocatalytic process and assessing possible inhibiting/toxic effects of CBZ and oxidation by-products.

The performances of the adopted catalyst in CBZ oxidation were investigated in a previous study (Laera et al., 2011). With an optimal catalyst loading of 0.5 g/L, the apparent rate constant (k_{app}) for a pseudo-first order linearization of the Langmuir–Hinshelwood kinetic was found to be about 0.8 h^{-1}. In this study the same catalyst loading resulted in k_{app} of about 0.2 h^{-1}, and the difference can be explained considering that the same lamp provided UV light to a reactor with quadruple volume. Based on these results, a reaction time of 6 h was adopted to obtain at least 70% CBZ removal in each cycle, as can be calculated applying the pseudo-first order kinetic:

$$\begin{aligned}\mathrm{CBZ_{removal}} &= \left(1-\frac{\mathrm{CBZ_{effluent}}}{\mathrm{CBZ_{influent}}}\right)\times 100\% \\ &= (1-\exp(-k_{app}\times t))\times 100\% \qquad (1)\end{aligned}$$

Considering that with the adopted recycling ratio (4:1) most of the effluent will be further submitted to the photocatalytic oxidation, higher overall removal efficiency can be expected.

Preliminary respirometric tests were performed using un-acclimated sludge mixed 1:1 with filtered supernatant (control), untreated MBR effluent (5 mg/L of CBZ in the respirometric vessel) and effluent treated with TiO_2/UV photocatalysis (about 1.5 mg/L of CBZ plus oxidation by-products). The endogenous respiration rates were found to be 43 ± 9, 68 ± 6 and 45 ± 6 $mg_{O_2}/g_{VSS}/d$ for control, untreated and treated effluent, respectively. Considering that the removal of CBZ during the respiration tests was found to be negligible, the significant increase in respiration rate in absence of other external substrates cannot be associated to the biodegradation of CBZ and may only be related to the presence of sub-lethal concentration of a chemical stressor. Indeed, as clearly demonstrated by Ray and Peters (2008), an excess of carbon and/or energy is required in presence of stressing conditions for the biomass, beyond the amounts needed for normal cell maintenance and decay. This need is manifested as an increase in the endogenous respiration rate, as found in this study and in similar investigations on different chemical compounds (Chen et al., 2008; Delgado et al., 2010). Therefore, CBZ can be considered a chemical stressor influencing the biomass metabolism, with stressing effects negligible at concentrations lower than 1.5 mg/L.

The variations in maximum respiration rate of the heterotrophic biomass (obtained after the addition of sodium acetate) were not significant for control, untreated and treated effluents (all values around 380 $mg_{O_2}/g_{VSS}/d$). Ray and Peters (2008) also found that the stressor compounds can have inhibiting effect at certain concentrations, which would slow down the maximum rates of growth and substrate utilization. Therefore, it can be concluded that CBZ and its oxidation by-products did not reached inhibiting concentrations for the heterotrophic biomass, as the maximum oxygen uptake rate remained unvaried.

As pointed out in Section 1, the main goal of the chemical oxidation in the integrated process was to increase the biodegradability of CBZ. The enhancement of biodegradability due to oxidation reactions is typically associated to the formation of smaller and more hydrophilic molecules (Mantzavinos and Psillakis, 2004). HPLC analysis of samples collected during the photo-degradation process confirmed that the disappearance of CBZ corresponded to the formation of more hydrophilic molecules (i.e. compounds with lower retention times in the C_{18} column), and negligible amounts of a hydrophobic compound. Therefore, an increase of biodegradability can be expected.

3.2. Performances of the biological process in the integrated system

The MBR–TiO_2 system was initially run without UV lamp and catalyst slurry (i.e. with MBR and permeate recycling only), so to better evidence the effect of the subsequent introduction of the photocatalytic process. As shown in Fig. 1, once the UV/TiO_2 system was turned on, the biomass reached a higher steady concentration. As all other operating parameters remained unchanged, this can be related to the decreased CBZ concentration in the recycled stream with consequent reduction in the biological tank.

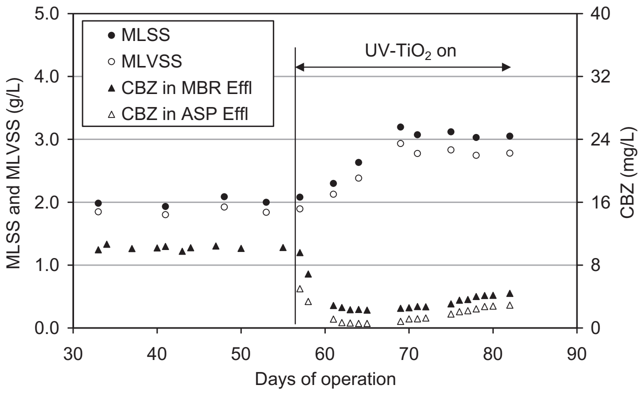

Fig. 1. Biomass suspended solids and effluent CBZ concentration in absence and presence of the photocatalytic process.

