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PHOTOCATALYTIC MEMBRANE REACTOR PERFORMANCE TOWARDS OXYTETRACYCLINE REMOVAL FROM SYNTHETIC AND REAL MATRICES

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INTRODUCTION

The use of photocatalytic membrane reactors (PMRs), as tertiary treatment of urban wastewaters, have been reported as a very promising solution to remove or transform contaminants of emerging concern (CECs) into less harmful compounds. PMRs can be divided into two main groups: (i) systems with the photocatalyst in suspension and (ii) systems with the photocatalyst immobilized on the membrane (nano-engineered membranes-NEM). Despite the growing scientific interest on the use of PMRs for pollutants removal, there is still a lack of an in-depth analysis on the influence of important process parameters as well as a comparison between the immobilized and suspended photocatalyst configurations. This way, the main objective of the present work is to assess the efficiency of an integrated hybrid system coupling microfiltration with UVA photolysis (UVA-MF) or TiO_2 photocatalysis (UVA/TiO_2-MF) (PMR) for the oxidation of oxytetracycline (OTC), as a model CEC. The matrix effect was analysed by spiking a secondary effluent from a real urban wastewater treatment plant with OTC.

THE 'PMR' CONCEPT

Photocatalytic advantages + Membrane technologies

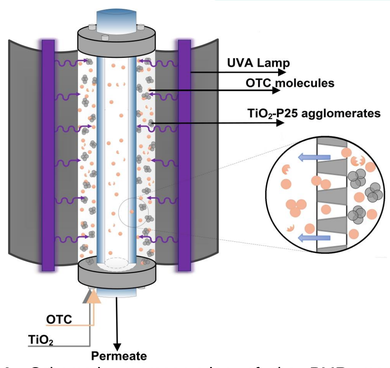


Fig. 1. Schematic representation of the PMR membrane module with TiO_2-P25 in suspension.

Membrane:
- plays the role of pollutants barrier;
- ensures the photocatalyst particles separation from the treated solution.

TiO_2:
- photocatalytic activity.

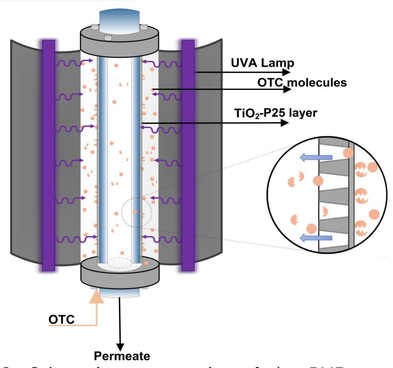


Fig. 2. Schematic representation of the PMR membrane module with TiO_2-P25 immobilized on the membrane shell-side.

Membrane:
- plays the role of pollutants barrier;
- *in-situ* pollutants oxidation/reduction.

TiO_2:
- photocatalytic activity.

EXPERIMENTAL METHODS

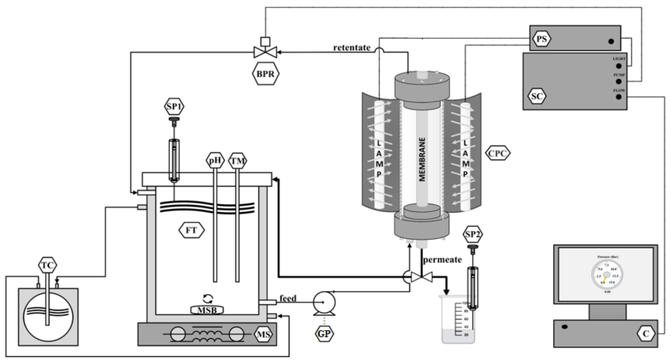


Figure 3. Schematic representation of the laboratory-scale PMR.

The installation can be set up in two configurations: (i) TiO_2-P25 nanoparticles in suspension (ii) or immobilized on the external surface of the membrane.

The membrane module ends are tightly sealed by two movable polypropylene flanges with 36 water inlets, allowing a more uniform distribution of the water.

