# D4.2: Benchmarking and Analysis of current aspects, requirements, specifications & conceptual architecture

## Task 4.2: Technical Specifications

## WP4: Demonstration of innovative technologies to achieve removal and remediation of chemical pollutants

Authors: Enrique del Río, David Lucio, David González, Rodrigo Sedano, ITCL Technology Centre

Date: 31st January 2024

Funded by
the European Union

| | |
|---|---|
| GRANT AGREEMENT NUMBER | 101112824 |
| ACRONYM/ FULL TITLE | iMERMAID/ Innovative solutions for Mediterranean Ecosystem Remediation via Monitoring and decontamination from Chemical Pollution |
| START DATE | 01 June 2023 |
| END DATE | 31 May 2026 |
| PROJECT URL | www.imermaid.eu |
| DELIVERABLE TITLE | 'Benchmarking and Analysis of current aspects, requirements, specifications & conceptual architecture' |
| WORK PACKAGE | 4 |
| CONTRACTUAL DATE OF DELIVERY | 31/01/2024 |
| ACTUAL DATE OF DELIVERY | M8 (January 2024) |
| NATURE | Report |
| DISSEMINATION LEVEL | Public |
| LEAD BENEFICIARY | ITCL Technology Centre |
| RESPONSIBLE AUTHOR | Enrique del Río, David Lucio, David González, ITCL |
| CONTRIBUTORS | EDEN, WF, IRIS, UA, CMMI, NEIG, UNIFI, SOCAMEX, ZEN, SMAT, ESDAK, AIG, CUB, OP, BIOS, NTUU KPI |
| ABSTRACT | The document makes a comprehensive state of the art for the incumbent remediation technologies. It also describes the technical specifications and requirements for both the monitoring sensors and the remediation technologies developed in the iMERMAID project. The data architecture and the related tools are also described as well as the addressed contaminants and the project outcomes and reusable work. |

Disclaimer

Copyright message

# Document Revision Log

| Version | Description of changes | Author | Role in the project |
|---|---|---|---|
| 0.1 | Draft | Enrique del Río, David González (ITCL) | Project Coordination Team |
| 0.2 | Project Benchmarking and Contaminants sections | Enrique del Río, David Lucio (ITCL) | Project Coordination Team |
| 0.3 | Technological platforms and tools section | Enrique del Río, David González (ITCL) | Project Coordination Team |
| 0.4 | Technological platforms and tools section | Vladan Gligorijevic (CUB) | Beneficiary |
| 0.5 | Technological platforms and tools section | Nenad Gligoric, Uros Dasic, Marija Vasic, Ivan Djurkov (ZEN) | Beneficiary |
| 0.6 | AKVO Technology | Abhilash Venkateshaiah, Wei Zhao (EDEN) | Beneficiary |
| 0.7 | 4D Scavenger Technology | Saara Tuhkanen (Weeefiner) | Beneficiary |
| 0.8 | PDP Technology | Giulia Molinari, Simone Barletta (IRIS) | Beneficiary |
| 0.9 | RROM Technology | Ahmed Hannachi, Sabrine Chamam (ENIG) | Beneficiary |
| 0.10 | Use Case 1 | Esther Gómez, Yolanda Ballesteros (SOCAMEX) | Beneficiary |
| 0.11 | Use Case 2 | Imen Ellefi (OPALIA) | Beneficiary |
| 0.12 | Use Case 3 | Camilla Burdizzo (SMAT) | Beneficiary |
| 0.13 | Use Case 4 | Louis Hadjioannou, Nikolas Flourentzou, Eleni Christoforou (CMMI) | Beneficiary |
| 0.14 | Use Case 5 | Kalliopi Bormpoudaki (ESDAK) | Beneficiary |
| 0.15 | Electrochemical Sensor | Maxime Pontié (UA) | Beneficiary |
| 0.16 | Oil Sense Sensor | Boris Brkic, Djordje Vujic (BIOS) | Beneficiary |
| 0.17 | Metalsens Sensor | Ilaria Palchetti (UNIFI) | Beneficiary |
| 0.18 | Monitorization with satellite data | Nataliia Kussul (NTUU KPI) | Beneficiary |
| 0.19 | Final first draft | Enrique del Río, David Lucio, David González, Rodrigo Sedano | Project Coordination Team |

| | | | |
|---|---|---|---|
| 0.20 | First review | Louis Hadjioannou, Nikolas Flourentzou, Eleni Christoforou, Myrsini Lymperaki (CMMI) | Beneficiary |
| 0.21 | Second review | Vladimir Urošević (ZEN) | Beneficiary |
| 0.22 | Third review | Marcela Permann-Doubkova, Eric Armengaud (AIG) | Beneficiary |
| 0.23 | Comments from reviewers merged in the Deliverable | David González, Rodrigo Sedano (ITCL) | Project Coordination Team |
| 1.0 | Final review and formatting | Rodrigo Sedano (ITCL) | Project Coordinator |

# Executive Summary

This document, entitled '*Benchmarking and analysis of current aspect, requirements, specifications & conceptual architecture*', corresponding to *Task 4.2 Technical specifications* of the iMERMAID project, is the reference for the future development of the project. Additional to the benchmarking on the water treatment of the incumbent technologies, an introduction to the iMERMAID project is included in *Section 1.0*, where an overview of the objectives and strategies that motivate the project tasks is explained. Moreover, a summary of related projects is provided with the aim of presenting the alignment with the global strategy of the EU regarding the improvement of the water quality. Furthermore, it is important to mention the participation of iMERMAID in the Lighthouse BlueMissionMed.

*Section 2.0* is dedicated to the state of the art regarding the water treatment technologies focused on those procedures closest to the technologies that will be developed during the project. Following is a summary of the different remediation techniques used in the wastewater treatment. A comprehensive review of the literature regarding the technologies developed in iMERMAID is provided focusing on environmentally friendly technologies in the sense that no hazardous chemical agents are used in the remediation procedure, and no additional pollutants or dangerous by-products are generated in the process. Regarding photocatalysis, the section covers the different catalysts, the photoreactors and the factors influencing the degradation effectiveness. The plasma technology section covers the structures and features of different reactors. Finally, a subsection dedicated to filtration technologies describes the different types of filtration strategies existing in the literature. In all of them, a section dedicated to the treatment of contaminants of emerging concern with the different technologies is included.

*Section 3.0* is dedicated to the technical specifications of the sensors and, in the same way, *section 4.0* is concentrated on the technical specifications of the water treatment technologies. The seven subsections, three sensors and four treatment technologies, are divided into four items: i) description of the sensor or technology, ii) contaminants to be monitored or treated, iii) the technical specifications and iv) the incorporation in the project. *Section 5.0* presents the description of different Use Cases. Furthermore, the uses of each sensor and/or technology, in each Use Case, is specified.

*Section 6.0* is dedicated to the contaminants present in the water, as the project focuses on the priorities defined by the European water directives, such as the 'Water Framework Directive' and the 'Marine Strategy Framework Directive'. A subsection is dedicated to the contaminants of emerging concern. Finally, another subsection is focused on the contaminants that will be the objective of the project. Those contaminants have been selected taking into account the water directives, particular characteristics of each Use Case, and the limitations derived from the TRL of the technologies.

In *section 7.0*, a description of the different alternative platforms and tools to enhance the value of the project results is analysed, approaching it from the point of view of the data lifecycle as a key unifying element of the different elements, sources of information and needs of the project. The data generated within the project will be analysed, shared, and stored following the architecture specifically designed for the project.

Subsequently, *section 8.0* presents an analysis of the upstream technologies. Considering the natural cycle of the water and the contaminants in the water bodies, the lifecycle of the contaminants in the different water bodies is described. The reusable work generated during the project is also reported from the different technologies to the data lifecycle architecture.

Lastly, in the final section of conclusions, the main findings cited in this document and considerations to be taken into account are mentioned in order to use this document as a knowledge basis for the development of the following tasks of the project.

## Table of Contents

## List of Figures

## List of Tables

# Acronyms

| | |
|---|---|
| 4DS | 4D Scavenger |
| AAS | Absorption Atomic Spectroscopy |
| AC | Alternating Current |
| AOP | Advanced Oxidation Processes |
| API | Application Programming Interface |
| BWRO | Brackish Water Reverse Osmosis |
| CAPEX | Capital Expenditures |
| CC | Closed-Circuit |
| CCI | Climate Change Initiative |
| CMEMS | Copernicus Marine Environment Monitoring Service |
| COD | Chemical Oxygen Demand |
| CoEC | Contaminant of Emerging Concern |
| CPE | Carbon Paste Electrode |
| DAF | Dissolved Air Flotation |
| DB | Database |
| DBD | Dielectric Barrier Discharge |
| DC | Direct Current |
| DLT | Distributed Ledger Technology |
| DNA | Deoxyribonucleic acid |
| DWD | Drinking Water Directive |
| ECS | Electrochemical Sensor |
| ENTS | Enhanced Natural Treatment Solutions |
| ESA | European Space Agency |
| ESI | Electrospry Ionization |
| EU | European Union |
| FO | Forward Osmosis |
| GC | Gas Chromatography |
| GCE | Glassy Carbon Electrode |
| GES | Good Environmental Status |
| GO | Graphene Oxide |
| HM | Heavy Metals |
| HPLC | High Performance Liquid Chromatography |
| HUME | Homemade Ultramicroelectrode |
| IBP | Ibuprofen |
| ICP | Inductively Coupled Plasma |
| IoT | Internet of Things |
| Irg | Irgarol |
| LC | Liquid Chromatography |
| LF | Low Frequency |
| LoD | Limit of Detection |
| LTP | Leachate Treatment Plant |
| MAEX | Maintenance Expenditures |

| | |
|---|---|
| MB | Microbubbles |
| MBR | Membrane Bioreactor |
| MIMS | Membrane Inlet Mass Spectrometry |
| MODBUS | Modular Digital Bus |
| MODIS | Moderate Resolution Imaging Spetroradiometer |
| MQTT | Message Queuing Telemetry Transport |
| MS | Mass Spectrometry |
| MSFD | Marine Strategy Framework Directive |
| MWF | Microwave Frequency |
| MWCO | Molecular Weight Cut-Off |
| NF | Nanofiltration |
| NMC | N-Methyl Carbamate |
| NSAID | Non-Steroidal Anti-Inflammatory Drug |
| NTP | Non-Thermal Plasma |
| OLCI | Ocean and Land Colour Instrument |
| OP | Organophosphates |
| OPEX | Operational Expenditures |
| PB | Plasma Bubbles |
| PDP | Pulse Discharge Plasma |
| PFAS | Polyfluoroalkyl Substances |
| PFOS | Perfluorooctane Sulfonate |
| PLC | Programmable Logic Controller |
| PPB | Parts Per Billion |
| PPT | Pulse Plasma Technology |
| PS | Persulfate |
| PV | Photovoltaic |
| RF | Radiofrequency |
| RO | Reverse Osmosis |
| RSD | Relative Standard Deviation |
| RSG | Rotary Spark Gap |
| RTD | Residence Time Distribution |
| SAR | Synthethic Aperture Radar |
| SLSTR | Sea and Land Surface Temperature Radiometer |
| SPE | Screen Printed Electrode |
| SQL | Structured Query Language |
| SWRO | Seawater Reverse Osmosis |
| TOC | Total Organic Carbon |
| TOF | Time of Fly |
| TPD | Temperature-Programmed Desorption |
| TRL | Technology Readiness Level |
| TTP | Travancore Titanium Products |
| UF | Ultrafiltration |
| UV | Ultraviolet |
| UWWTD | Urban Wastewater Treatment Directive |

| | |
|---|---|
| VOC | Volatile Organic Compound |
| WFD | Water Framework Directive |
| WP | Work Package |
| WWTP | Wastewater Treatment Plant |

# 1.0 Project Benchmarking

## 1.1 Introduction to iMERMAID

iMERMAID project is focused on safeguarding the health of the Mediterranean Sea basin through monitoring and elimination of contaminants of emerging concern (CoEC), but also by creating a social conscience and boosting policies oriented to minimize the use of substances of concern and avoiding their disposal into the environment. As a research project, it will combine several innovative sensors and remediation technologies in the different Use Cases, with the aim of providing new tools for monitoring and reduction of contaminants in the Mediterranean Sea basin.

A total of five Use Cases will be studied, four of which will be implemented in wastewater treatments of different natures and all of them will be equipped with a new treatment technology along with an innovative contaminants' sensors. The fifth Use Case is a buoy containing several sensors related to the monitoring of contaminants in the Mediterranean Sea.

## 1.2 Related projects

iMERMAID project is the product of the experience of previous projects and explorations. Furthermore, a new philosophy is being applied to face the challenge of chemical pollution from a holistic approach. Among the 26 partners involved, all of them have proven previous experience with active participation in related projects. Hence previous projects will be a perfect starting point for iMERMAID and their products will be used and refined within iMERMAID.

For instance, the methods developed in **AQUAlity** for the removal of contaminants of emerging concern (CoEC) present in wastewater will be further matured in iMERMAID.

Within the project **Nanosenso**, the first portable kit dedicated to pesticides monitoring in the environment was developed to TRL4. This technology will be used in iMERMAID project and extended to other organic micropollutants, isolated and/or in mixtures, and further developed to an electrochemical sensor box adapted for on-site experiments, complementary to remediation operations.

**WATERAGRI** brings innovative and sustainable Water Retention solutions technologies to European farmers, including farm-constructed wetlands, remote sensing pipeline, irrigation and agrometeorological monitoring, biochar for water retention, etc. Eden Microfluidics introduced its ultra-compact and energy-saving technology for water treatment in the agricultural environment and for the removal of agricultural-specific micro-pollutants. This technology will also be implemented in iMERMAID.

**SEArcularMINE** aimed at recovering energy and critical raw materials such as magnesium, lithium, rubidium, and other trace elements, from waste brines in Mediterranean basin saltworks. The project will target very low energy consumption, while using novel technology to generate electricity from salinity gradients of seawater. The circular approach maximizes resource efficiency and economic viability.

iMERMAID will build on one of the advanced technologies developed in the **H2020 project Ô**, further developing the HiNaPEF plasma technology for water treatment and exploiting the User Collaborative Platform as a starting point to develop the Solutions' Showcase from Task 5.5.

[9513/31/2021 - Sustainable manufactured 4D Scavengers for water intensive industry (1/2022- 6/2023)] is an innovation project co-funded by Business Finland, focusing on using innovative waste materials as "building blocks" for 4D Scavengers. It has relevance to iMERMAID as it also includes scale-up of the 4D Scavenger technology, however, the context is totally different.

The EU-funded **aqua3S** project aimed to standardise existing sensor technologies complemented by state-of-the-art detection mechanisms for drinking water networks, with the combination of complex sensors with videos from unmanned aerial vehicles, satellite images and social media observations from citizens reporting low-quality water. This helped to create social awareness and promote interactive knowledge transfer. The proposed technical solution is an integrated platform designed to offer a standardised detection system. Similar philosophy will be followed by iMERMAID for the monitoring of contaminants in the Mediterranean Sea basin.

