# Photocatalytic nanofiltration reactor for agricultural wastewater purification and reuse

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**Abstract.** The agrofood industry utilizes a large amount of pesticides for improving the agricultural production. Nevertheless, the presence of pesticide residues in agro-wastewater can cause adverse impact on water reservoirs and have harmful effects on human health. Conventional wastewater treatment methods are inefficient to confront pesticides, therefore intensive actions are required for their elimination. Herein, a novel pilot-scale photocatalytic nanofiltration reactor (PNFR) was designed and fabricated for the demands of agricultural wastewater purification and reuse, relying on a previous engineering study of a patented photocatalytic membrane reactor concept. The PNFR pilot unit consists of multi-channeled photocatalytic nanofiltration monoliths, prepared via a wash-coating technique. Additionally, the rector hosts a high number of polyvinylidene fluoride porous hollow fibers stabilized with $TiO_2$ photocatalyst nanoparticles. The active surface of the photocatalytically reactor effectively irradiated by an elegant illumination system is capable to produce up to 1.2 $m^3$/day clean water. The experimental evaluation was performed involving various concentrations (6-55 ppb) of the frequently detected Acetamiprid (ACT) and Thiabendazole (TBZ) pesticides in fruit-industry wastewater, in different feed flow rates and transmembrane pressures. In about 2 h, 95% of the wastewater was recovered, while the amount of ACT and TBZ was reduced by 25 and 42%, respectively.

**Keywords:** Pesticides; Titania; PNFR; Agricultural wastewater treatment

## 1. Introduction

Nowadays, the effective usage of pesticides has expanded the agro-production and harvesting; however, the existence of agroindustrial wastewater raised many concerns. Till now, most of the proposed wastewater purification technologies cannot respond efficiently, while raising drawbacks are limiting their usage [Oller et al. 2011]; ozonation is a cost-effective method in terms of required equipment and operation cost, the management of the final solid waste using activated carbon cannot compensate the efficient sorption of the contaminants, the filtration treatment technology involves periodic cleaning and regeneration steps of the membranes, the slurry bed reactors with heterogeneous photocatalysts demands separation steps of the catalyst from the treated effluent after the process. Nevertheless, the integration of heterogeneous photocatalysis with the aforementioned technologies could overpass any undesired effects through their synergetic interaction.

Membrane filtration and photocatalysis with $TiO_2$ are considered as the most efficient wastewater purification technologies and subsequently, their integration could raise significant assets. Indeed, such a combination was designed and patented, developing lab-scale photoreactor module [Falaras et al., 2012]. The main aspect of the so-called photocatalytic nanofiltration reactor (PNFR) is the ability to coat the membrane surfaces (internal and external) with any type of nanostructured photocatalyst, including modified titania nanoparticles [Athanasekou et al., 2015]. During the operation and the examination of the PNFR system, significant removal efficiencies were achieved against common azo-dye target pollutants, emphasizing the potential use of this innovative purification technology against a plethora of contaminated matrices with personal care products (PCPs), pharmaceuticals, pesticides, etc. Concerning the different pesticide substances, the neonicotinoid insecticide acetamiprid (ACT) and the azole fungicide thiabendazole (TBZ) are occasionally selected for crops in Greece and Spain,

suggesting them as them ideal candidates for the PNFR validation in real-life conditions.

This examination focuses on the design and fabrication of a photocatalytic nanofiltration reactor unit, in pilot-scale, for the purification and reuse of agroindustrial wastewater. The main innovations of PNFR module is both the accumulation of titania photocatalyst onto 12 multi-channeled nanofiltration ceramic membranes through a wash-coating method and the embedding of $TiO_2$ onto the matrix of 240 polyvinylidene fluoride (PVDF) hollow fibers. The intelligent assembly of the module generates enormous number of photocatalytic activated flow channels, resulting in 1.2 $m^3$/day clean water production capacity. The evaluation demonstrated 25% and ~ 41.5% removal of the recalcitrant ACT and TBZ, respectively, after two hours operation, while there was no obvious retentate condensation. These results imply that 95% water recovery is feasible under consecutive recycling and treatment steps of the effluent.

## 2. Materials and Methods

Based on design and operation simulations, the exact configuration of PNFR (in terms of composition, flow and pressure control, illumination system) was elucidated [Athanasiou et al., 2016]. In particular, 12 tubular ceramic monoliths, with dimensions 40 cm effective length, 2.5 cm external diameter and 7 internal cylindrical channels of 6 mm internal diameter, were selected. The photocatalytic activation of these monoliths was implemented using a simple and flexible wash-coating modification route, adapted to the requirements of the present project [Du et al., 2008].

Moreover, the PNFR blueprints comprise polymeric hollow fibers (HFs) surrounding the monoliths. Totally, 120 m of PVDF HFs, embedded with nanoparticulate titania ($TiO_2$), were fabricated using a dry-jet wet phase inversion process in a spinning set-up, as described previously [Chatzidaki et al., 2007].

The PNFR operation is based in a tangential flow mode, in which the wastewater is gradually transferred from a feed tank (volume from 70 to 105 L) to the reactor unit. Consequently, wastewater flows inside the reactor and subjected to the cleaning stages; photocatalysis in HFs during the upwards direction, photocatalysis/nanofiltration in the modified monoliths during the downward direction. Then, the filtrated wastewater is collected in the permeate outlet, while the retentate wastewater is transferred back to the feed tank and subjected again to the described process. By repeating the retentate utilization for several flow cycles in the PNFR, a total recovery of ~95% can be achieved. The number of cycles (or crosses) can be estimated by calculating the residence time of an infinitesimally thin slice of the water column of height Δh.

