

Novel, sustainable filtering solution for bacteria and pesticides removal from water

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Water is, undeniably, one of the most valuable resources on earth. The universal right to access safe drinking water and enhanced public health are among the objectives of the 2030 Agenda for Sustainable Development (Goals 3 and 6). The incorrect management of urban, industrial, or agricultural wastewater affects the quality of millions of people's drinking water, which is dangerously contaminated or chemically polluted. Microbial contamination is especially relevant in the least developed countries or specific situations (*e.g.*, conflict zones) where water-borne diseases are more prevalent. On the other hand, the European Green Deal sets targets to reduce the use of and risks from chemical pesticides by 50% by 2030 in the Zero Pollution Action Plan since pesticides can contaminate surface waters and groundwater, aiming to protect ecosystems.

Decontamination (either microbial or chemical) strategies are, therefore, of utmost importance for the environment and human health and have a huge socioeconomic impact. Herein, we aim to develop innovative and effective bioactive filtering solutions that contribute to safer environments using sustainable technologies.

The use of versatile, biocompatible 2-oxazoline-based oligomers (OOXs) (Aguiar-Ricardo et al. 2015) with broad biocidal activity and fast killing rates is a suitable alternative for membrane functionalization (Correia et al. 2011). OOXs can be synthesized using supercritical carbon dioxide (scCO₂), using a greener approach when compared to the commonly used conventional synthesis (Table 1). For bacteria removal from water samples, a bioactive approach will be used, where antimicrobial OOXs will be immobilized at the surface of a membrane using plasma treatment and supercritical carbon dioxide, two environmentally friendly techniques (Correia et al. 2015).

Table 1. Comparison between OOXs conventional and scCO₂ synthetic route from a green chemistry point of view (Aguiar-Ricardo et al. 2015).

Parameter	Conventional synthesis	scCO ₂ synthesis	Green chemistry principles
Solvents involved	6	1	Safer solvents
Purification steps	3	0	Less hazardous synthesis
Time consumption (h)	72-120	44	Design for separation
Waste production	yes	no	Time efficiency
			Prevention

For pesticide removal, different commercial nanofiltration membranes will be initially screened to assess their ability to remove relevant pesticides (in accordance with the Watch List of substances to be monitored in EU surface waters and the European Environment Agency), aiming to select the most efficient ones. We have a vast experience in pollutants removal using different technologies including nanofiltration for water treatment (Couto et al. 2015; Dionísio et al. 2021). In this work, commercially available NFm will be screened for pesticides removal

using (i) initially water samples spiked with 5 target pesticides (e.g. Diflufenican, Imidacloprid; Table 2) and (ii) later real water samples contaminated with pesticides (e.g. fresh water near agricultural fields) where 200 pesticides will be monitored. Basically, the pesticides will be extracted from water using solid phase extraction (SPE). The pesticides analysis will be performed by GC-QqQ-MS employing multiple-reaction-monitoring tandem mass spectrometry (GC-QqQ-MS/MS) validated 200 pesticides and adapted for the 5 target pesticides. If needed, untargeted analysis of the water samples (not spiked) will be performed by GC-TOFMS.

Table 2. Target five pesticides to be studied. Three pesticides (all selected as targets: a fungicide, an herbicide and an insecticide; highlighted in grey) are referred in the Watch List substances under the Water Framework Directive and the other four are referred in an European Environment Agency report (two selected as targets: an insecticide and a herbicide; assessed between 2013 and 2021; highlighted in green). The table shows for candidate substances the group/class, CAS number and use, considering water as the environmental matrix. PPP: Plant Protection Product.

Substance/group name	CAS number	Use
Azoxystrobin	131860-33-8	Fungicide used as PPP and biocide
Diflufenican	83164-33-4	Herbicide used as PPP
Fipronil	120068-37-3	Insecticide
Imidacloprid	138261-41-3	Insecticide found in surface water
Metolachlor	51218-45-2	Herbicide found in surface water
Atrazine	1912-24-9	Herbicide found in groundwater
Bentazone	25057-89-0	Herbicide found in groundwater

Herein, we propose a bioactive and combined approach that departs from standard methods (which solely include physical barriers to microorganism passage), where the final coupled filter rapidly kills the bacteria upon contact and efficiently removes pesticides.

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