The **NextGen** initiative evaluated champion innovative and transformational circular economy solutions and systems that challenge embedded thinking and practices around resources used in the water sector. The project produced new understandings to underpin the exploitation of techniques and technologies that enhance our ability to recover, refine, reuse, repurpose, capture value from, and extend the usage life of an ever-increasing range of resources and products, thereby projecting the European water and allied sectors as global circular economy pioneers. The NextGen developed approaches, tools and partnerships, could be transferred and upscaled in the iMERMAID project.

The EU **MULTISOURCE** project will be focused on enhanced natural treatment solutions (ENTS) of urban waters by natural procedures to improve water reusability and reduction of contaminants, and to minimize residual untreated water.

In the **SMURBS/ERA-PLANET** project, products were created for monitoring and assessing the quality of water bodies for the city of Kyiv with Sentinel-3 data. In the iMERMAID project, they will be adapted to maritime polluted waters and tested in different pilot environments.

The EU **ENERGYWATER** project analysed energy efficiency in industrial water processes, developing insight into the project and the water life cycle within the industry. It also generated a benchmarking methodology to classify process that may be reused for project purposes.

Furthermore, the **Mediterranean basin Lighthouse,** built on existing governance structures, initiatives and networks, public and/or private organisations and networks able to align priorities, policies and initiatives of the 22 Countries of the basin, was established to maximize the deployment of the Mission objectives in the area.

**BlueMissionMed** supports the Mission Mediterranean Lighthouse project through a series of Coordination and Support Actions, in combination with the other Lighthouse initiatives, like the Innovation Actions. In this way, the main goals and objectives of the project are:

- To act as a hub to mobilise all local actors and help them in setting up their plans and initiatives in line with the targets of the lighthouse.
- To enhance synergies among different national, regional, and local initiatives/projects.
- To mobilise key stakeholders to align resources.
- To work hand-to-hand with the Mission secretariat to align priorities, activities and awards.
- To support the European Commission to mobilise the uptake of the Mission Charter.

Together with iMERMAID, the projects RHE-MEDiation, SeaClear2.0 and REMEDIES are also some of the stakeholders of the BlueMissionMed. As part of our goals and objectives, the iMERMAID project will be actively participating in the BlueMissionMed project, aiming to create a greater impact and reach a larger community.

**RHE-MEDiation** EU project, also funded under the same call as the iMERMAID project, will support the work of policymakers by providing advanced remediation solutions for the Mediterranean Sea basin, as well as modalities and tools for monitoring and control, enabling parallel citizen empowerment in the action.

For this purpose, RHE-MEDiation sets itself three strategic goals:

- To prevent chemical pollution from reaching the Mediterranean Sea and address environmental challenges with innovative solutions along the entire discharge networks, spanning from urban, industrial, and rural water flow to the sea.
- To minimize and control pollution, by enabling prompt reactions in the Mediterranean hot spots, promoting data sharing with stakeholders at demo-sites.
- To eliminate and remediate existing polluted hot spots by working at the source of major pollution to enable a return to a 'good environmental status' in the long term through improved dilution conditions.

The EU **SeaClear2.0** project supports the achievement of the EU Mission ‘Restore our Oceans and Waters’ by preventing and eliminating seabed and floating marine pollution. **SeaClear2.0** aims to prevent and reduce marine litter pollution, particularly plastics and microplastics, in the Mediterranean through (i) Community activation, (ii) Scaling up and demonstrating an innovative solution with teams of autonomous, intelligent robots for effective monitoring and collection of marine seafloor and surface litter, (iii) Providing solutions for valorisation of the collected litter, (iv) Adding novel dimensions in policy making, and (v) Accelerating the uptake of our solution by demonstrating its scalability and replicability to the Mediterranean basin and beyond.

**REMEDIES** EU project aims to restore our seas and rivers through deploying (micro)plastic litter valorisation and prevention pathways. Project activities will revolve around monitoring and detection, collection and valorisation, and prevention and reuse of plastic waste. The REMEDIES movement is striving to co-create a plastic-conscious society by applying cutting-edge technology and circularity approaches, underpinned by a holistic citizen engagement framework.

## 2.0 Water remediation technologies

The European Union has strict standards and regulations for water quality control with the aim of protecting human health and the environment. The **Water Framework Directive** (WFD)[1] is one of the key legislations in the EU that established a framework for sustainable water management. Various contaminants in water are monitored and controlled within this framework. Some of the main contaminants monitored by the European Union include microbiological parameters such as *Escherichia coli* (*E.coli)* or Intestinal enterococci (indicatives of faecal contamination), chemical parameters (nitrates and nitrites mainly derived from agriculture and livestock and heavy metals), polycyclic aromatic hydrocarbons (PAHs) from incomplete combustion of organic materials, priority hazardous substances (persistent organic compounds, pesticides, and pharmaceuticals), water priority substances that may pose a significant risk to the aquatic environment and new hazardous substances and emerging priority pollutants.

On the other hand, the **Marine Strategy Framework Directive** (MSFD)[2] is aimed to maintain clean, healthy, productive and resilient marine ecosystems while securing a more sustainable use of marine resources. The Directive requires Member States to develop national marine strategies in order to achieve, or maintain where it exists, good environmental status.

The Directive defines Good Environmental Status (GES) as 'The environmental status of marine waters where these provide ecologically diverse and dynamic oceans and seas which are clean, healthy and productive'. In Annex I the Directive sets out eleven qualitative descriptors which describe what the environment will look like when GES has been achieved. Descriptors 8 and 9 are most related with the iMERMAID project:

- Descriptor 8: Concentration of contaminants gives no pollution effects.
- Descriptor 9: Contaminants in seafood are at safe levels.

Both directives WFD and MSFD are revised every six years.

Other two Directives related with water quality in the EU are also worth to consider: the **Drinking Water Directive** (DWD)[3], which is the EU's main law on drinking water concerning its accessibility to the population, and the quality of water intended for human consumption to protect human health. Finally,

---

[1] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal Legislation 327, 22/12/2000, P. 0001 – 0073.

[2] Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy. Official Journal Legislation 164, 25/6/2008, p. 19 – 40.

[3] Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. Official Journal Legislation 435, 23/12/2020, p. 1 – 62.

the **Urban WasteWater Treatment Directive** (UWWTD)[4] concerns the collection, treatment and discharge of urban wastewater and the treatment and discharge of wastewater from certain industrial sectors.

As it can be observed, EU water legislation is extensive and regularly updated to address new challenges and scientific discoveries. However, each EU member state may have additional specific regulations at the national level to address local conditions and specific concerns.

There are several water decontamination methods[5], designed to address different types of contaminants and specific water conditions. The most common methods are briefly described below:

Filtration

- Mechanical Filtration uses porous materials to trap solid particles and organisms in the water.
- Membrane Filtration uses semipermeable membranes to remove small particles and microorganisms.

Disinfection

- Chlorination: Chlorine is added to water to kill bacteria, viruses, and other microorganisms.
- Ultraviolet (UV) Disinfection: UV radiation is used to deactivate microorganisms present in the water.
- Ozone: Ozone is introduced to disinfect the water and eliminate contaminants.

Precipitation and Coagulation

- Coagulation: Chemicals (coagulants) are added to group particles to form flocs.
- Flocculation: Formed flocs are grouped to facilitate their removal.

Adsorption

- Water passes through activated carbon to adsorb impurities and organic contaminants.

Ion Exchange

- Ion Exchange resins remove unwanted ions by exchanging them for more benign ions.

Distillation (simple or multiple)

- Water is evaporated, and vapor is condensed to obtain purified water, leaving contaminants behind.

Reverse Osmosis

---

[4] Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. Official Journal Legislation 135, 30/5/1991, p. 40 – 52.

[5] Hasan, H. A., & Muhammad, M. H. (2020). A review of biological drinking water treatment technologies for contaminants removal from polluted water resources. Journal of Water Process Engineering, 33, 101035.

- Water is forced through semipermeable membranes to remove salts and other contaminants.

Bioremediation

- Treatment Ponds: Use microorganisms to break down organic contaminants.

Phytoremediation

- Some aquatic plants have the ability to absorb and accumulate water contaminants.

Ozone Treatment

- Ozone is used to break down persistent organic contaminants in advanced oxidation.

The combination of these methods might be of high importance in the treatment of different types of contaminants and to ensure the quality of drinking water as well as to achieve the necessary levels of remediation of different wastewater effluents before its discharge into the environment. The choice of method will depend on several factors, such as the nature and concentration of contaminants present in the water.

## 2.1 Technology: Photocatalysis

Photocatalysis is a process in which a catalytic reaction occurs as a result of radiation absorption by a catalyst. When this photoreaction takes place at the catalyst surface, at the solid (catalyst)–liquid or solid (catalyst)–gas interface, the process is known as heterogeneous photocatalysis[6], which leads to the degradation and even mineralisation of organic compounds, using a light-sensitive semiconductor as a catalyst. The process develops according to the following reaction:

$$\text{Organic matter} + O_2 \xrightarrow{\text{Semiconductor}} CO_2 + H_2O + \text{mineral acids}$$

The semiconductors used as photocatalysts are solids in which the atoms constitute an infinite three-dimensional lattice, whose electronic configuration is expressed as bands. This is because of the bonds between the atoms that form the solid lattice. In these atoms the atomic orbital overlap goes beyond the first atoms and extends throughout the lattice, resulting in a configuration of delocalised states in which the difference between two electronic states is practically null, and bands of allowed electronic states form. Between the bands there are energy ranges containing forbidden electronic states, each of which corresponds to a forbidden energy band or band gap. The bands involved in photocatalysis are the valence band with the lowest energy and greatest electron density, and the conduction band with the highest

---

[6] Peiró, A.M. Nuevas aportaciones al desarrollo de metodologías en química verde: Eliminación fotocatalítica de contaminantes fenólicos y preparación de fotocatalizadores mediante procesos químicos suaves. Barcelona: Universitat Autónoma de Barcelona, 2003. Doctoral dissertation.

energy and empty levels. The difference in energy between both is known as the bandgap energy or potential.

The photocatalytic process begins with the light-induced generation of electron–hole pairs in the semiconductor particles[7]. When a photon with an energy, ‘hv’, equal to or larger than its bandgap energy, impinges on the semiconductor, an electron (e-) is promoted from the valence band to the conduction band, leaving a hole (h+) in the valence band. The electrons that reach the conduction band can move through the semiconductor lattice, as can the holes generated in the valence band (*Figure 1*).

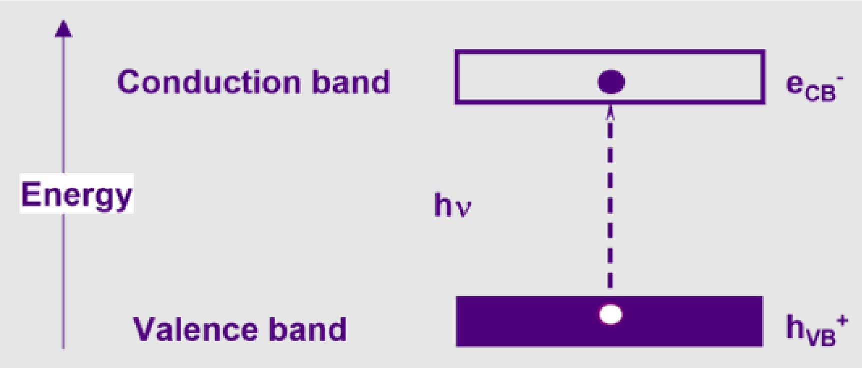


Figure 1: Generation of an electron–hole pair in a semiconductor.

The electrons and arising holes can migrate to the semiconductor surface, effecting an electronic transfer with the substances adsorbed on the particle surface. The electrons that reach the surface reduce an electron acceptor (usually oxygen), while the holes can accept an electron from an electron-donor species, causing this species to oxidise, according to the reactions:

$$e^-_{CB} + A \rightarrow A^{\cdot -}$$

$$h^+_{VB} + D \rightarrow D^{\cdot +}$$

The capture of an electron by species A gives rise, therefore, to a radical $A^{\cdot -}$, while the interaction between species D and the hole gives rise to a radical $D^{\cdot +}$. These radicals are highly reactive and can react with each other and with other adsorbed species or diffuse from the semiconductor surface and participate in a chemical reaction in the aqueous phase, if the semiconductor is in contact with a solution. The most widely used semiconductor photocatalyst is titanium dioxide ($TiO_2$), due to its stability, as discussed further below. The photocatalytic reactions that develop at the $TiO_2$ surface in the presence of oxygen and water, in which

---

[7] Fox, M. A.; Dulay, M. T. Heterogeneous Photocatalysis. Chem. Rev., 93, 341-357, 1993.

radicals are generated and organic substances are degraded, unfold according to the following sequence [8,9]:

1. The electrons reduce the oxygen and generate the superoxide ion, $O_2^{\cdot -}$

$$O_2 + e^-_{CB} \rightarrow O_2^{\cdot -}$$

2. The holes oxidise the water adsorbed on the $TiO_2$ surface and generate the hydroxyl radical, $OH^{\cdot}$

$$H_2O + h^+_{VB} \rightarrow OH^{\cdot} + H^+$$

3. The superoxide anion radical gives rise to hydrogen peroxide:

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2$$

4. The hydrogen peroxide decomposes and gives rise to hydroxyl radicals:

$$H_2O_2 + e^-_{CB} \rightarrow OH^{\cdot} + OH^-$$

5. The organic compounds oxidise through the hydroxyl radicals:

$$R + OH^{\cdot} \rightarrow R'^{\cdot} + H_2O$$

6. The holes oxidise the organic matter:

$$R + h^+_{VB} \rightarrow R^{+\cdot} \rightarrow \text{reaction products}$$

### 2.1.1 Semiconductor Photocatalysts

Different semiconducting materials may be used as photocatalysts, since they have appropriate band potentials to allow the photocatalytic reactions (oxygen reduction and generation of hydroxyl radicals) to be developed (*Figure 2*).

---

[8] Wold, A. Photocatalytic properties of TiO2. Chem. Mater., 5, 280-283, 1993.

[9] Houas, A.; Lachleb, H.; Ksibi, M.; Elaloui, E.; Guillard, C.; Hherrmann, J.M. Photocatalytic degradation pathway of methylene blue in water. Applied Catalysis B: Environmental, 31, 145-157, 2001.

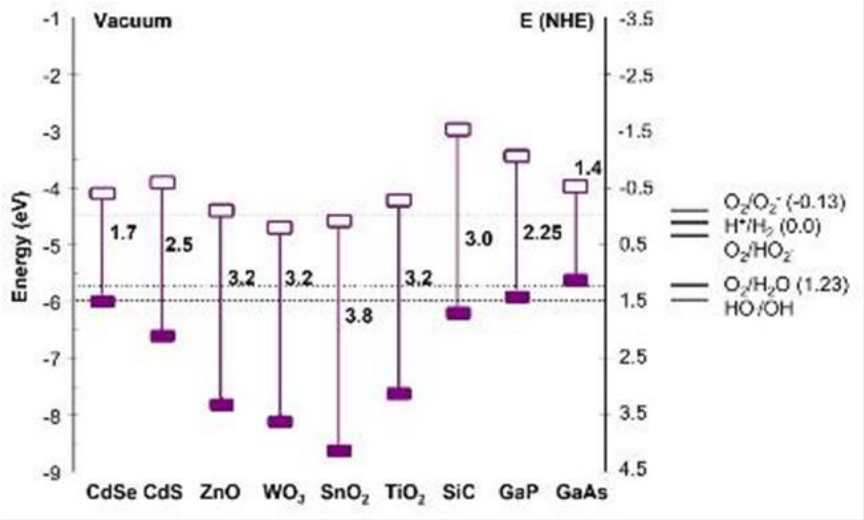


Figure 2: Band potentials of different semiconductors in an aqueous electrolyte (pH=1). The left axis shows the energy scale with respect to the vacuum, the right axis with respect to the normal hydrogen electrode.

