Pollutant photo-nf remediation of agro-water

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Abstract

We describe the deployment of a novel water purification technology, which was initially conceptualized in the context of a readily successful FP7 project (CLEAN WATER, Grant Agreement no 227017, 2009-2012) and is now in the progress of been upgraded and upscaled thanks to the grants awarded by a LIFE Environment and Resource Efficiency project (LIFE PureAgroH2O, LIFE17 ENV/GR/000387, 2018-2021). The technology is currently recognizable with the term "Photocatalytic Nanofiltration Reactor" (PNFR) and combines in a synergetic way the processes of nanofiltration (NF) and photocatalysis in a single-stage, targeting to the complete elimination of pesticides and other organic and inorganic (heavy metals) pollutants from the wastewater of the Fruits & Vegetables Industry (F&VI) and to the reuse of 15 m^3 of treated water on a daily basis.

Keywords: Photocatalysis; Nanofiltration; Titania; Chlorpyrifos degradation; Optical Fibers.

1. Introduction

In early 2012, a European Patent was published, describing an innovative water purification device, where the processes of nanofiltration and photocatalysis were for the first time occurring simultaneously and in a synergetic way, concluding to a significant enhancement of the clean water productivity and organic pollutants degradation efficiency (Falaras *et al.*, 2012). Upon Patent's granting, there was the possibility to disseminate the work done in a lab scale prototype, making the public sphere aware on the importance of the the novel technology and keeping the scientific community and industry up-to-date on the process intensification and transferability of the novel PNFR reactor. The first publication (Romanos *et al*., 2012) reported on the benefits gained by meeting with the challenge of effectively irradiating both photocatalytic surfaces (lumen and shell) of the NF monolith during nanofiltration. The results concluded that double-side active TiO_2-modified monoliths photodegraded almost double amount of a common pollutant like methyl orange (MO). Further enhancement (x2) of the MO abatement efficiency was achieved by increasing the photocatalytic surface inside the PNFR module *via* incorporation of alginate fiber stabilized TiO_2 nanoparticles (Papageorgiou *et al*., 2012). Since then, photocatalytic monoliths have been developed with various methodologies, encompassing the nanoparticles growth and layer-by-layer chemical vapour deposition CVD (Athanasekou *et al*., 2012) and the dip coating sol-gel techniques, while novel materials and photocatalysts, including graphene (Athanasekou *et al.*, 2014) and N-doped Titania (Moustakas *et al*., 2014), endowed the process with vis-light photocatalytic activity and mitigated the energy required to power up artificial light sources. Relevant to the latter was our effort to report the PNFR's results on an energy consumption basis (Romanos *et al*., 2013, Athanasekou *et al*., 2015) and to implement process design studies with the scope to reduce the pressure drop along the length of the photocatalytic monoliths (Athanasiou *et al*., 2016). In this paper, we present the optimized design of the PNFR, with a focal on the reactor's internals and the way of irradiation using side glowing fiber optics (AmbientFiber®, LEONI GmbH); we refer to the process selected for deploying the upscaled photocatalytic monoliths having as major indicators the cost and the amount of TiO_2 deposited per m^2 of monolith's surface; we make a brief description on the optimized conditions of the spinning process to derive the PVDF hollow fibers (HFs) with embedded TiO_2 nanoparticles and we highlight the high potential of the technology emanating from the readily high water permeability and chlorpyrifos abatement efficiency of the PNFR reactor with the novel materials.

2. Results-Conclusions

2.1. Results

For the photocatalytic membrane development, a 7-channeled, ZrO_2 NF monolith was subjected to the all-titania washcoating process, consisting on dipping the dried monolith into a TiO_2 slurry for 10 min, followed by excess slurry blown out, drying at 150°C and heating up to 450°C. The slurry was prepared by adding TiO_2 powder into a gel synthesised by heating a transparent TiO_2 colloidal solution at 80°C under stirring.

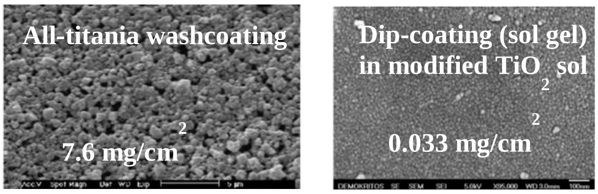

Figure 1. SEM images of the deposited photocatalyst. Comparison between the two coating approaches.

As can be noticed in Fig. 1, the all-titania washcoating concludes to higher amount of TiO_2 deposit as compared to the technique of dip-coating in modified TiO_2 sol, described in a previous work (Moustakas *et al*., 2014) and most importantly, it costs less (162 €/m^2 *vs* 1360 €/m^2). Furthermore the optimized dry/wet spinning conditions to derive the PVDF HFs with embedded TiO_2 nanoparticles (Fig. 2) in a spinneret setup were as following: dope solution PVDF/TiO_2/DMAC %wt. (15/3/82); bore fluid, H_2O %v/v (100); dope flow rate (1.8 ml/min); bore liquid flow rate (2 ml/min); air gap (25 cm); take-up velocity (2.2 m/min); dope solution temperature (25 °C).

Figure 2. PVDF hollow fibers with embedded TiO_2.

Fig. 3 presents the PNFR reactor's internal. Distinguishable are: (A) the photocatalytic monolith, (B) the glass-tube, which divides the reactor volume into several flow paths and bears the mounts (C) for accomodating the PVDF/TiO_2 hollow fibers and (D) the glass cell, which acts as sleeve for the UV sources. The fiber optics (AmbientFiber®) are passed through the channels (E) of each 7-channeled monolith and powered on their tips to irradiate the lumen surface.

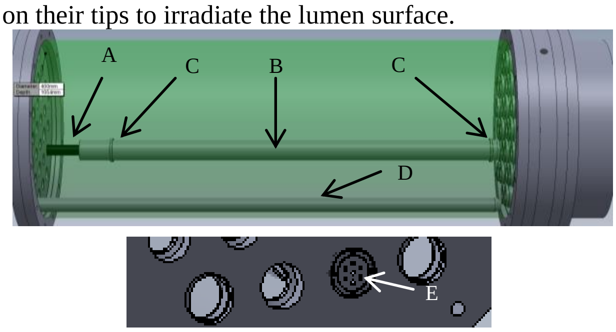

Figure 3. Design of the PNFR reactor internals.

The experimental campaign encompassed photocatalytic nanofiltration tests, conducted using a chlorpyrifos solution of 1 ppm as the feed stream and the results showed that the photocatalytic monolith exhibited higher water permeability than the unmodified one (10 L/m^2/h/bar *vs* 7.5 L/m^2/h/bar), due to phenomena of photoinduced hydrophilicity and a much higher chlorpyrifos rejection efficiency at the permeate side (99% *vs* 73%).

2.2. Conclusions

A novel PNFR reactor was designed and developed and its capacity demonstrated for the elimination of chlorpyrifos from the F&VI waste water effluent. Further work with other types of pesticides and mixtures of pesticides, in the presence of natural organic matter (NOM), is expected to validate the transferability of the proposed technology.

Acknowledgments

The research leading to this work was funded by the European Commission, Environment, LIFE17 ENV/GR/000387-PureAgroH2O Programme. P. Falaras also acknowledges funding from Prince Sultan Bin Abdulaziz International Prize for Water—Alternative Water Resources Prize 2014.

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