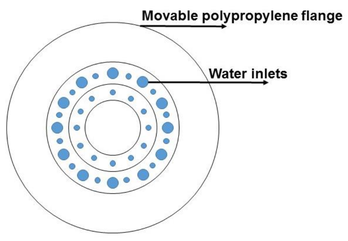


Figure 4. Schematic representation of the reactor movable polypropylene flanges, .

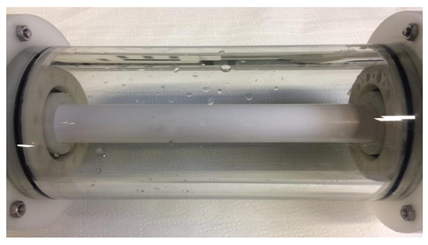


Table 1. PMR reactor dimensions.

Photocatalytic Membrane Reactor	
Length (cm)	15.5
Inner diameter - outer tube (cm)	6.0
Outer diameter – membrane (cm)	2.0
Hydraulic diameter (cm)	4.0
Effective membrane area (m^2)	84×10^{-4}
Photonic flow (J_{UV} s^{-1})	0.5
Total volume illuminated (cm^3)	0.5

RESULTS

Effect of transmembrane pressure and TiO_2-P25 loading using the catalyst slurry system

TMP

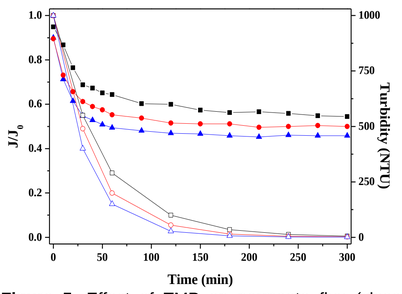


Figure 5. Effect of TMP on permeate flux (closed symbols) and turbidity (open symbols). TMP: (■) 0.1, (●) 0.15 and (▲) 0.2 MPa. [TiO_2-P25] = 0.2 g L^{-1}.

TMP: Low cross flow velocity value (0.01 m s^{-1}) - denser catalyst cake layer on the membrane surface with increasing TMP.

[TiO_2]: An increase on photocatalyst amount led to a flux decline and to an increment on permeate quality.

Catalyst loading

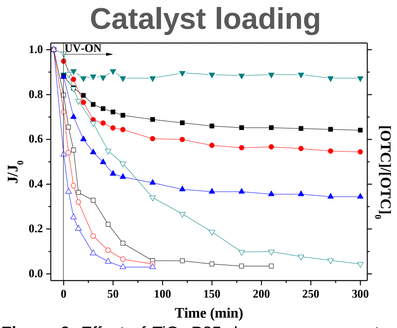


Figure 6. Effect of TiO_2-P25 dosage on permeate flux (closed symbols) and OTC removal (open symbols). [TiO_2-P25]: (▼) 0 – photolysis (■) 0.1, (●) 0.2 and (▲) 0.4 g L^{-1}. TMP = 0.1 MPa.

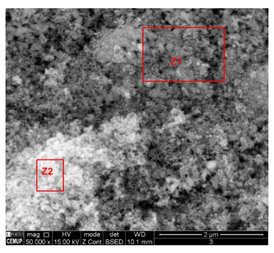
Table 2. OTC degradation times and permeate flux deterioration when using ultrapure water (UPW) and urban wastewater (UWW) as solution matrices.

Matrix	System	TMP (bar)	[TiO_2] (g L^{-1})	nº of dip coatings	OTC degradation time[a] (min)	J_5/J_0[b]
UPW	UVA/TiO_2-MF	1.0	0.2	-	60	0.54
	UVA/TiO_2-MF	1.5	0.2	-	60	0.50
	UVA/TiO_2-MF	2.0	0.2	-	60	0.46
	UVA-MF	1.0	-	-	240	0.87
	UVA/TiO_2-MF	1.0	0.1	-	90	0.64
	UVA/TiO_2-MF	1.0	0.2	-	60	0.54
	UVA/TiO_2-MF	1.0	0.4	-	30	0.34
	UVA/TiO_2-MF	1.0	-	3	180	0.92
	UVA/TiO_2-MF	1.0	-	6	150	0.99
	UVA/TiO_2-MF	1.0	-	9	150	0.95
	UVA/TiO_2-MF	1.0	-	9	150	0.98
	UVA/TiO_2-MF	1.0	-	9	150	0.99
UWW	UVA-MF	1.0	-	-	>300	0.10
	UVA/TiO_2-MF	1.0	0.1	-	180	0.26
	UVA/TiO_2-MF	1.0	0.2	-	90	0.22
	UVA/TiO_2-MF	1.0	0.4	-	60	0.18
	UVA/TiO_2-MF	1.0	-	9	>300	0.34