Of all semiconductors, titanium dioxide ($TiO_2$) is the most extensively used, because of its greater stability. Other photocatalytically active semiconductors, such as zinc oxide (ZnO) and cadmium sulphide (CdS), are not stable in the entire pH range and undergo photocorrosion processes that lead to catalyst inactivation.

$TiO_2$ is widely used as a photocatalyst for the following reasons:

- Many organic compounds have a less positive oxidation potential than the $TiO_2$ valence band limit, which is why their oxidation by the photogenerated holes is thermodynamically permitted (reduction of free energy, ΔG).
- The redox potential of the $H_2O$/OH. (OH-) pair lies within the material's bandgap energy domain.
- The redox potential of the electron excited to the conduction band is thermodynamically appropriate for the reduction of oxygen.
- It is chemically stable on exposure to acids and alkalis.
- It is stable under illumination.
- It is chemically harmless.

Titanium dioxide is used as a raw material in numerous industries, such as paints (white pigment), cosmetics, ceramics (opacifier), etc. It can usually be chemically activated by light, hence its photoactivity is well known, and is a cause of serious problems, particularly in paints, since light tends to cause $TiO_2$ to decompose organic compounds in the paints [10,11].

---

[10] Frazer, L. Titanium dioxide: environmental white knight? Environmental health perspectives 109, 174-177, 2001.

[11] Fujishima, A.; Zhang, X.; Tryk, D.A. TiO2 photocatalysis and related surface phenomena. Surface Science Reports 63, 515-582, 2008.

The $TiO_2$ used as an industrial raw material and the $TiO_2$ used as a photocatalyst differ mainly in their crystal shape and particle size. Thus, in the foregoing industrial processes, the crystal shape used is that of rutile and the particle size is larger than that of the $TiO_2$ used as a photocatalyst. $TiO_2$ achieves its highest efficiency in photocatalytic reactions, when it is present as anatase and has a nanometre particle size.

### 2.1.2 Photocatalytic Reactors

Any photocatalytic setup, disregarding the scale, consists of reagents, a light source, and the reactor with its operating system. As with any other conventional reactor, the photoreactor can be operated in batch or continuous regime, and this will be an important parameter in sizing the system. The fabrication of an effective photocatalytic reactor must consider several specific design parameters such as reactor geometry/area, radiation source, type of photocatalyst, and operational parameters, such as catalyst concentration, rate transfer of pollutants/reaction kinetics, light wavelength, and intensity, pH, temperature and dissolved oxygen concentration[12,] , among others.

As complex as it might be, there are some general aspects that can be emphasized: (i) Most used photocatalytic reactors, as reported in the literature, are batch or semi-batch-operated, characterized by small volumes (up to 100 L for some pilot-scale plants); (ii) The radiation source can be either natural (the sun), or artificial, consisting of UV-lamps; both are widely investigated and used even in the same system, but the second option will provide a constant radiation flux with the cost of additional energy consumption; (iii) Appropriate oxidations rates are obtained when the dissolved oxygen concentration is maintained near to saturation. The oxygen can be supplied by direct contact with atmospheric air (for small reaction volumes) or by air compressors[13].

In a simplified approach, photocatalytic reactors can be divided into two major categories by the state of the photocatalyst, i.e., dispersed systems (stirred) and immobilized systems. The efficiency of suspended $TiO_2$ catalysts has been demonstrated to be superior compared to the same catalysts immobilized on a substrate [10]. This can be attributed to the enhanced mass transport in suspended form. However, using immobilized catalyst permits to avoid the separation step of the particles[14].

---

[12] Isopencu, G.O., Mocanu, A., Deleanu, I.M. A Brief Review of Photocatalytic Reactors Used for Persistent Pesticides Degradation. ChemEngineering 6, 89, 2022.

[13] Puma, G.L., Machuca-Martínez, F., Mueses, M., Colina-Márquez, J., Bustillo-Lecompte, C. Scale-Up and Optimization for Slurry Photoreactors. In Advanced Oxidation Processes; IntechOpen: London, UK, 1–22, 2020.

[14] Ahmed, S., Rasul, M.G., Brown, R., Hashib, M.A. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. Journal of Environmental Management, 92, 311–330, 2011.

### 2.1.3 Factors influencing the Photocatalytic degradation process

Traditionally, tertiary treatments have been considered as refining processes to remove pollutants that could not be removed in the previous treatment stages. However, in some cases, tertiary treatment is now the only treatment used for the removal of certain very specific pollutants. Among the processes used are those of advanced oxidation, which include heterogeneous photocatalysis with titanium dioxide ($TiO_2$), being of special interest the use of solar radiation as a source of energy necessary for its activation[15].

Photocatalytic processes are green advanced techniques consisting of the usage of light to modify the reaction rate of a process, in the presence of a photocatalyst. The photocatalytic oxidation of pollutants requires high potential, thus the valence band location at the semiconductor-electrolyte interface must be more positive, as exhibited by $TiO_2$ for the photogenerated holes to have sufficient energy to oxidize the organic pollutants through the generation of hydroxyl radicals. The redox potential must lie within the band gap of the photocatalyst.

Designing an optimal photocatalytic process/system depends on a wide spectrum of independent and interdependent variables: pH, catalyst dose, irradiation intensity and type, pollutants concentration and type, reaction time, temperature, mixing conditions, and so more[16].

The effect of the most important operational variables on the photocatalytic degradation of pollutants in the aqueous phase is shown below.

Type of photocatalyst

The photocatalytic activity of $TiO_2$ depends on surface and structural semiconductor properties such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density. Particle size is of primary importance in heterogeneous catalysis because it is directly related to the efficiency of a catalyst through the definition of its specific surface area. A number of commercially available catalysts have been tested for the photocatalytic degradation of various organic compounds in an aqueous environment. The following table (Table *1*) presents the specification and characteristics of some commercial $TiO_2$ samples[17].

The photocatalyst titanium dioxide Degussa P25 has been widely used in most of the experimental conditions; other catalyst powders, namely, Hombikat UV100, PC500, PC 10, PC 50, Travancore Titanium Products (TTP), India, were also used for degradation of toxic organic compounds. Physico-chemical characteristics of different tinanium oxides are summarised in *Table 1*. P25 contains 75% anatase and 25% rutile with a specific BET surface area of 50 $m^2/g$ and a primary particle size of 20 nm. Hombikat UV100

---

[15] Blanco Gálvez, J. et al. Descontaminación y desinfección de agua y aire mediante procesos solares de oxidación avanzada. Madrid: CIEMAT, 2009.

[16] Al-Nuaim, M.A., Alwasti, A.A., Shnain, Z.Y. The photocatalytic process in the treatment of polluted water. Chemical Papers, 77, 677–701, 2023.

[17] Ahmed, S., Rasul, M.G., Brown, R., Hashib, M.A. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. Journal of Environmental Management, 92, 311–330, 2011.

consists of 100% pure and smaller anatase with a specific BET surface area of 250 $m^2/g$ and a primary particle size of 5 nm. The photocatalyst PC500 has a BET surface area of 287 $m^2/g$ with 100% anatase and primary particle size of 5-10 nm and $TiO_2$ obtained from TTP, India has a BET surface area of 9.82 $m^2/g$. It has been demonstrated that the degradation rate of pollutants proceeds much more rapidly in the presence of P25 as compared to other photocatalysts. The efficiency of photocatalysts was shown to follow the order: P25 > UV100 > PC500 > TTP for the degradation of various pesticides and herbicides derivatives. The differences in the photocatalytic activity are likely to be related to the differences in the BET surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface, since these factors could affect the adsorption behaviour of a pollutant or intermediate molecule and the lifetime and recombination rate of electron-hole pairs. The higher photoactivity of P25 has been attributed to its crystalline composition of rutile and anatase which slows down the recombination between electrons and holes.

Table 1: Physico-chemical characteristics of available commercial products.

| Sample | Specific surface area BET ($m^2/g$) | Crystal size (nm) | Composition | Producer |
|---|---|---|---|---|
| **P25** | 50 | 21 | 75% Anatase<br>25% Rutile | Evonik Industries |
| **PC500** | 287 | 5-10 | 100% Anatase | Millenium Chemicals |
| **PC50** | 54 | 20-30 | 100% Anatase | |
| **PC10** | 10 | 65-75 | 100% Anatase | |
| **Hombikat UV100** | 250 | 5 | 100% Anatase | Sachtleben Chemie |
| **TTP** | 9.82 | N/A | N/A | Travancore Titanium Products |

ZnO is a semiconductor whose activity as a photocatalyst has been investigated in the degradation of organic pollutants. The main practical problem when using ZnO is that this semiconductor suffers photodissolution induced by self-oxidation, according to the following equation:

$$ZnO + 2\,h^+ \rightarrow Zn^{2+} + \tfrac{1}{2}O_2$$

Consequently, toxicity in the illuminated ZnO system can be magnified by the increase of $Zn^{2+}$ in the solution. This problem can be solved by adjusting the pH of water to about 9.5 after heterogeneous photocatalytic treatment to form the insoluble hydroxide salt. Zinc removal is not complete until the solid is physically removed from the water, by subsequent sedimentation and filtration [18,19].

## Effect of pH

Characteristics of organic pollutants in wastewater differ greatly in several parameters, particularly in their speciation behaviour, solubility in water and hydrophobicity. While some compounds are uncharged at common pH conditions, which is typical of natural water or wastewater, other compounds exhibit a wide variation in speciation (or charge) and physico-chemical properties. Some compounds can exist in positive, neutral, and negative forms in aqueous solutions. This variation can also significantly influence their photocatalytic degradation behaviour. Wastewater pH varies significantly and can play an important role in the photocatalytic degradation of organic contaminants since it determines the surface charge of the photocatalyst and the size of aggregates it forms. The surface charge of the photocatalyst and the ionization or speciation (pKa) of an organic pollutant can be profoundly affected by the solution pH. Electrostatic interaction between a semiconductor surface, solvent molecules, substrate and charged radicals formed during photocatalytic oxidation strongly depends on the solution pH. In addition, protonation and deprotonation of the organic pollutants can take place depending on the solution pH. Sometimes protonated products are more stable under UV-radiation than its main structures. Therefore, the pH of the solution can play a key role in the adsorption and photocatalytic oxidation of pollutants.

The point of zero charge of the $TiO_2$ (Degussa P25) is widely investigated/reported at pH 6.25. While under acidic conditions the positive charge of the $TiO_2$ surface increases as the pH decreases; above pH 6.25 the negative charge at the surface of the $TiO_2$ increases with increasing pH. Moreover, the pH of the solution affects the formation of hydroxyl radicals by the reaction between hydroxide ions and photo-induced holes on the $TiO_2$ surface. The positive holes are considered as the major oxidation steps at low pH, whereas hydroxyl radicals ($\cdot OH$) are considered as the predominant species at neutral or high pH levels. It would be expected that the generation of OH is higher due to the presence of more available hydroxyl ions on the $TiO_2$ surface. Thus, the degradation efficiency of the process will be logically enhanced at high pH. To elucidate the effect of pH on the photocatalytic degradation of organic compounds and adsorption on the $TiO_2$ surface, numerous investigations have been carried out.

## Interfering substances

Generally, the removal of organic pollutants by heterogeneous photocatalysis is largely influenced by the quality of the water matrix to be treated, and the influence of the dissolved substances, which can provoke neutral, inhibitory or promoting effects. Photosensitizers (organic and inorganic species) in the water

---

[18] Fenoll, J., Martínez-Menchón, M., Navarro, G., Vela, N., Navarro, S. Photocatalytic degradation of substituted phenylurea herbicides in aqueous semiconductor suspensions exposed to solar energy. Chemosphere, 91(5), pp. 571–578, 2013.

[19] Fenoll, J., Sabater, P., Navarro, G., Pérez-Lucas, G., Navarro, S. Photocatalytic transformation of sixteen substituted phenylurea herbicides in aqueous semiconductor suspensions: Intermediates and degradation pathways. Journal of Hazardous Materials, 244-245, 370–379, 2013.

matrix can promote the production of reactive oxygen species by UV irradiation, leading to indirect photolysis[20]. Since wastewater composition can vary with time, the basic understanding of the effect of organic and inorganic constituents present in wastewater on the performance of photocatalytic systems is crucial to ensure operational stability of a prototype photocatalytic water purification process. A number of studies have demonstrated that water components like calcium, magnesium, iron, zinc, copper, bicarbonate, phosphate, nitrate, sulphate, chloride, and dissolved organic matters can affect the photocatalytic degradation rate of organic pollutants since they can be adsorbed onto the surface of $TiO_2$. Depending on the solution pH, they can also compete with the target pollutant for the active sites.

Some authors have pointed out an inhibitive effect of anions in the order $SO_4^{2-}<NO_3^-<Cl^-$ during the photolytic degradation of some pesticides attributing to the detrimental effect to their competition for the active sites on the $TiO_2$ surface[21].

The adsorption of water components can reduce the formation of OH· radicals. Although hydroxyl radical scavenging by bicarbonate, phosphate, nitrate, sulphate, and chloride results in corresponding anion radicals, they have lower oxidation potential. Consequently, all these reactions can influence the overall rate of photocatalytic oxidation.

Oxidants/electron acceptor:

One practical problem in using $TiO_2$ as a photocatalyst is the undesired electron-hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and thus represent the major energy wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron–hole pair recombination is to add other (irreversible) electron acceptors to the reaction. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of additives to enhance the degradation rate may often be justified [22].

Addition of external oxidant/electron acceptors into a semiconductor suspension has been shown to improve the photocatalytic degradation of organic contaminants by (1) removing the electron-hole recombination by accepting the conduction band electron; (2) increasing the hydroxyl radical concentration and oxidation rate of intermediate compound; and (3) generating more radicals and other oxidizing species to accelerate the degradation efficiency of intermediate compounds. Since hydroxyl radicals appear to play an important role in photocatalytic degradation, several researchers have investigated the effect of addition of electron acceptors such as $H_2O_2$, $KBrO_3$, and $K_2S_2O_8$ or $Na_2S_2O_8$ on the photocatalytic degradation of various pesticides and herbicides to enhance the formation of hydroxyl

---

[20] Gambín, M., Pérez-Lucas, G., Navarro, S. Removal Kinetics of Four Leacher Herbicides Through Solar Heterogeneous Photocatalysis as Influenced by Water Matrix Components. Bulletin of Environmental Contamination and Toxicology, 106, 989–995, 2021.

[21] Mahmoodi, N.M., Arami M., Limaee, N.Y., Gharanghij, K. Photocatalytic degradation of agricultural N-heterocyclic organic pollutants using immobilized nanoparticles of titania. Journal of Hazardous Materials, 145, 65-71, 2007.

