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

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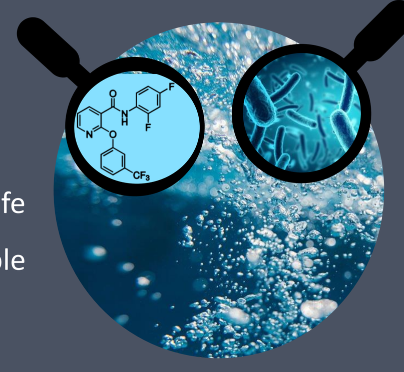
Introduction



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 – *Good health and well-being* and 6 –*Clean water and sanitation*).

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. We aim to develop innovative and effective bioactive filtering solutions that contribute to safer environments using sustainable technologies.

Methods

1. Biocompatible 2-oxazoline-based oligomers (OOXs) immobilization onto filtration membranes

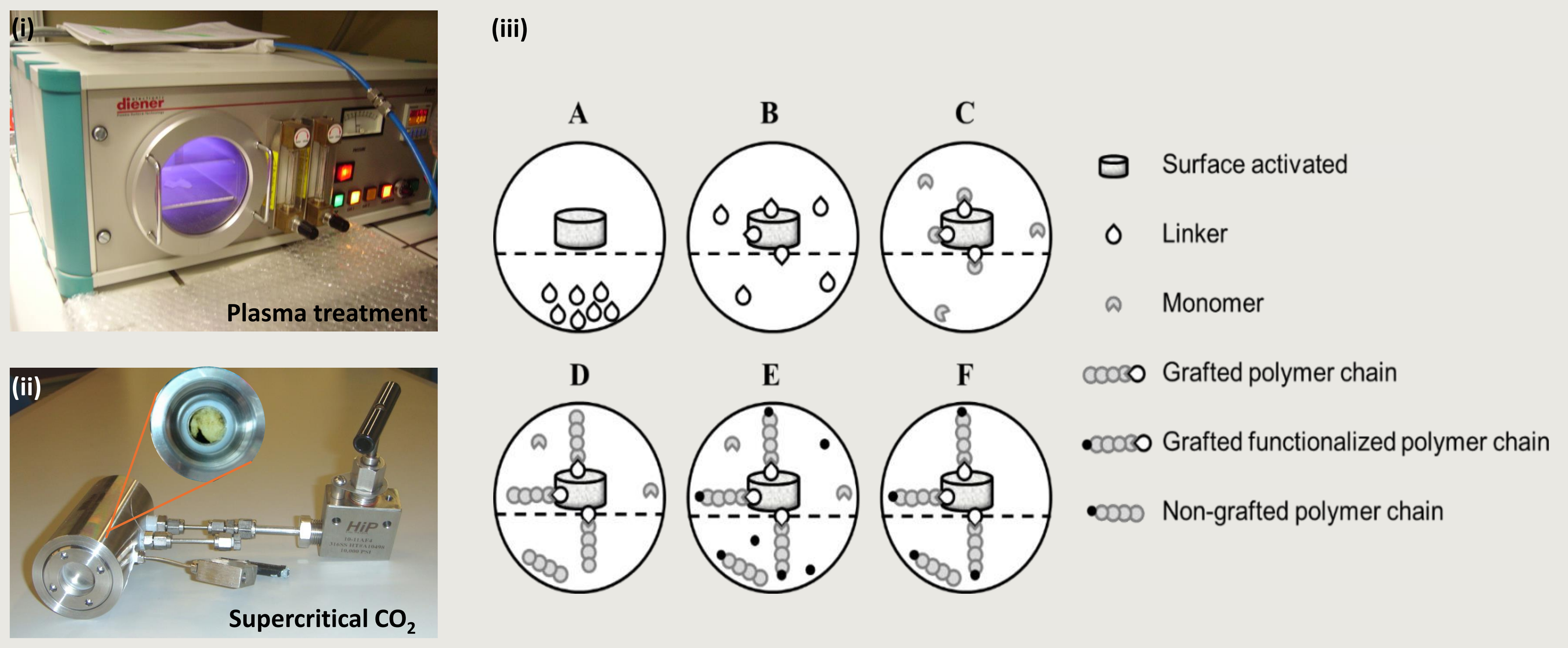


Figure 1. Schematic illustration of the grafting procedure comprising (*i*) plasma surface activation and (*ii*) oligomerization and functionalization in $scCO_2$. The (*iii*) high-pressure cell is divided in two parts with a porous structure in the middle. A) activated polymeric structure (in the upper part) is separated of the linker molecule, 2-isopropenyl-2-oxazoline (placed in the lower part). B) $scCO_2$ is added to the high pressure cell, an homogeneous distribution of the linker molecule is attained in the reactor and the linker reacts with the activated surface; C) unreacted linker molecules are vented from the cell, 2-substituted-2-oxazoline monomer and initiator are added to the reactor and oligomerization takes place; D) oligomerization ends, and free oligomer is precipitated at the bottom of the reactor; E) functionalization molecule, *N,N*-dimethyldodecylamine, is added to the reactor and end-caps both grafted and free oligomer; F) unreacted monomer and functionalization molecule are washed out from the reactor and purified antimicrobial OOXs-grafted scaffold and antimicrobial OOXs are obtained.