[a] Defined as the time required to reduce above 90% of the initial OTC concentration (in feed).
[b] Defined as the ratio between the permeate flux after 5 h of experiment (J_5) and the initial one (J_0).

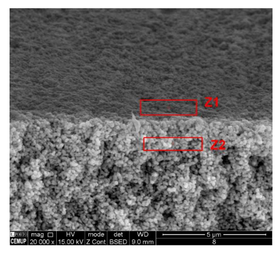
Effect of the amount of catalyst deposited on/in the membrane

Membrane surface



NEM reduced the membrane fouling through *in-situ* organic compounds oxidation - **permeate flux decline < 8%.**

Membrane cross-section



Membrane:
- TiO_2-P25 particles were successfully deposited on the membrane surface and within the pores.

TiO_2:
- Increase on the catalyst film thickness enhances the reaction rate until a point where the light is completely absorbed by the catalyst layer.

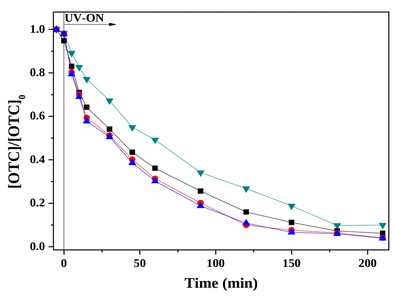


Figure 7. Effect of TiO_2-P25 amount deposited over the MF on OTC removal. Immobilized TiO_2-P25 amount: (▼) 0 – photolysis (■) 31 mg (3 immersions), (●) 39 mg (6 immersions) and (▲) 43 mg (9 immersions).

Effect of urban wastewater matrix

Table 3. Main physicochemical characteristics of the urban wastewater (UWW).

Parameter (units)	UWW
pH	7.2
Total dissolved carbon (mg L^{-1})	29.7
Dissolved inorganic carbon (mg L^{-1})	25.1
Chemical oxygen demand (mg O_2 L^{-1})	15.0
Total suspended solids (mg L^{-1})	1.3

UWW: Higher decline in the permeate flux when compared to UPW.

Cake layer: TiO_2-P25 particles + particulate organic and inorganic matter from the UWW.

Dual effect of the NEM-MF system when compared with the slurry system:
- Lower membrane fouling
- Lower permeate quality

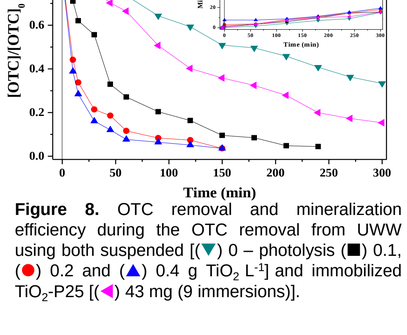


Figure 8. OTC removal and mineralization efficiency during the OTC removal from UWW using both suspended [(▼) 0 – photolysis (■) 0.1, (●) 0.2 and (▲) 0.4 g TiO_2 L^{-1}] and immobilized TiO_2-P25 [(◀) 43 mg (9 immersions)].

CONCLUSIONS

The permeate flux and OTC removal efficiency are significantly influenced by the catalyst loading. The use of NEM reduced the membrane fouling through the *in-situ* organic compounds oxidation. UWW matrix showed a negative effect on OTC removal and permeate flux when compared with UPW, mainly due to the presence of organic/inorganic matter. Despite the advantages of NEMs in terms of membrane performance, the OTC removal efficiency was higher when using TiO_2-P25 slurry conditions due to the higher photocatalyst surface area.

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