[22] Haque, M.M., Muneer, M. Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide. Journal of Environmental Management, 69(2), 69–176, 2003.

radicals as well as to inhibit electron-hole (e_/h+) pair recombination. In all cases the addition of oxidants has resulted in higher pollutant degradation rates compared to the molecular oxygen. In most of the cases, the order of enhancement is UV/ $TiO_2/BrO_3^-$> UV/ $TiO_2/S_2O_8^{2-}$> UV $TiO_2/H_2O_2$. The enhancement of degradation rate is due to reaction between $BrO_3^-$ and conduction band electron. This reaction reduces the recombination of electron-hole pair.

$$BrO_3^- + 6e_{CB}^- + 6H^+ \rightarrow Br^- + 3H_2O$$

$S_2O_8^{2-}$ can generate sulphate radical anions ($SO_4\cdot^-$) both thermally and photolytically in aqueous solution. $SO_4\cdot^-$ then reacts with $H_2O$ to produce ·OH radicals.

$$S_2O_8^{2-} \rightarrow 2SO_4\cdot^-$$

$$SO_4\cdot^- + H_2O \rightarrow \cdot OH + SO_4^{2-} + H^+$$

With the addition of $H_2O_2$, the enhancement of degradation is due to the increase in the hydroxyl radical concentration as shown by the following Eqs.

$$H_2O_2 + e_{CB}^- \rightarrow \cdot OH + OH^-$$

$$H_2O_2 \rightarrow \cdot OH + \cdot OH$$

### 2.1.4 Photocatalytic degradation of selected CoEC

The following list described in this section shows the information found in the literature on the elimination of the selected contaminants using the photocatalytic technique.

Phenylurea pesticides

In the photocatalytic treatment, the mineralization of the pollutants is the goal. Here also, the central oxidation species is non-selective (·OH), but the less reactive free radical ($H_2O\cdot$) and its conjugate ($O_2\cdot$) have their contribution as well. The pollutants react with the free radicals and numerous distinctive intermediates are forming until total mineralization, achieved through different oxidation paths.

Very slow degradation of TOC (Total Organic Carbon) from phenylurea pesticides after 80–90% mineralisation and very slow mineralisation of urea have been reported previously[23]. Urea could therefore be expected as an intermediate originating from phenylurea pesticides. Urea contains only one C atom and two N atoms, with the C atom being fully oxidised (oxidation state +IV). This impedes hydrogen abstraction as electrophilic attack as well by hydroxyl radicals at the carbon atom. Furthermore, several resonance structures are possible making the molecule very stable and the oxidative attack on the amine groups very slow. Hydroxylamine could be an intermediate product leading to the formation of nitrate.

---

[23] Parra, S., Olivero, J., Pulgarin, C. Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO2 suspensions. Appl. Catal. B: Environ. 36, 75–85, 2002.

Mainly, the formation of urea could justify not only the remaining TOC, but also the incomplete release of N as $NH_4^+$ or $NO_3^-$ [24].

*Annex 1* shows the information on the photocatalytic degradation of the pesticides diuron, isoprotorun and fenuron found in the literature. They detail the operational variables used in the investigations carried out, as well as the degradation obtained in terms of percentage of elimination and mineralisation of the pesticide and irradiation time required to achieve them.

N-methyl carbamate (NMC) pesticides

The photocatalytic degradation of carbofuran in aqueous media has been investigated using different photocatalysts ($TiO_2$ and ZnO) and UV radiation sources [25,26]. The studies found in this search conclude that photocatalytic technology can be used for the degradation of carbofuran in aqueous media. Mahalakshmi et al. reported complete mineralisation of carbofuran as determined by TOC analysis. Based on their research, a possible degradation pathway was proposed: the carbamate group is the main site of attack by the hydroxyl radical producing carbamic acid, which is a known unstable compound and hence decomposes rapidly to gaseous products such as methyl amine and carbon dioxide. The decomposition of the benzene ring and subsequent mineralisation resulting in water and carbon dioxide was visualised by the decrease of TOC during the photocatalytic process [27].

*Annex 1* includes the information on the photocatalytic degradation of the pesticide carbofuran found in this literature revision. It shows the operational variables used in the investigations carried out, as well as the degradation obtained in terms of percentage of elimination and mineralisation of the pesticide and irradiation time required to achieve them.

Triazine pesticides

Different studies have shown that photocatalytic degradation of triazine herbicides takes place by several steps leading to formation of cyanuric acid (trihydroxy s-triazine) as final stable product. Several authors refer to the ultimate formation, in heterogeneous photocatalytic degradation of atrazine, of very recalcitrant compounds, bearing 3/8 of the organic carbon of the original molecule and the triazine ring. The high stability of the s-triazine ring prevents a further degradation to achieve the full mineralization

---

[24] Maldonado, M.I., Passarinho, P.C., Oller, I., Gernjiak, W., Fernández, P., Blanco, J., Malato, S. Photocatalytic degradation of EU priority substances: a comparison between TiO2 and Fenton plus photo-Fenton in a solar pilot plant. J. Photochem. Photobiol. A: Chem. 185, 354-363, 2007.

[25] FENOLL, J., HELLÍN, P., FLORES, P., MARTÍNEZ, C.M., NAVARRO, S. Degradation intermediates and reaction pathway of carbofuran in leaching water using TiO2 and ZnO as photocatalyst under natural sunlight. Journal of Photochemistry and Photobiology A: Chemistry, 251, 33-40, 2013.

[26] TOMAŠEVIC, A. MIJIN, D. MARINKOVIC, A., CVIJETIC, GAŠIC, S. Photocatalytic degradation of carbamate insecticides: effect of different parameters. Pestic. Phytomed. (Belgrade), 34, 193-200, 2019.

[27] MAHALAKSHMI, M., ARABINDOO, B., PALANICHAMY, M., MURUGESAN, V. Photocatalytic degradation of carbofuran using semiconductor oxides. Journal of Hazardous Materials, 143, 240-245, 2007.

even upon addition to the solution of oxidants such as peroxydisulphate ($Na_2S_2O_8$). As a consequence of the formation of such compounds, mineralisation is deficient, and nitrogen released from atrazine is incomplete.

Chu et al. conducted a study on the degradation and mineralisation of simazine by photocatalytic oxidation in a $TiO_2$ suspension[28]. Examination of the intermediate and final products provided information on the feasibility and optimisation of the photocatalytic process in terms of simazine degradation. As a result, the authors concluded that cyanuric acid is the final product in this process.

*Annex 1* details the information obtained on the photocatalytic degradation of atrazine, cybutryne (named also as irgarol), simazine and terbutryn, including the main operating variables used and the degree of degradation and mineralisation of these compounds in the examined studies.

### Dihydrofolate reductase inhibitor

Several studies deal with the removal and mineralisation of the pharmaceutical compound Trimethoprim d-9 in synthetic water and in the effluent from wastewater treatment plants, using reactors with different commercial $TiO_2$ dispersed photocatalysts.

Marquez et al. found that while the trimethoprim compound was completely removed with a relatively low radiation exposure (90 min), no more than c.a. 70% TOC removal was achieved after the application of long radiation exposure, suggesting the formation of recalcitrant organic products. Complete transformations of sulphur to sulphate, chlorine to chloride and fluorine to fluoride were achieved. On the other hand, no complete conversions of organic carbon to carbon dioxide and organic nitrogen to ammonium or nitrate were observed even for the higher radiation exposure times tested. The formation of very stable transformation products was also identified by Sirtori et al. in experiments performed to monitor the formation of inorganic nitrogen compounds ($NH_4^+$ and $NO_3^-$) during the degradation of Trimethoprim. In this study, the nitrate concentration showed a continuous increase during the photocatalytic degradation process. Only 20% of the N in the compound was mineralised to nitrate and ammonia by $TiO_2$ photocatalysis, indicating a significant amount of nitrogenous transformation products at the end of the treatment[29].

*Annex 1* shows the best results from the literature reviewed on the photocatalytic removal and mineralisation of Trimethoprim using commercially available photocatalysts.

### Non-Steroidal Anti-Inflammatory Drugs (NSAIDs)

Ibuprofen is a non-steroidal anti-inflammatory drug (NSAID). One of the main entryways of ibuprofen into the aquatic environment is the effluent from secondary sewage treatment plants, which are ineffective in

---

[28] CHU, W., RAO, Y., HUI, W.Y. Removal of simazine in a UV/TiO2 heterogeneous system. Journal of Agricultural and Food Chemistry, 57, 6944-6949, 2009.

[29] SIRTORI, C., AGÜERA, A., GERNJAK, W., MALATO, S. Effect of water-matrix composition on Trimethoprim solar photodegradation kinetics and pathways. Water Research, 44, 2735–2744, 2010.

removing this drug. Some studies have been conducted using photocatalysis processes to degrade ibuprofen, but only a few of them have been carried out with industrial wastewater of pharmaceutical origin and using UV or solar radiation on $TiO_2$ systems.

Jallouli et al. reported the photocatalytic degradation of ibuprofen in ultrapure water, municipal wastewater and wastewater from the pharmaceutical industry[30]. The results showed that, although the removal of ibuprofen was complete, at the end of the experiments the mineralisation was incomplete. Results from other studies, with different water matrixes, $TiO_2$, artificial UV lamps or sunlight indicate that photocatalysis is efficient in degrading this drug but leads to the formation of a number of recalcitrant products such as substituted phenolic compounds and aromatic carboxylic acids.

*Annex 1* includes the information on the photocatalytic degradation of ibuprofen found in this literature revision. It shows the operational variables used in the investigations carried out, as well as the degradation obtained in terms of percentage of removal and mineralisation of this NSAID and the irradiation time required to achieve them.

Benzamide

Very few references on the photocatalytic degradation of amisulpride benzamide with commercial photocatalysts were found in the literature search. The reviewed studies were carried out in real complex water effluents from hospital wastewater treatment plants and drinking and lake waters with pharmaceuticals mixtures. The results of these studies, shown in *Annex 1* focus on the determination of the removal rates of amisulpride achieved in the different water sources investigated. However, no information is reported on the mineralisation of the compound.

## 2.2 Technology: PDP

Plasma, also known as the ‘fourth state of matter’, plays an increasingly significant role in industrial, commercial, domestic and even space and fusion research. The evolution of new plasma applications continues to accelerate at a notable pace, with its versatility spanning in various fields such as medicine, textile treatment, solar cells, electrohydraulic water treatment, paper production, packaging and corrosion protection, among many others[31]. To generate plasma, sufficient energy must be applied to a gas. This energy is typically provided by an electrical source, which can be direct current (DC), radiofrequency (RF), low frequency (LF) or microwave frequency (MWF).

The use of plasma in water disinfection is an area of research and development where various applications are being explored. Plasma is a state of matter composed of electrically charged particles, electrons and

---

[30] JALLOULI, N., PASTRANA-MARTÍNEZ, L.M., RIBEIRO, A.R., MOREIRA, N.F.F., FARIA, J.L., HENTATI, O., SILVA, A.M.T., KSIBI, M. Heterogeneous photocatalytic degradation of ibuprofen in ultrapure water, municipal and pharmaceutical industry wastewaters using a TiO2/UV-LED system. Chemical Engineering Journal, 334, 976–984, 2018.

[31] Harry, J. E. (2013). Introduction to plasma technology: science, engineering, and applications. John Wiley & Sons.

ions, capable of generating reactive oxygen and nitrogen species. These reactive species possess disinfectant properties and can contribute to the elimination of microorganisms and contaminants in water.

Some potential applications of plasma in water disinfection are described below:

- Inactivation of microorganisms: Plasma can generate free radicals and other reactive species with the ability to deactivate pathogenic microorganisms such as bacteria, viruses, and fungi in water.
- Decomposition of organic contaminants: Plasma can break down organic compounds present in water, including persistent organic pollutants and industrial chemicals.
- Elimination of odours and flavours: Plasma can aid in removing compounds responsible for unpleasant odours and flavours in water.
- Wastewater treatment: Plasma has been explored as a technology for wastewater treatment, helping to disinfect water before its release into the environment.
- Surface and pipeline disinfection: Plasma can be applied directly to pipeline systems and surfaces to disinfect and prevent biofilm growth.
- Reduction of chemical usage: Compared to some disinfection methods involving chemical products, the use of plasma can reduce the reliance on chemicals in water treatment.

Different plasma technologies exist based on the type of plasma used, whether continuous or pulsed, pressure, electrodes in contact with water or not, their arrangement, etc. In all these technologies, *E. coli* was used to determine disinfection capacity.

### 2.2.1 Plasma technologies reactors.

In 2013, Zheng, Huang, Zhang, Liu, Yan, and Zhu employed a 2.5 L plasma reactor to assess the efficiency of a non-thermal pulsed plasma technique for water disinfection. The experimental setup and system specifications, as illustrated in *Figure 3*, provide a schematic representation of the pulsed plasma system[32].

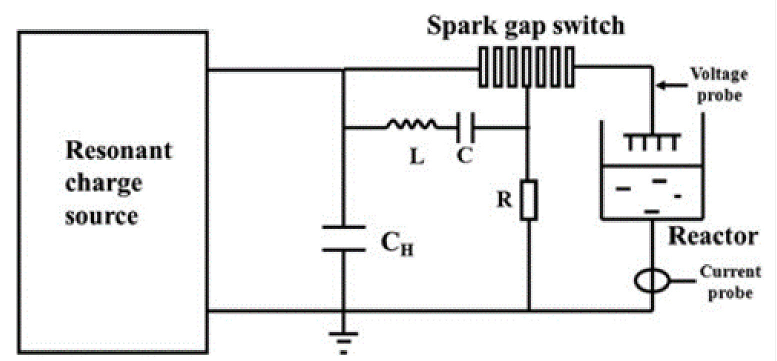


Figure 3: Scheme of experimental configuration [32].

---

[32] Zheng, C., Xu, Y., Huang, H., Zhang, Z., Liu, Z., Yan, K., & Zhu, A. (2013). Water disinfection by pulsed atmospheric air plasma along water surface. Aiche journal, 59(5), 1458-1467.

This configuration includes a plasma reactor, a resonant charging source, a high-voltage capacitor (CH), a multi-gap spark switch, an inductor (L) combined with a capacitor (C) and a resistor (R) forming an LCR trigger. The 39.2 $nF_H$ capacitor is charged within the range of 10 to 30 kV. The *Figure 4* displays a photo of the reactor with an inner diameter of 150 mm and a volume of 2.5 L.

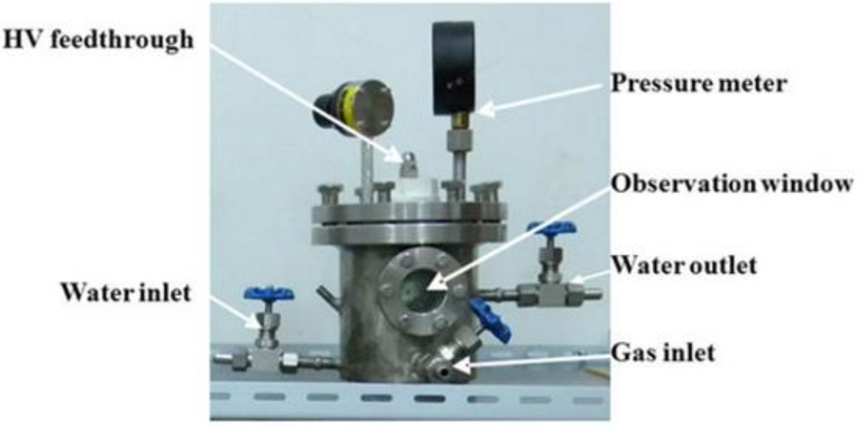


Figure 4: Image of reactor [32].