Finally, the frequently detected recalcitrant pesticides TBZ and ATC in fruit agroindustry wastewater were selected as target pollutants for the PNFR evaluation. The examined parameter were ranging from 6 to 55 ppb for the initial feed concentration, from 2.3 to 3.3 L/min for the flow rates and from 3 to 4.5 bar for the transmembrane pressure (TMP). The photocatalytic removal efficiencies were estimated using the equation:

$$\Delta C_0 \text{ (\%)} = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

where $C_0$ is the pollutant's initial concentration (after the adsorption-desorption equilibrium) and $C_t$ the pollutant's concertation during the respective time intervals. All the concentrations, expressed in mg/L, were determined with a UHPLC-QqLIT-MS/MS analyzer.

## 3. Results

### 3.1. Operation and photocatalytic performance of PNFR unit

As referred in section 2, ACT and TBZ were employed as model pollutants in order to investigate the photocatalytic performance of the pilot-scale PNFR unit. In Table 1, the total experimental conditions concerning the experimental expedition are illustrated. At this point it could be mentioned that the PNFR cleaning procedure between the experimental runs had a vital role to the overall efficiency of the unit.

**Table 1.** Experimental conditions of the PNFR unit during the synergistic photocatalytic filtration procedure

| Run | Pressure (bar) | Feed flow (L/min) | Pollutant (ppb) | UV illumination |
|-----|----------------|-------------------|-----------------|-----------------|
| 1 | 4.1 | 3.3 | ACT (50.0) | on |
| 2 | 4.4 | 3.3 | ACT (54.6) | on |
| 3 | 3.0 | 2.5 | ACT (54.8) | on |
| 4 | 3.1 | 2.4 | ACT (48.0) | off |
| 5 | 3.3 | 2.3 | TBZ (7.6) | on |
| 6 | 3.3 | 2.3 | TBZ (5.8) | off |

Furthermore, a crucial studied parameter was the water permeance during the synergistic photocatalytic filtration procedure.

The water permeance Pe (L/$m^2$·h·bar) is a significant property of membranes and can be calculated as:

$$Pe = \frac{F}{P*S} \quad (2)$$

where F (mL/min) is the water flux through the membrane, P (bar) is the TMP, and S ($m^2$) is the surface of the membrane, which, in our study, matches with the photocatalytic shell surface of the monoliths. The active photocatalytic surfaces of the HFs and monoliths (shell surface and lumen surface in the channels) were 0.45, 0.38, and 0.63 $m^2$, respectively.

The evolution with time of the normalized water permeance (compared to the initial value) is depicted for each run in Figure 1. The initial water permeance fluctuated between 2.2-15.6 L/$m^2$·h·bar, depending on the hydrodynamic conditions (feed flow and TMP). Here, a remarkable observation is the sharp decrease of membranes permeance (60% of the initial value) during

the runs under lower feed flow (2.4 L/min and 3 bar) and TMP conditions. This was noticed within the first 10 minutes of flooding of each experiment and after that the permeance was stabilized derived from steady state conditions. In addition, the lower flow rate of the feed inlet resulted in lower crossflow velocity advancing a possible membranes' fouling. In any case, cake layer formation or pore blocking were excluded.
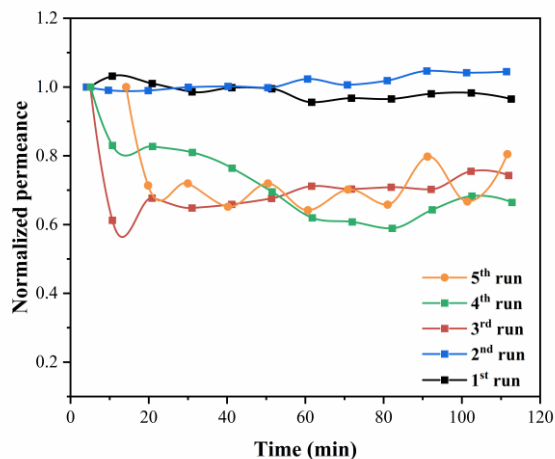


**Figure 1.** Temporal evolution of the normalized water permeance of membranes

Moreover, from Figure 1 it could be referred that the run under dark conditions (4th run) presented differences compared to those under UV illumination. Specifically, after 50 minutes on stream, the flux through membranes under illumination appeared to show an uprising tendency. This could be explicated by the presence of photo-induced hydrophilicity effects on the titania photocatalytic layers [Papageorgiou et al., 2012].

Lastly, the rejection percentage was calculated by the fraction of the total amount of the pollutant removed to the initial amount. The maximum rejections of ACT and TBZ reached up to 25 and 42%, respectively.

## 4. Conclusions

The outcomes of this study are focusing on the construction and validation of the novel hybrid photocatalytic nanofiltration reactor (PNFR), with a recycling capacity of agro-industrial effluent equal to1.2 $m^3$/day. The photocatalytic performance of the PNFR unit was examined using different experimental parameters for feed flow rate (2.3–3.3 L/min), TMP (3.0–4.5 bar) or contaminants' concentrations. The experimental campaigns point out that the frequently detected pesticides TBZ and ACT in fruit industry were reduced to 42 and 25%, respectively, in about 2 h operation. These promising results confirm the effective incorporation of photocatalysis and nanofiltration as an advanced oxidation technology (AOT) in the field of wastewater purification and reclamation. Moreover, the replicability, transferability and upscalability of the novel of PNFR technology constitute a strong motivation to validate PNFR in additional wastewater

matrices, reinforcing its exploitation and commercialization opportunities.

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