2. Pesticides removal from water samples by nanofiltration membranes - targeted analysis

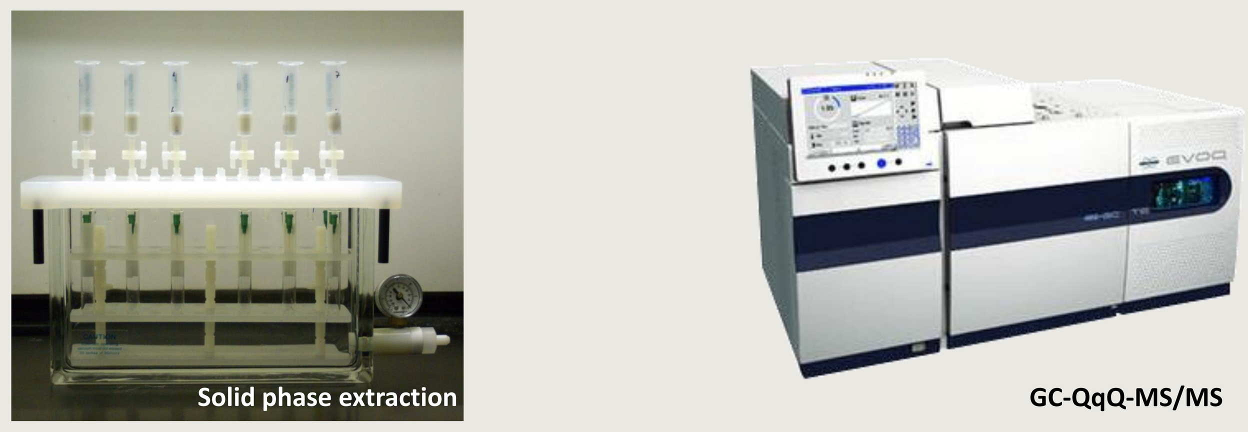


Table 1. Selection of the target five pesticides to be studied. Three pesticides (all selected as targets: a fungicide, an herbicide and an insecticide; highlighted in green) are referred in the Watch List substances under the Water Framework Directive and the other four are referred in a European Environment Agency report (two selected as targets: an insecticide and an herbicide; assessed between 2013 and 2021; highlighted in blue). 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

Preliminary Results

OOXs surface immobilization using sustainable technologies

Preliminary data shows that OOXs can be covalently linked to a polymeric material (chitosan, CHT) using a *grafting from* approach (adapted from *Biomacromolecules, 2015*).

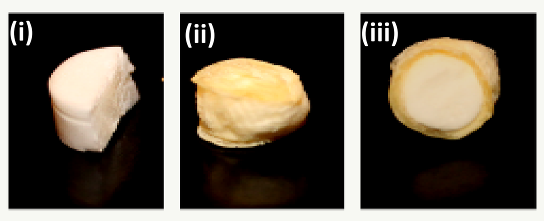


Figure 2. Photographs of (i) a polymeric (chitosan, CHT) native scaffold (white) and (ii) OOXs-grafted scaffold (yellow) showing the OOXs immobilization at the top and lateral side of the scaffold and (iii) not in the interior of the scaffold after cross-section.

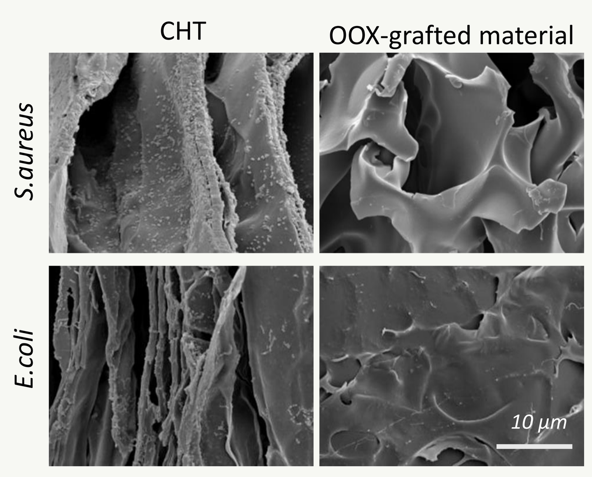


Figure 3. SEM micrographs of CHT polymeric material and OOXs-grafted material after 18 h of direct contact with *S. aureus* and *E. coli* cells (models gram-positive and gram-negative bacteria, respectively).