An air distributor is located at the base to inject air, and both air pressure and water flow can be adjusted individually. Typically, the water volume inside the reactor is 1.6 L. The entire reactor is grounded, except for the high-voltage electrode, which is insulated by Teflon. The high-voltage electrodes consist of four stainless steel needles, usually positioned 1 to 10 mm above the water surface. Atmospheric air plasma is generated between the high-voltage electrodes (AT) and the reactor wall grounded through the water surface. All experiments are conducted with a pulse repetition frequency of 2 pulses per second. The optical emission spectrum of the plasma is captured using a fiber optic spectrometer (Ocean optics HR2000+). To monitor the current distribution, two current probes as shown in *Figure 5* (A) are employed.

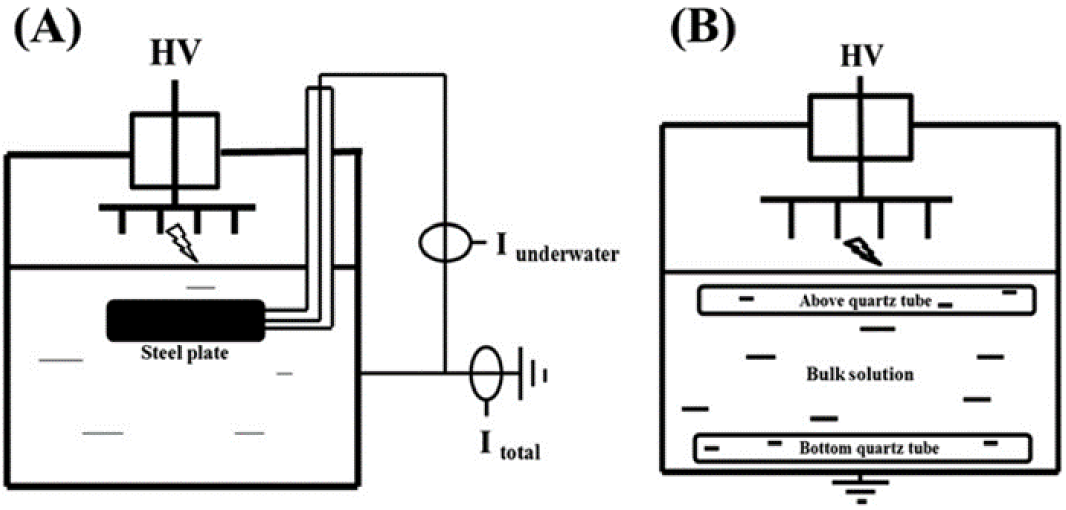


Figure 5: System configuration: A. Underwater current probe, B. Two quartz tubes [33].

The plate current probe is located 2 cm below the water surface, measuring the underwater current. The difference between the total current and the underwater current represents the plasma current along the water surface. All electrical measurements are recorded with a Tektronix oscilloscope (DPO 7054, 500 MHz).

Rashmei, Bornasi, and Ghoranneviss assessed water disinfection using atmospheric cold plasma spark treatment. The experimental setup for this water disinfection process[33] involved a spark discharge plasma system consisting of two separate needle electrodes and a pulsed power supply delivering 10 kV at 30 Hz. Non-thermal plasma (NTP) was generated using a simple outdoor apparatus. The two needle electrodes were positioned 5 cm apart, with a 4 mm gap between the electrodes and the water surface. In this system, bacteria were suspended in a shallow container containing approximately 10 mL of water and NTP was applied to the liquid surface.

In 2016, Singh, Philip, and Ramanujam investigated in detail the disinfection mechanism using pulsed plasma technology (PPT), with *E. coli* as the model bacteria[34]. The schematic diagram of the corona discharge reactor and the setup for experimental studies are shown in *Figure 6*.

---

[33] Rashmei, Z., Bornasi, H., & Ghoranneviss, M. (2016). Evaluation of treatment and disinfection of water using cold atmospheric plasma. Journal of water and health, 14(4), 609-616.

[34] Singh, R. K., Philip, L., & Ramanujam, S. (2016). Disinfection of water by pulsed power technique: a mechanistic perspective. RSC advances, 6(15), 11980-11990.

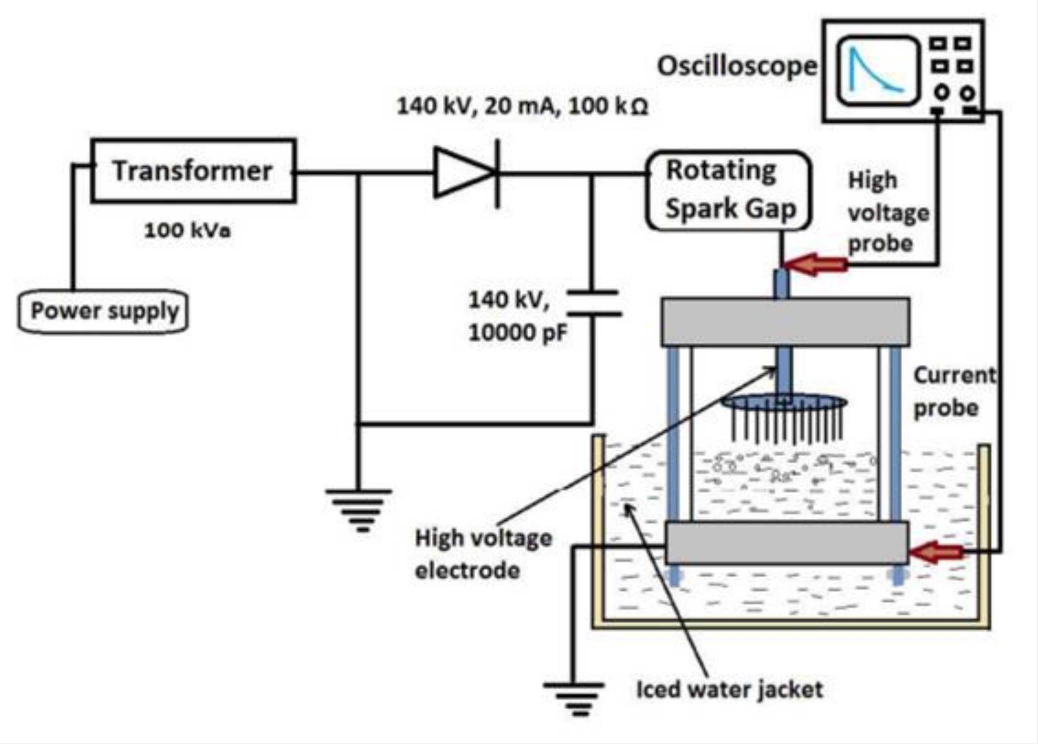


Figure 6: A schematic diagram of the experimental setup and the multi-pin plane geometry corona discharge reactor [34].

The corona discharge was initiated by employing a tungsten electrode with a needle-plane configuration. Needles, with a fine tip radius of 50 µm, were used to maintain a continuous discharge. Within a 50 mL glass container, both the high-voltage electrode and the ground electrode were securely fixed. A rotary spark gap (RSG) was used to generate square pulses, with pulse duration controlled by altering the RSG speed. The applied voltage was adjusted to a level where visible serpentine propagation could be observed during testing. To prevent temperature rise, chilled water continuously circulated around the reactor. The upper electrode was equipped with a port for the collection and analysis of various physicochemical parameters.

In 2021, Abramov et al. reported on a novel water treatment method involving simultaneous hydrodynamic cavitation and plasma discharge[35]. The hybrid reactor used in the experiment consists of two tanks (contaminated water and treated water), a high-pressure pump, a discharge chamber with two electrodes, a hydrodynamic cavitation unit, and a closed safety container for the collection of gases and vapours (*Figure 7*).

---

[35] Abramov, V. O., Abramova, A. V., Cravotto, G., Nikonov, R. V., Fedulov, I. S., & Ivanov, V. K. (2021). Flow-mode water treatment under simultaneous hydrodynamic cavitation and plasma. Ultrasonics Sonochemistry, 70, 105323.

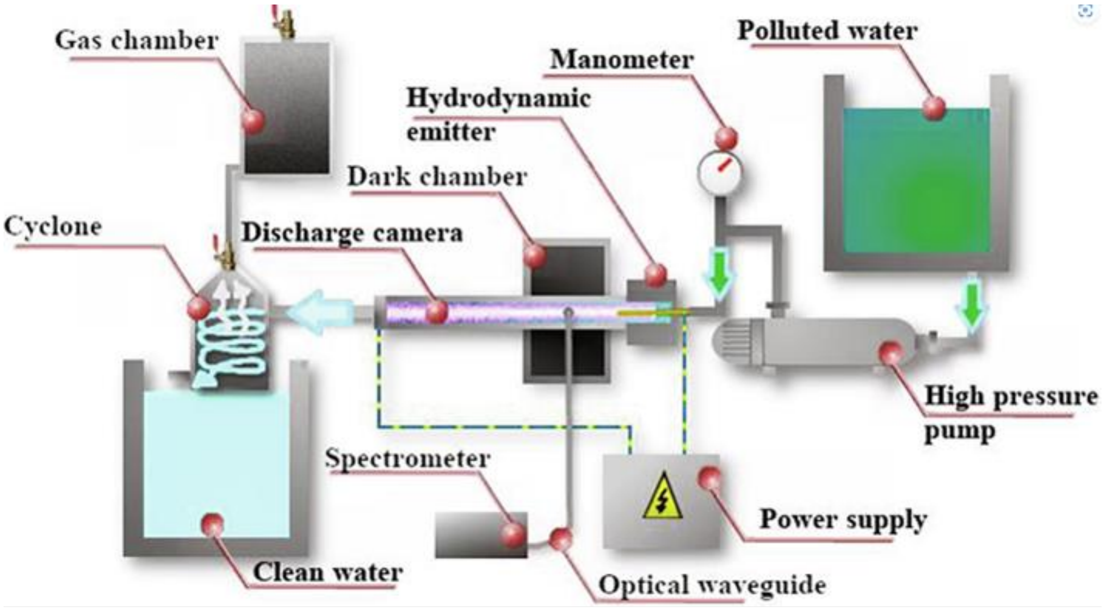


Figure 7: Diagram of the laboratory setup for water treatment using hydrodynamic cavitation and plasma discharge [35].

The laboratory setup operated at a flow rate of 1 $m^3/h$ and maintained a constant voltage of 15 kV. The reactor used replaceable electrodes made of graphite, silver and brass. Hydrodynamic cavitation in the liquid flow was generated by an efficient unit known as the emitter. The emitter's operation involved generating oscillations in a liquid medium when a jet from a nozzle interacted with a specific barrier. This disturbance caused self-oscillations in the jet. In the experimental setup, an annular slotted nozzle was used, forming a barrier consisting of cantilever plates arranged circumferentially. The hydrodynamic emitter, located at the entrance of the discharge chamber, circulated the contaminated water through a high-pressure pump. For safety reasons, the electric potential could not be applied directly to the emitter. Therefore, an electrode (ring-shaped, matching the internal and external diameter of the discharge chamber) was placed near the hydrodynamic emitter, while the second electrode was fixed at the end of the chamber. Cavitation was induced throughout the discharge chamber due to hydrodynamic flows leading to pressure reduction.

The cavitation number of the system confirmed the hypothesis (0.0027) and was calculated based on various parameters. A cyclone was used to separate the gas produced during treatment and its composition was analysed using a gas chromatograph. Approximately 500-1000 $cm^3$ of gas per minute were generated during water treatment. Emission spectra were recorded to examine discharge parameters in relation to electrode materials. The setup included a QE65000 spectrometer, and a sensor mounted in a sealed light chamber. Cavitation noise spectra were measured using a dynamic pressure sensor PS 01-03 with a single crystalline element, operating over a wide dynamic range with a sensitivity of 400 nC/bar and nonlinearity <2% at a signal frequency exceeding 20 kHz, placed at the chamber's entrance. The concentration of silver ions in treated water was determined using a potentiometric method, and the disinfection efficacy was assessed using *E. coli* in pre-sterilized water samples. The study found that the method exhibited powerful disinfection capabilities, although it is essential to note that disinfection, unlike sterilization, does not necessarily eliminate bacterial spores.

Hijosa-Valsero, Molina, Schikora, Müller, and Bayona investigated the removal of water microcontaminants[36]. They evaluated the efficacy of two different non-thermal plasma reactors operating at atmospheric pressure to eliminate atrazine, chlorfenvinphos, lindane (pesticides) and 2,4-dibromophenol (a flame-retardant by-product) from aqueous solutions. *Figure 8* shows an illustrative diagram of reactor R1, which is a discontinuous DBD (dielectric barrier discharge) reactor.

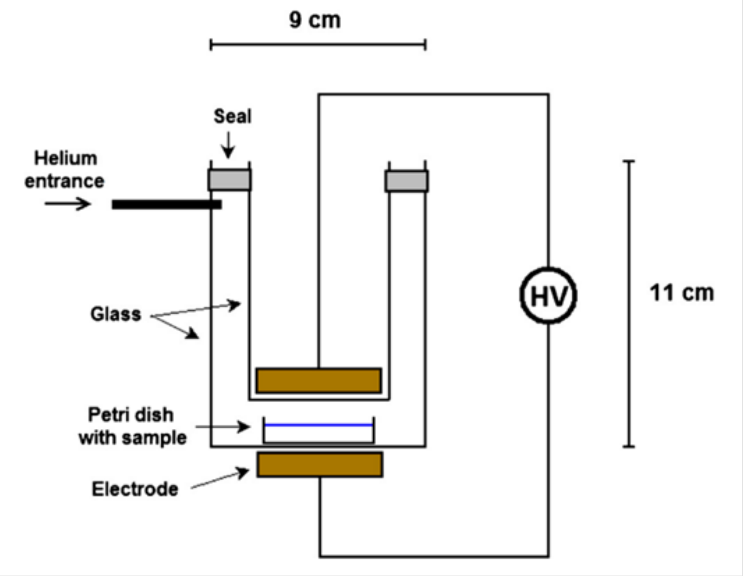


Figure 8: Scheme of the atmospheric plasma discontinuous reactor R1. HV (High Voltage). The operating conditions were as follows: AT ≈ 20 kV, frequency of 100 kHz, and power of 30 W [36].

The physical boundaries of the reactor were defined by using two Pyrex glass containers with a wall thickness of 2 mm, serving as dielectric barriers. Helium gas was introduced into the reactor chamber using gas mass flow meters and controllers from Bronkhorst (Ruurlo, Netherlands) at a flow rate of 5 L per minute. Continuous helium injection was necessary due to gas leaks, despite attempts to seal the system, a Promax GF-855 function generator (L'Hospitalet de Llobregat, Spain) connected to a linear amplifier AG-1012 from T&C Power Conversion Inc. (Rochester, NY, USA), generated a continuous sinusoidal wave at a frequency of 100 kHz. The linear amplifier maintained a constant forward power (dissipated) of 30 W, while the reflected power oscillated between 50 and 70 W.