Respirometric tests on the acclimated biomass confirmed the trend found for un-acclimated sludge, i.e. the reduction of CBZ concentration resulted in reducing endogenous respiration rate and no significant variations of the maximum respiration rate (Table 1). Therefore, also with acclimated biomass, the chemical stress due to the presence of CBZ was strongly reduced when the UV/TiO_2 process started reducing CBZ concentration in the system. 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. This was experimentally observed as increase of biomass concentration and sludge yield (Table 1). The theoretical COD associated with the presence of CBZ can be calculated in 2.17 mg_{O_2}/mg_{CBZ}, according to the following reaction:

$$C_{15}H_{12}N_2O + 16O_2 + 2H^+ \rightarrow 15CO_2 + 2NH_4^+ + 3H_2O \qquad (2)$$

If all removed CBZ would be mineralized in the integrated process, the removal of 9.3 mg/L of CBZ (Table 1) should correspond to the removal of about 20 mg/L of COD. Therefore, based on the average experimental variation of about 17 mg/L of COD, it can be inferred that most of the CBZ oxidation products was biodegradable and was removed in the membrane bioreactor, after effluent recycling.

3.3. Performances of the photo-catalytic process in the integrated system

The results reported in Section 3.1 were obtained in batch tests with fresh catalyst. In the integrated system, the same catalyst was used in automated cycling operation (fill, reaction, settling, and discharge) and kept in the ASP for a total of about 80 cycles. The catalyst recovery after each cycle was almost complete and less than 1% per day was found to escape the ASP as fine particles in the effluent, possibly due to mechanical friction and breaking up of the nanofiber particles. The lost catalyst was weekly replenished, in order to maintain the optimal concentration of 0.5 g/L in the slurry photo-reactor.

As shown in Fig. 1, during the first days of operation of the photocatalytic oxidation, most of the CBZ present in the integrated system was degraded and the effluent CBZ reached its minimum value (max CBZ removal of 95%). However, after about 2 weeks of operation (corresponding to 42 cycles), CBZ removal started to decrease. Direct monitoring of the catalyst activity was done by sampling the ASP at regular intervals during the cycle and fitting the CBZ degradation kinetics according to the pseudo-first order linearization of the Langmuir–Hinshelwood model. After few

Table 1
Comparison of operating parameters of MBR alone and integrated system.

Parameter	Unit	MBR alone	MBR–TiO_2	Variation
MLSS	gSS/L	2.0 ± 0.1	3.1 ± 0.3	+55%
MLVSS/MLSS	%	92 ± 1	91 ± 1	n.s.
Y_{obs}	g_{VSS}/g_{CODrem}	0.0284	0.0435	+53%
Endogenous OUR	$mg_{O_2}/g_{VSS}/d$	97 ± 7	60 ± 5	−38%
OUR_{max} heterotrophs	$mg_{O_2}/g_{VSS}/d$	960 ± 70	920 ± 70	n.s.
OUR_{max} nitrifying bacteria	$mg_{O_2}/g_{VSS}/d$	110 ± 14	110 ± 20	n.s.
Effluent COD	mg/L	46 ± 5	29 ± 4	–37%
COD removal	%	98.1 ± 1.3	98.8 ± 0.5	n.s.
Effluent CBZ	mg/L	10.1 ± 0.3	0.8 ± 0.3	–92%

n.s. = not significant.

cycles of operation, the apparent constant rate stabilized around $0.175\ h^{-1}$, i.e. about 87% of the initial value. Similar reduction was found in a previous study with CBZ in municipal MBR effluent, which was related to the effluent content of organic matter and divalent ions (Laera et al., 2011). However, in this study, long term operation resulted in further decline of the catalytic activity starting after about 40 cycles of operation and, at the end of the experimental run, k_{app} was found to be about 33% of the initial value. Prolonged treatment of the exhausted nanofibers with UVA in deionized water resulted in progressive recovery of its photocatalytic activity. This suggests that reversible organic fouling had occurred and that it could be counteracted by periodic catalyst regeneration or proper increase of the UV lamp intensity. Further studies are required to optimize the catalyst performances and its mechanical properties.

4. Conclusions

The main conclusions of this study can be resumed as follows:

- Under the adopted conditions and for CBZ concentration below 10 mg/L, CBZ was not biodegradable nor inhibitor of biomass activity and substrate removal. However, the drug demonstrated to be a chemical stressor influencing the biomass metabolism with consequent effects on both endogenous respiration and observed sludge yield.
- The integration of MBR with TiO_2/UV photocatalysis in a system with recycling ratio of 4:1 resulted in CBZ removal up to 95%.
- The beneficial synergic action obtained with the integration of biological and chemical oxidation processes was evidenced.

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