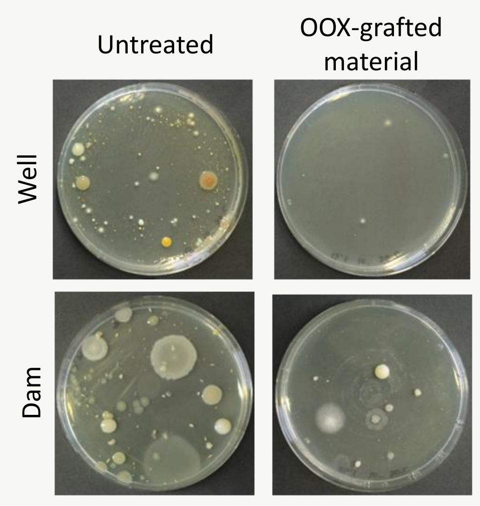


Figure 4. Reduction in microorganism viability for two different environmental water samples (a well, an underground source, and another one from a dam, surface water) after direct contact with OOX-grafted material (time of contact = 5 min) and incubation 36 °C (ISO 6222:1999). Images show the initial variety of culturable microorganisms present in each water sample (plated volume: 400 µL).

Method development and chromatographic identification of 200 pesticides

Preliminary data shows that a library of 200 pesticides can be analysed by GC-MS technique.

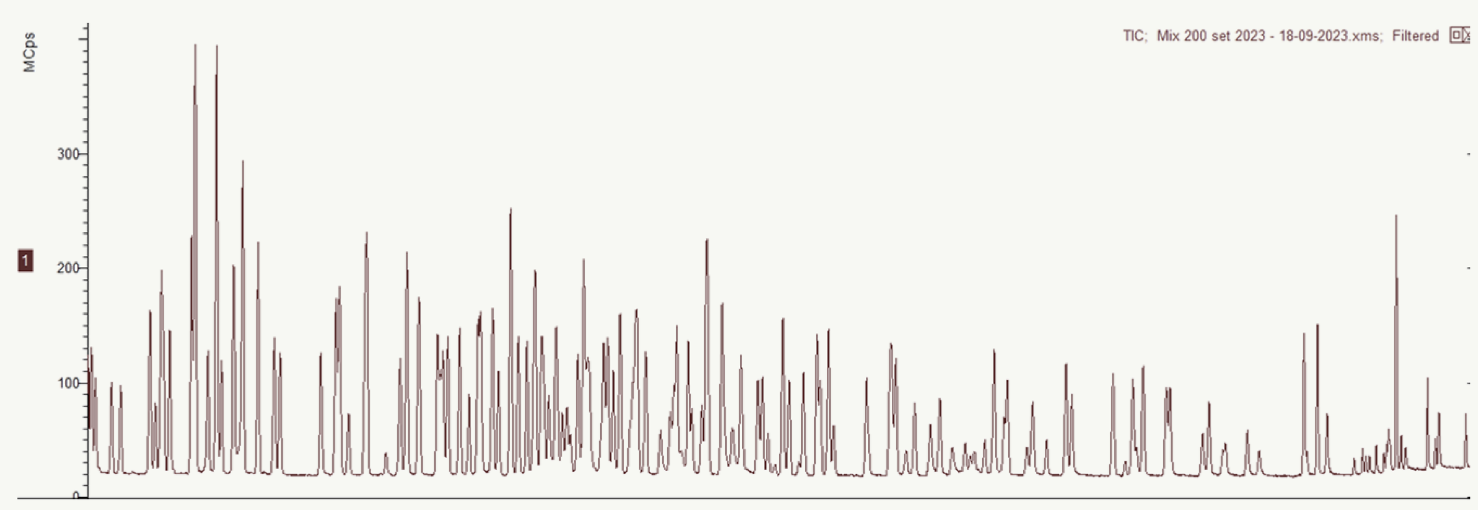


Figure 5. Representative chromatogram of GC-MS analysis in full scan mode of 200 pesticides using SCION GC-TQMS with 451 GC (Bruker).

Discussion

Antimicrobial filtration membrane

OOXs are biocompatible and versatile oligomers (properties and bacterial killing efficacies can be tunned).

OOXs can be covalently grafted to a surface using green technologies, rendering stable materials.

OOXs-grafted materials have antimicrobial and antibiofouling properties.

Nanofiltration membrane

Nanofiltration membranes can be used for pesticides removal.

Pesticides can be extracted from water samples using solid phase extraction and analysed by GC-QqQ-MS employing multiple-reaction-monitoring tandem mass spectrometry (GC-QqQ-MS/MS) validated for 200 pesticides and adapted for the 5 target pesticides.

Prototype validation

A prototype (containing both coupled filters) can be tested and validated for water decontamination applications.

Conclusion

Novel filtering solution: a **disruptive bioactive combined approach** that departs from standard methods (which solely include physical barriers to microorganism passage), where the **final coupled filter rapidly kills bacteria upon contact** and **efficiently removes pesticides**.

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