---

[36] Hijosa-Valsero, M., Molina, R., Schikora, H., Müller, M., & Bayona, J. M. (2013). Removal of priority pollutants from water by means of dielectric barrier discharge atmospheric plasma. Journal of hazardous materials, 262, 664-673.

A corresponding network and two transformers from HR-Diemen S.A. (Sant Hipòlit de Voltregà, Spain) were connected in series at the amplifier's output to increase the voltage to approximately 20 kV. The distance between the two electrodes was about 16 mm and both electrodes were high-voltage electrodes, as they were connected in antiphase to the output of the transformers. The experiments were carried out at room temperature and the sample temperature during plasma treatment did not exceed 40°C. Inside the reactor, a Steriplan Petri dish from Grupo Duran (Wertheim, Germany) was placed without a lid. The distance between the Petri dish (with an outer diameter of 32 mm, an inner diameter of 28 mm, a height of 10 mm, and a glass thickness of 2 mm) and the upper dielectric barrier was kept constant at 2 mm. The Petri dish was filled with four mL of an aqueous solution containing 1-5 mg/L of the target compound. Subsequently, the reactor was sealed, high voltage was applied, and plasma was generated on the sample surface. To analyse the degradation kinetics, various samples, all with the same initial concentration for each experiment, underwent individual treatments with different durations (0 seconds, 10 seconds, 30 seconds, 2 minutes, 5 minutes, and 15 minutes). The final volumes of the treated samples were measured to account for water losses due to evaporation during plasma treatment.

Sarangapani, Misra, Milosavljevic, Bourke, O'Regan, and Cullen conducted a study on the degradation of pesticides (diclorvos, malathion and endosulfan) in water using a high-voltage dielectric barrier discharge plasma reactor that employed atmospheric air as the inducing gas [37]. The experimental setup is illustrated in *Figure 9*.

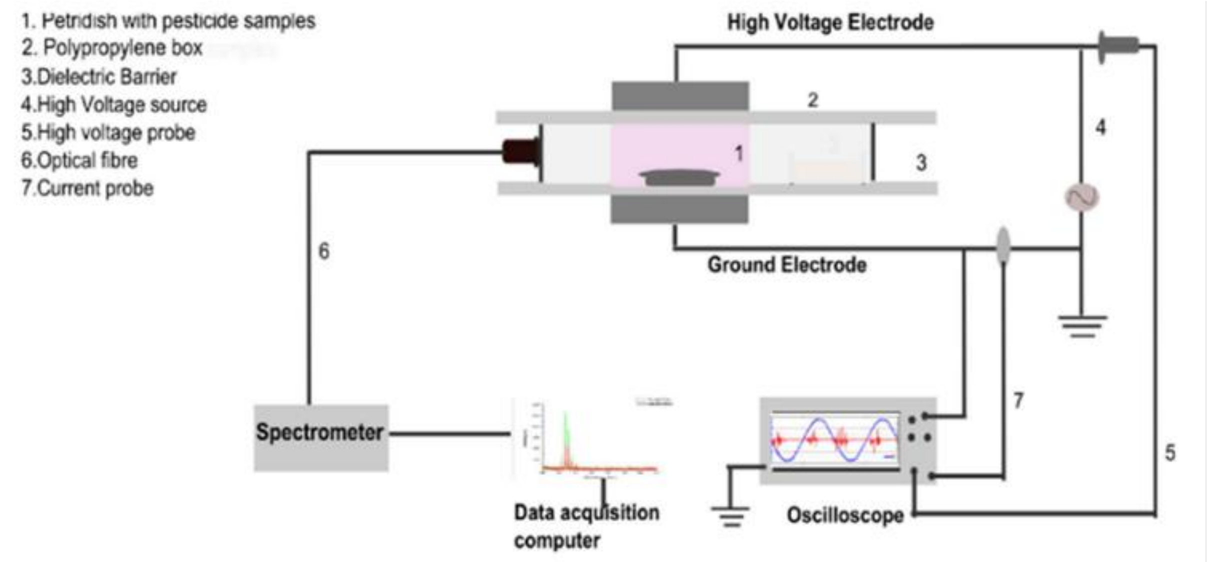


Figure 9: Scheme of the experimental setup with electrical and optical diagnostics [37].

It consisted of two circular electrodes made of aluminium plates (with an outer diameter of 158 mm), one placed beneath a 2 mm thick dielectric for grounding and the other placed on a 10 mm thick methacrylate

---

[37] Sarangapani, C., Misra, N. N., Milosavljevic, V., Bourke, P., O'Regan, F., & Cullen, P. J. (2016). Pesticide degradation in water using atmospheric air cold plasma. Journal of Water Process Engineering, 9, 225-232.

for high-voltage input. A rigid polypropylene container (310 mm × 230 mm × 22 mm) was placed within the space between the dielectrics. Each of these removable containers contained a Petri dish with 20 mL of the pesticide cocktail positioned between the electrode spaces. The container served as a sealed chamber and an additional dielectric. To prevent the escape of reactive species generated during and after treatment, the containers were sealed within a high-barrier Cryovac BB3050 film. It is noteworthy that no specific measures were taken to optimize the infusion of the generated species into the sample. Atmospheric air was used as the working gas. The electrodes were connected to a high-voltage step-up transformer (Phenix Technologies, Inc., USA), with its primary winding receiving input at 230 V and 50 Hz, delivering a high-voltage output within the range of 0-120 kVRMS. Treatment durations of 0 minutes (control), 2 minutes, 4 minutes, 6 minutes, and 8 minutes were tested at 60 kVRMS, 70 kVRMS, and 80 kVRMS. After treatment, the containers were stored at 16°C for 24 hours to ensure that the generated reactive species had sufficient time to react with the samples. All sample treatments were conducted in duplicate at an ambient temperature of 25±2 °C.

In the context of the investigation into the degradation of pentoxifylline, a model pharmaceutical compound, in aqueous solution, a coaxial DBD reactor (*Figure 10*), was employed by Magureanu, Piroi, Mandache, David, Medvedovici, and Parvulescu[38].

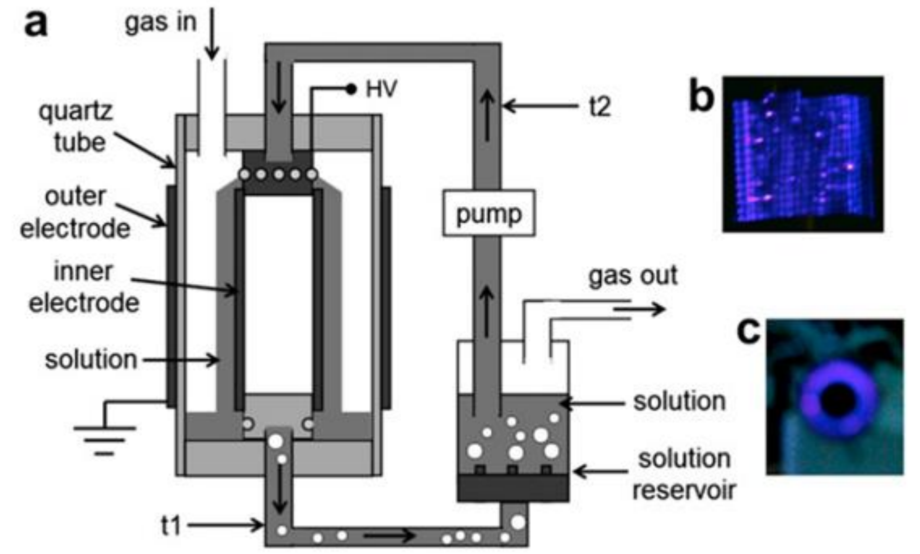


Figure 10: Experimental configuration [38].

The external electrode had a 100 mm section coated with silver paste on the outer surface of the quartz tube. In contrast, the internal electrode was a 16 mm diameter cylinder made of sintered stainless-steel fibers. To facilitate the experiment, a peristaltic pump maintained a flow rate of 40 mL/min, ensuring that

---

[38] Magureanu, M., Piroi, D., Mandache, N. B., David, V., Medvedovici, A., & Parvulescu, V. I. (2010). Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment. Water research, 44(11), 3445-3453.

the pentoxifylline solution cascaded as a thin film through the internal electrode. This film exited the reactor through several openings at the top and was then channelled through a lower tube, returning to the solution reservoir. For oxygen infusion, a separate entry point on the reactor's top cover allowed a flow rate of 600 sccm. After passing through the plasma reactor, the outlet gas, carrying the ozone generated within the discharge, converged with the liquid. This integration aimed to promote the interaction of ozone with contaminant molecules in the solution. The effluent gas was introduced into the solution reservoir through six needles arranged at the base of the reservoir. Solution samples after plasma treatment were extracted by removing the reservoir cover. Notably, active cooling was not required, given the relatively low power used in the experiments (approximately 1 W).

Additionally, gas circulation contributed to cooling effects. The discharge was performed in pulsed mode, using high-voltage connections for the internal electrode and grounding for the external electrode. A negative-polarity direct current (DC) high-voltage generator (Spellman SL600) with a 190-pF capacitor discharged through a rotary spark gap switch (RSG). The RSG governed the pulse frequency. Discharge voltage monitoring was conducted through a high-voltage probe (Tektronix P6015, 1000x), while discharge current was determined by measuring the voltage drop across a non-inductive shunt resistor ($R_s = 3\ \Omega$) connected in series with the external electrode. In each experiment, a 200 mL solution containing pentoxifylline at concentrations ranging from 25 to 150 mg/L in tap water was used to simulate real-world conditions. The initial solution had a conductivity of 775 µS/cm and a pH of 7. Pentoxifylline, being a xanthine derivative, exhibits structural stability due to its extended aromaticity and a long aliphatic chain. UV-visible absorption spectra of these aqueous solutions were analysed using a spectrophotometer (Varian Cary 100) within a wavelength range of 200 to 400 nm. The spectrophotometer cells had a width of 10 mm. A linear correlation was established between the pentoxifylline concentration in the aqueous solution (c in mg/L) and the absorbance (A) measured at a wavelength of 273 nm. Furthermore, the solution underwent liquid chromatography-mass spectrometry (LC-MS) using a Zorbax Eclipse XDB-C8 column (3.5 µm, 2.1 mm inner diameter x 100 mm length) at 35°C. The injection volume was 1 mL, and the mobile phase flowed at a rate of 0.6 mL/min. A linear gradient elution was applied over 20 minutes, starting with an aqueous component at 95% (0.1% formic acid in water) and methanol at 5% (with 0.1% formic acid) and concluding with a final mobile phase composition of 75% aqueous component and 25% methanol.

In 2021, Li and his research team conducted a study focused on the development of an effective technology for ibuprofen (IBP) removal using a pulsed power-driven water film DBD plasma system[39] (*Figure 11*).

---

[39] Li, Z., Wang, Y., Guo, H., Pan, S., Puyang, C., Su, Y., & Han, J. (2021). Insights into water film DBD plasma driven by pulse power for ibuprofen elimination in water: performance, mechanism and degradation route. Separation and Purification Technology, 277, 119415.

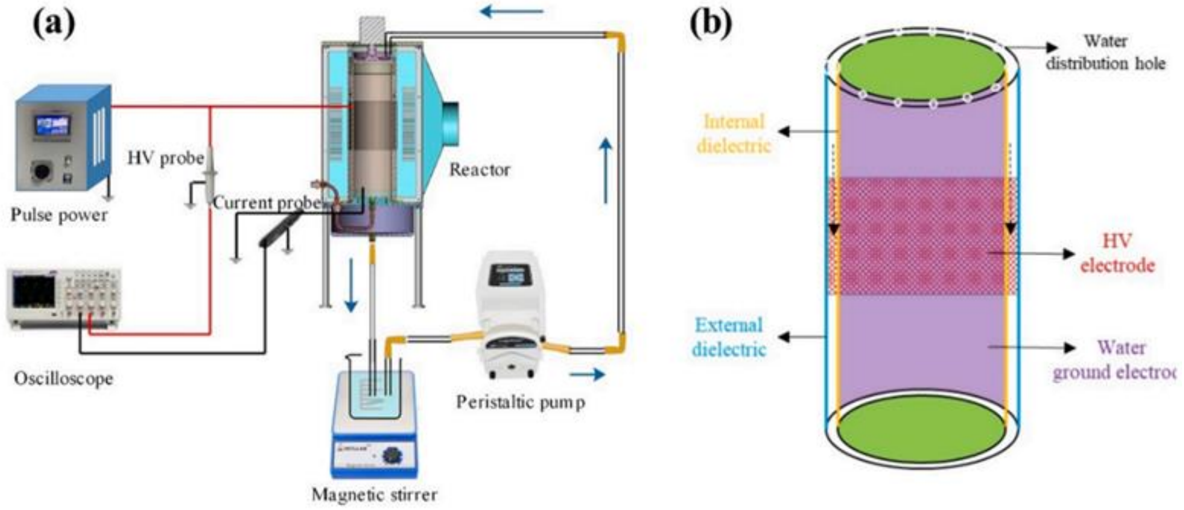


Figure 11: Experimental system: a) flow chart; b) Diagram of the structure of the reactor electrodes [39].

Nanjing Propect Electronic Technology Co., Ltd. provided a pulse power source (PSPT-2000C) with adjustable pulse frequency and duty cycle. Discharge characteristics were measured using an oscilloscope (Tektronix, MDO3012) equipped with a high-voltage probe (Tektronix, P6015A) and a current probe (Tektronix, P6021). Water circulation was maintained using a peristaltic pump (Longer, BT600-2 J) and a magnetic stirrer (Sile, B11-1) was employed to mix the treated water. The dielectric barrier discharge (DBD) reactor was designed with a double water film dielectric structure grounded with water. The reactor had leg height of 25 cm, main body height of 40 cm, and a width of 25 cm. Details of the electrode structure can be seen in *Figure 11 (B)*. The high-voltage electrode was constructed with stainless steel mesh, wrapped by an external dielectric. The entire internal dielectric was filled with water, serving as the ground electrode. The discharge occurred between the outer and inner dielectric layers. Treated water samples were guided through a water distributor with small evenly spaced holes before passing through the discharge zone. This process effectively removed organic contaminants from the water.

Zhou et al. devised a catalytic plasma bubble column reactor to generate submerged plasma bubbles (PB) to efficiently introduce reactive oxidative gas species generated by plasma into the liquid phase for subsequent applications[40]. The experimental setup consisted of several components, including an AC power supply, a plasma bubble column reactor, an electrical diagnostic system, and an optical emission spectroscopy system (*Figure 12*).

---

[40] Zhou, R., Zhou, R., Alam, D., Zhang, T., Li, W., Xia, Y., Mai-Prochnow, A., An, H., Lovell, E.C., Massod, H., Amal, R., Ostrikov, K.K., & Cullen, P. J. (2021). Plasmacatalytic bubbles using CeO2 for organic pollutant degradation. Chemical Engineering Journal, 403, 126413.

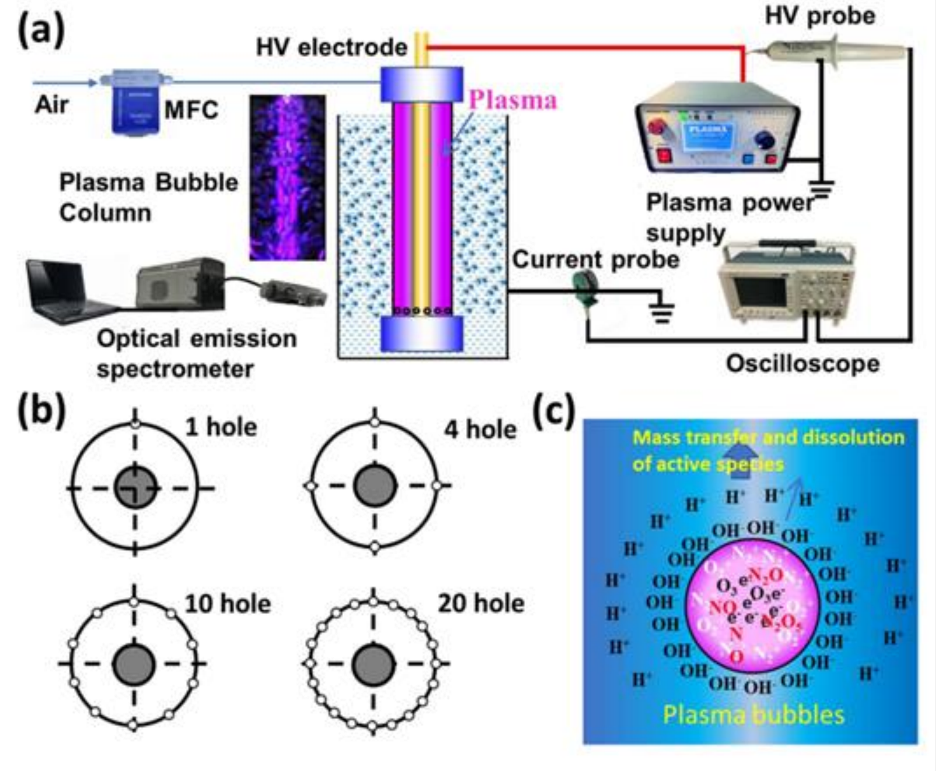


Figure 12: Schematic representation of the experimental setup of the plasma bubble column. a) Plasma bubble column system; b) Cross-sectional view of the plasma column with an outer dielectric tube with one or more holes; c) Plasma bubbles for mass transfer and dissolution of active species [40].

The power supply (Leap100, PlasmaLeap Technologies, Sydney, Australia) could provide a high-voltage output with a discharge power ranging from 0 to 400 W at an AC frequency of 50 Hz to 3000 Hz. The plasma bubble column reactor comprised a 5.0 mm diameter stainless steel rod (serving as the high-voltage electrode), an inner dielectric tube with inner and outer diameters of 5.0 mm and 8.0 mm, respectively and an outer dielectric tube with a 12.0 mm inner diameter. The outer dielectric tube was equipped with 1, 4, 10, and 20 holes (500 µm in diameter, in four different tubes) evenly distributed around the base of the outer quartz tube (see *Figure 12*). These holes allowed atmospheric air to flow through the tube and enabled the resulting bubbles to diffuse into the wastewater, which acted as the grounded electrode. The length of the column submerged in water for plasma generation during water purification was 8 cm. Air was introduced as the plasma-inducing gas into the space between the outer and inner quartz tubes at a flow rate of 2.0 L min standard-1 (MST).

These studies showcase various experimental setups and methodologies for water disinfection using different plasma technologies. The effectiveness of plasma-based water treatment depends on factors such as the type of plasma, reactor design, applied voltage, treatment duration, initial microbial load in the water and the type of contaminant to be treated. Thus, different approaches have been designed depending on the contaminant to be eliminated.

### 2.2.2 PDP degradation of CoECs

Pesticides phenylurea.

The Phenylurea pesticides [41,42] are organic compounds derived from urea (carbonyl diamide or carbamide with the chemical formula $CO(NH_2)_2$). These compounds belong to the herbicide group, meaning they are chemical substances, usually of organic origin, used as pesticides to destroy and/or control the growth of weeds, undesirable plants and in pre-emergence treatments. The issue with these contaminants is their persistence, making their elimination necessary. This group includes Diuron, Isoproturon, and Fenuron.

In 2008, Feng et al. presented a study in which the degradation of diuron was carried out in an aqueous solution in a dielectric barrier discharge reactor[43]. *Figure 13* shows a schematic diagram of the system.

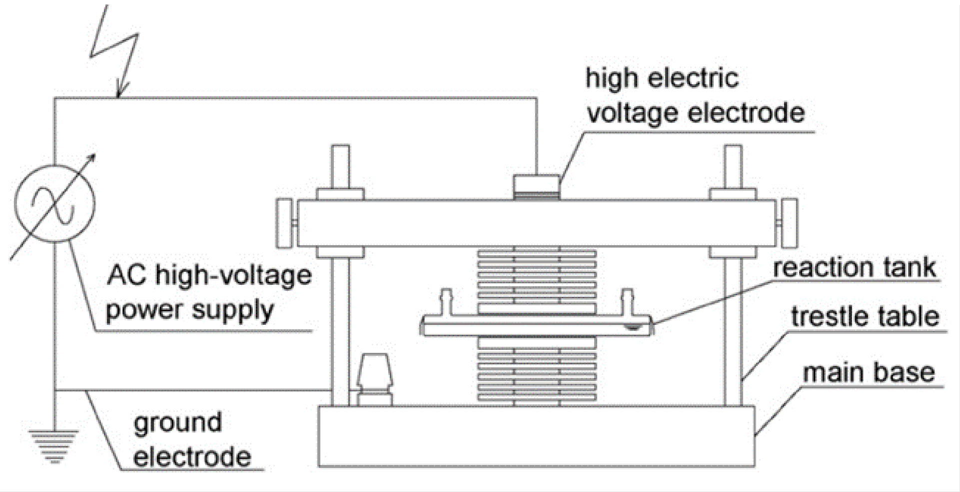


Figure 13: Diagram of the experimental equipment [43].

The diuron solution was primarily treated with a quartz reaction tank that had two distinct sections. The upper part of this tank was slightly larger in size compared to the lower part. The lower section was specifically designed to contain the solution and had dimensions of 84 mm inner diameter, 88 mm outer diameter and 6 mm height. This reaction tank was strategically placed between two aluminium electrodes. Energy was supplied through an AC source, which provided adjustable amplitude voltage settings. The discharge intensity within the reaction tank was determined by the input power, which could be calculated

---

[41] National Center for Biotechnology Information (2023). PubChem Compound Summary for CID 7560, Fenuron. Retrieved October 2, 2023.

[42] EU Pesticides Database. Fenuron. Reg. (EC) No 1107/2009. Retrieved October 2, 2023.

[43] Feng, J., Zheng, Z., Sun, Y., Luan, J., Wang, Z., Wang, L., & Feng, J. (2008). Degradation of diuron in aqueous solution by dielectric barrier discharge. Journal of hazardous materials, 154(1-3), 1081-1089.

based on the voltage and average current from the AC power supply. All samples were meticulously prepared using purified water obtained from a Millipore Milli-Q system. In each experimental configuration, 10 mL of the solution was introduced into the reaction tank. The gaseous component present above the water surface inside the reaction tank was simply ambient air. Additionally, the solution was not buffered unless specific requirements dictated otherwise.

The degradation efficiency of diuron increased as the discharge time extended. Several factors, including the intensity of the input power, the initial pH level, and the introduction of $H_2O_2$ and $Fe^{2+}$, significantly affected it. Throughout the reaction process, the pH of the treated solution experienced a decrease. The presence of $Fe^{2+}$ led to a greater removal of TOC. Additionally, during the reaction, various substances such as $Cl^{-,}$ $NO^{3-}$, $NH^{4+}$, acetic, formic, and oxalic acids were identified, aiding in deducing the degradation pathways of diuron.

The same researchers investigated, for the first time, the degradation of diuron in aqueous solution using hybrid gas-liquid discharge. Like their previous study 'Degradation of diuron in aqueous solution by dielectric barrier discharge', they examined the effect of output power intensity, pH value, $Fe^{2+}$ concentration, $Cu^{2+}$ concentration, initial conductivity, and air flow rate on the diuron degradation efficiency. The results demonstrated that the efficiency of diuron degradation improved as the output power intensity increased and pH values decreased.

In 2018, Magureanu, Bradu, and Parvulescu attempted to summarize the results on plasma removal of various classes of pesticides from water[44]. From the consulted literature, they conducted research and found that non-thermal plasma generated in a liquid or gas-liquid environment could be successfully used to degrade these contaminants, including isoproturon.

In the same year, Vanraes et al. optimized a downward film dielectric barrier discharge plasma reactor in combination with adsorption on activated carbon textile to minimize the production of potentially harmful oxidation by-products during the treatment of persistent pesticides (alachlor, diuron, and isoproturon) in water[45]. The generation of these by-products and the underlying reaction mechanism were examined through HPLC-TOF-MS analysis. Within the first 10 minutes of treatment, the maximum concentration of each by-product was at least two orders of magnitude lower than the initial pesticide concentration. After 30 minutes of treatment, the concentrations of these individual by-products had dropped to levels at least three orders of magnitude below the initial pesticide concentration. The proposed oxidation pathways revealed five primary stages of oxidation: dechlorination, dealkylation, hydroxylation, addition of a double-bond oxygen, and nitrification. Nitrification was highlighted as one of the main oxidation mechanisms for diuron and isoproturon during air plasma treatment. Additionally, it is noteworthy that this study was the

---

[44] Li, Z., Wang, Y., Guo, H., Pan, S., Puyang, C., Su, Y., ... & Han, J. (2021). Insights into water film DBD plasma driven by pulse power for ibuprofen elimination in water: performance, mechanism and degradation route. Separation and Purification Technology, 277, 119415.

[45] Magureanu, M., Bradu, C., & Parvulescu, V. I. (2018). Plasma processes for the treatment of water contaminated with harmful organic compounds. Journal of Physics D: Applied Physics, 51(31), 313002.

first case where the formation of nitrified intermediates in the plasma treatment of non-phenolic compounds was documented.

In the case of Fenuron, there is a scarcity of literature on this topic, which can be attributed to the restriction of fenuron use in 2008 within the European Union, likely discouraging further research on this subject. However, while experiments specifically focused on fenuron removal using plasma technology may not have been conducted, we can potentially extrapolate knowledge from research involving compounds belonging to the same family as fenuron, such as diuron.

In their study, Oturan et al. applied the advanced electrochemical oxidation method 'electro-Fenton process,' which follows a similar oxidation procedure to plasma, to three phenylurea herbicides, namely diuron, monuron, and fenuron[46]. The reactivity of these phenylurea herbicides toward hydroxyl radicals was observed to depend on the amount of chlorine substituents within the aromatic ring. The results indicated a degree of mineralization exceeding 90% after a 3-hour treatment period. Numerous aromatic by-products were identified, primarily resulting from the oxidation of the N-terminal group. These by-products were accompanied by hydroxylation of the aromatic ring and/or lateral methyl groups, as well as the dehalogenation of aromatic compounds. Subsequent reactions involved the oxidative fragmentation of the aromatic ring, leading to the formation of carboxylic acids and inorganic ions.

Subsequently, Kovács et al. comparatively evaluated various advanced oxidation processes (AOP), including UV photolysis, ozonation, heterogeneous photocatalysis, and their combinations, in a custom-made reactor using the same energy input[47]. The study focused on the oxidative transformation of phenylurea herbicides, namely fenuron, monuron, and diuron. Initial transformation rates revealed that UV photolysis was highly efficient for diuron and monuron. Ozonation demonstrated significantly higher effectiveness in fenuron transformation compared to monuron and chlorine-containing diuron. In heterogeneous photocatalysis, the decomposition rate decreased as the number of chlorine atoms in the target molecule increased.

The addition of ozone to UV-irradiated solutions and/or suspensions containing $TiO_2$ substantially improved initial degradation rates. The dehalogenation of monuron and diuron indicated that each of these methods is suitable for the simultaneous removal of chlorinated pesticides and their chlorinated intermediates. Heterogeneous photocatalysis proved effective in achieving mineralization.

---

[46] Oturan, M. A., Edelahi, M. C., Oturan, N., & Aaron, J. J. (2010). Kinetics of oxidative degradation/mineralization pathways of the phenylurea herbicides diuron, monuron and fenuron in water during application of the electro-Fenton process. Applied Catalysis B: Environmental, 97(1-2), 82-89.

[47] Kovács, K., Farkas, J., Veréb, G., Arany, E., Simon, G., Schrantz, K., ... & Alapi, T. (2016). Comparison of various advanced oxidation processes for the degradation of phenylurea herbicides. Journal of Environmental Science and Health, Part B, 51(4), 205-214.

N-methylcarbamates (NMCs)

The carbamates are a class of insecticides structurally and mechanically like organophosphate insecticides (OP)[48]. Carbamates have a toxicological presentation similar to OP poisonings, with a duration of toxicity typically less than 24 hours. Common agents resulting in toxic exposure include aldicarb, carbofuran, carbaryl, ethienocarb, fenobucarb, oxamyl, methomyl, pirimicarb, propoxur, and trimethacarb.

Regarding Carbofuran, in 2008, Lumei et al. investigated the oxidative degradation of aqueous carbofuran, a widely used toxic carbamate insecticide, by low-temperature plasma[49]. For this purpose, the authors designed an apparatus consisting of a high-voltage power supply and a reactor. The reactor vessel contained a needle-to-plate electrode system. A pointed platinum anode, with a diameter of 0.5 mm, enclosed within a quartz tube, was inserted into the bottom of the reactor from one side to initiate a glow discharge within the aqueous solution. The cathode, a 20 mm diameter graphite rod, was suspended about 40 mm above the anode. Energy was supplied by a DC power supply unit DH1722-6, providing a voltage ranging from 0 to 1000 V and a current range from 0 to 0.3 A. In the experiment, a voltage of 600 V was applied, resulting in a glow discharge and the release of a significant amount of gas (oxygen) at the tip of the anode. The reactor was equipped with an external water jacket to maintain a constant temperature of the reaction system. The carbofuran degradation process was monitored using an HPLC (Agilent 1100 LC) equipped with a diode array detector. A reverse-phase ODS-18 column (Krosmail, 250 mm×4 mm) was used for separation. The method employed a solvent mixture consisting of 40% acetonitrile in water with a pH adjusted to 3 using phosphoric acid and operated at a flow rate of 1.0 mL/min. Products were identified by comparison with known standards. The detector wavelength was set at 220 nm with a reference wavelength of 450 nm. Under these separation conditions, carbofuran showed a retention time of 3.6 minutes. The results showed that treatment and pH value alteration could lead to enhanced carbofuran degradation in solution. Furthermore, low-temperature plasma treatment efficiently demonstrated the removal of chemical oxygen demand (COD) of carbofuran in the solution.

Singh, Philip, and Ramanujam conducted a study focused on the application of plasma generated by pulsed corona discharge for the rapid degradation of carbofuran from an aqueous solution[50]. Carbofuran at concentrations ranging from 0.5 mg/L to 30 mg/L was effectively removed between 4 and 10 minutes after the treatment time, at an input power of 101.5 W. The degradation efficiency (2.95 g/kWh) was significantly higher for a carbofuran concentration of 10 mg/L compared to a degradation efficiency of 0.37 g/kWh for 0.5 mg/L of carbofuran. The impact of pulsed voltage, pulsed frequency, initial pesticide concentration, pH, and the influence of radical scavengers ($HCO_3$ and humic acid) were thoroughly

---

[48] National Center for Biotechnology Information (2023). PubChem Compound LCSS for CID 2566, Carbofuran. Retrieved September 28, 2023.

[49] Lumei, P., Jinzhang, G., Yusen, H., Huiguang, L., Wen, X., & Xingmin, W. (2008). Oxidation degradation of aqueous carbofuran induced by low temperature plasma. Plasma Science and Technology, 10(3), 348.

[50] Singh, R. K., Philip, L., & Ramanujam, S. (2016). Rapid removal of carbofuran from aqueous solution by pulsed corona discharge treatment: kinetic study, oxidative, reductive degradation pathway, and toxicity assay. Industrial & Engineering Chemistry Research, 55(26), 7201-7209.

investigated. The presence of certain key intermediates confirmed the possible formation of demethylated products due to the direct impact of electrons during the degradation process. Seven intermediates were identified, and a proposed mechanism for the degradation pathway of carbamates involving oxidation and reduction processes was established. An ecotoxicity study with microalgae validated the complete detoxification of carbofuran after 14 minutes of corona discharge treatment.

Regarding Trimetacarbo, in a conducted study by Moutiq et al. aimed to determine the degradation efficacy and transformation products of carbamates treated with cold plasma in water[51]. The dissipation of three carbamates, specifically carbaryl, methiocarb, and aminocarb, was assessed in relation to treatment voltage (70, 80, and 90 kV) and duration (1 to 5 minutes) using a dielectric barrier discharge. Substantial and rapid reductions in concentrations of carbaryl, methiocarb, and aminocarb were observed after treatment with cold plasma. The highest degradation reached 50.5% for carbaryl, 99.6% for methiocarb, and 99.3% for aminocarb after 5 minutes of treatment at an applied voltage of 90 kV. Plasma light emission was evaluated through optical emission spectroscopy, revealing the generation of reactive oxygen and nitrogen species, as well as gas temperatures close to ambient levels. Most reaction intermediates were identified as oxidation products originating from the respective carbamates, and reaction pathways were proposed. Additionally, the toxicity of degradation products was examined whenever data were available.

As in previous cases, it should be noted that the scarcity of literature on this topic may be attributed to restrictions on the use of 3,4,5-trimetacarbo within the European Union, which likely has discouraged further research on this subject.

### Pesticides Triazine

The triazines are a group of pesticides used to control weeds in intensive agriculture. From a chemical perspective, they are nitrogen heterocyclic derivatives. The most well-known subgroup of triazines includes the chlorotriazines, namely simazine, propazine, atrazine, cyanazine, and ciprazine[52]. The common form of application is as a spray. Atrazine is perhaps the most widely used triazine in herbicide formulations, extensively employed in crops such as corn, hazelnut, sorghum, olive, etc. Contamination of both surface and groundwater can occur due to discharges from companies manufacturing phytosanitary products, but primarily due to their use in intensive agriculture. Among the acute effects on human health (from exposures to high concentrations in a short period), notable conditions include skin and mucous membrane disorders. However, from an environmental and water quality perspective, given the low solubility of these pesticides in water, the most significant health effects occur through exposures to very

---

[51] Moutiq, R., Pankaj, S. K., Wan, Z., Mendonca, A., Keener, K., & Misra, N. N. (2020). Atmospheric pressure cold plasma as a potential technology to degrade carbamate residues in water. Plasma Chemistry and Plasma Processing, 40, 1291-1309.

[52] Kumar, R., Kumar, N., Roy, R. K., & Singh, A. (2017). Triazines—A comprehensive review of their synthesis and diverse biological importance. Curr. Med. Drug Res, 1(1), 173.

low concentrations over a lifetime. The study will focus on the following compounds: atrazine, cybutrine, simazine, and terbutrine.

Regarding Atrazine, Mededovic and Locke investigated a pulsed corona discharge with a combination of $FeSO_4·7H_2O$ electrolyte was employed for the degradation of atrazine in water[53]. The plasma was formed between the point-to-plane electrode immersed in the liquid. The authors claimed that the addition of $FeSO_4·7H_2O$ led to the complete removal of the target compound caused by the Fenton reaction between ferrous ions and hydrogen peroxide generated by plasma.

Vanraes et al. evaluated atrazine degradation induced by DBD plasma in the presence of nanofiber polyamide adsorption membranes[54]. The plasma was generated in dry air over a thick water film introduced into the membrane. Degradation was found to increase with the addition of the nanofiber polyamide membrane compared to plasma alone. The main influence of the membrane was to expose contaminants absorbed in the membrane to the plasma. They identified deethylatrazine and ammelide as by-products in the degradation process.

Subsequently, Feng and colleagues investigated the degradation of atrazine in aqueous solution using a plate-type DBD plasma reactor[55]. The DBD plasma was generated at the gas-liquid interface of the formed water film. After 14 minutes of discharge at a power level of 200 W, atrazine was efficiently degraded, exhibiting a degradation rate of 99%. It was confirmed that both the degradation rate and the G value (energy efficiency for 90% degradation of atrazine) increased dramatically with the addition of $Fe^{2+}$. However, a significant decrease in the rate constant and G value was observed with the addition of radical scavengers (tert-butyl alcohol, isopropyl alcohol, or $Na_2CO_3$). Aqueous levels of $O_3$ and $H_2O_2$ generated were determined, promoting atrazine degradation. Declorination, hydroxylation, dealkylation, and alkyl oxidation processes were involved in the atrazine degradation pathways.

In 2021, Wang et al. designed a persulfate (PS)-activated DBD integrated with microbubbles (MB) to decompose atrazine from aqueous solutions[56]. Under specific conditions, including a discharge power of 85 W, a PS concentration of 1 mM, and an air flow rate of 30 mL/min, the degradation efficiency reached 89% after a 75-minute treatment. The heat generated by the DBD process contributed to atrazine removal. Additionally, the impact of varying PS dosage, discharge power, and initial pH values on atrazine removal was evaluated. The calculated energy efficiency demonstrated cost-effectiveness and potential for treating

---

[53] Mededovic, S., & Locke, B. R. (2007). Side-chain degradation of atrazine by pulsed electrical discharge in water. Industrial & engineering chemistry research, 46(9), 2702-2709.

[54] Vanraes, P., Willems, G., Daels, N., Van Hulle, S. W., De Clerck, K., Surmont, P., & Leys, C. (2015). Decomposition of atrazine traces in water by combination of non-thermal electrical discharge and adsorption on nanofiber membrane. Water Research, 72, 361-371.

[55] Feng, J., Jiang, L., Zhu, D., Su, K., Zhao, D., Zhang, J., & Zheng, Z. (2016). Dielectric barrier discharge plasma induced degradation of aqueous atrazine. Environmental Science and Pollution Research, 23, 9204-9214.

[56] Wang, Q., Zhang, A., Li, P., Héroux, P., Zhang, H., Yu, X., & Liu, Y. (2021). Degradation of aqueous atrazine using persulfate activated by electrochemical plasma coupling with microbubbles: removal mechanisms and potential applications. Journal of Hazardous Materials, 403, 124087.

1 litre of atrazine-contaminated wastewater. The presence of $SO_4^{2-}$, $Cl^-$, $CO_3^{2-}$, and $HCO_3^-$ had adverse effects, while the presence of MBs and humic acid had a positive influence on the process.

In the study of Cybutrine, Giardina, Tampieri, Marotta, and Paradisi subjected Irgarol (Irg) to non-thermal plasma (NTP) treatment in air, both alone and in the presence of $TiO_2$[57]. A dielectric barrier discharge reactor, powered by AC voltage (18 kV, 50 Hz), was used to generate non-thermal plasma directly on the surface of the aqueous solution of Irgarol undergoing treatment. Given the rapid degradation of Irgarol observed under the experimental conditions used, kinetic experiments failed to identify any acceleration in the degradation rate attributed to titania-induced photodegradation. However, the authors demonstrated that pre-adsorption of Irgarol onto titania provides a way to substantially increase the efficiency of non-thermal plasma-induced Irgarol degradation, a finding that could have practical implications. This phenomenon seems to be related to the acidic nature of $TiO_2$, which increases the solubility of Irgarol by enhancing the ionization ratio, $[IrgH^+]/[Irg]$. Through product analysis using LC/ESI-MSn, they were able to detect and identify numerous intermediate products generated during the degradation of Irgarol. This allowed them to propose several competing reaction pathways for the non-thermal plasma-induced advanced oxidation process applied to Irgarol. The degree of mineralization to $CO_2$ was determined by Total Carbon analysis, and it was found to reach 95% after 5 hours of treatment of Irgarol solutions with an initial concentration of 5.10-6 M. These findings confirmed the ability of their NTP reactor prototype to mineralize persistent organic contaminants.

In 2015, Vanraes et al. described the effect of input power on the energy efficiency of atrazine degradation and the formation of by-products in a DBD reactor with activated carbon textile and additional ozonation[58]. As indicated by the decomposition kinetics from GC-MS analysis and power calculations, up to 40.5% of the total atrazine decomposition was attributed to plasma gas bubbling, and the energy removal efficiency of atrazine from the reactor remained relatively constant at around 3.7 mg/kWh when power was increased by a factor of 3.5. However, the abundance of all by-products (including simazine amide, atrazine amide, deethylatrazine, and diethylatrazine, detected through HPLC-MS analysis) was found to decrease significantly with the increase in power.

Studies by Roccamante et al. and Ruíz-Delgado et al., respectively, enhanced the degradation of a mixture of CoECs (diclofenac, terbutryn, pentachlorophenol, and chlorfenvinphos) through the application of

---

[57] Giardina, A., Tampieri, F., Marotta, E., & Paradisi, C. (2018). Air non-thermal plasma treatment of Irgarol 1051 deposited on TiO2. Chemosphere, 210, 653-661.

[58] Vanraes, P., Willems, G., Nikiforov, A., Surmont, P., Lynen, F., Vandamme, J., ... & Leys, C. (2015). Removal of atrazine in water by combination of activated carbon and dielectric barrier discharge. Journal of hazardous materials, 299, 647-655.

ozone in the presence of solar radiation[59], achieving 90% removal after 120 minutes of treatment at circumneutral pH[60].

## Inhibitor of dihydrofolate reductase

Some dihydrofolate reductase inhibitors are used to treat cancer, as they are substances that can accumulate in cancer cells and prevent them from using folate[61]. Folate is a nutrient needed by rapidly multiplying cells to synthesize DNA. Blocking the use of folate helps prevent the formation of cancer cells and can destroy them. A dihydrofolate reductase inhibitor is a type of antifolate. It is also called a DHFR inhibitor. One of the inhibitors is Trimethoprim-d9[62]. As in the previous cases, it should be noted that the scarcity of bibliographic material on this topic may be attributed to restrictions on the use of Trimethoprim-d9 within the European Union, which have likely discouraged further research on this subject.

## Non-Steroidal Anti-Inflammatory Drugs (NSAIDs)

Non-Steroidal Anti-Inflammatory Drugs are a chemically heterogeneous group of drugs that, in addition to their anti-inflammatory properties, also act to a greater or lesser extent as analgesics and antipyretics. NSAIDs work by relieving pain through their analgesic action, reducing inflammation through their anti-inflammatory action, and lowering fever through their antipyretic action. NSAIDs can be classified in various ways, with one of the most common classifications based on their chemical structure. They are grouped into salicylates, para-aminophenols, pyrazolic derivatives, propionic acid derivatives, etc. One of the most important NSAIDs currently is ibuprofen.

Li et al. investigated the removal of Ibuprofen using Dielectric Barrier Discharge (DBD) plasma in a water film through power pulses[63]. Firstly, the degradation performance of IBP was assessed based on various operating parameters. Improvements in input power, frequency, duty cycle, and solution flow led to enhanced ibuprofen removal. Higher degradation efficiency was achievable with low ibuprofen concentration and neutral pH conditions. The advantages of this technology for ibuprofen removal are evident, as 96.1% of the drug could be reduced in just 30 minutes and the energy efficiency in the study

---

[59] Roccamante, M., Salmeron, I., Ruiz, A., Oller, I., & Malato, S. (2020). New approaches to solar Advanced Oxidation Processes for elimination of priority substances based on electrooxidation and ozonation at pilot plant scale. Catalysis Today, 355, 844-850.

[60] Ruíz-Delgado, A., Roccamante, M. A., Oller, I., Agüera, A., & Malato, S. (2019). Natural chelating agents from olive mill wastewater to enable photo-Fenton-like reactions at natural pH. Catalysis Today, 328, 281-285.

[61] Schweitzer, B. I., Dicker, A. P., & Bertino, J. R. (1990). Dihydrofolate reductase as a therapeutic target. The FASEB Journal, 4(8), 2441-2452.

[62] Gangjee, A., Shi, J., Queener, S. F., Barrows, L. R., & Kisliuk, R. L. (1993). Synthesis of 5-methyl-5-deaza nonclassical antifolates as inhibitors of dihydrofolate reductases and as potential antipneumocystis, antitoxoplasma, and antitumor agents. Journal of medicinal chemistry, 36(22), 3437-3443.

[63] Li, Z., Wang, Y., Guo, H., Pan, S., Puyang, C., Su, Y., & Han, J. (2021). Insights into water film DBD plasma driven by pulse power for ibuprofen elimination in water: performance, mechanism and degradation route. Separation and Purification Technology, 277, 119415.

reached up to 0.243 g/kWh. In summary, it can be stated that the DBD plasma process with a water film is a potential technology for remediating ibuprofen-contaminated wastewater.

Benzamide

Benzamide is a white, slightly water-soluble organic solid compound with the molecular formula $C_7H_7NO$. The compound is used for the treatment of multiple sclerosis and ankylosing spondylitis[64]. A drug derived from benzamide is amisulpride. Oral tablets of amisulpride are used in European countries to treat acute and chronic schizophrenic disorders, as well as negative symptoms secondary to mental health disorders such as affective disorders, depressive mood, and mental retardation. As in previous cases, it should be noted that the shortage of bibliographic material on this subject may be attributed to restrictions on the use of Amisulpride within the European Union, which likely have discouraged further research on this topic.

## 2.3 Technology: Membrane Filtration

A membrane is, according to the European Membrane Society, an intermediate phase that separates two phases and/or acts as a passive or active barrier to the transport of substances between the phases. In practice, a membrane is a barrier that moderates the permeation of species in contact with it. This semi-permeable interface can be homogeneous or heterogeneous, dense or porous, organic or inorganic, liquid or solid, etc. The transport of substances from one phase to another occurs when a driving force (usually a pressure or concentration gradient) is applied. Finally, the unit containing the membrane is called module. The mixture to be treated is called feed, the retained is the fraction retained by the membrane and the permeate is the fraction that passes through the membrane.

### 2.3.1 Types of membrane filtration technologies

The most common membrane technology processes are microfiltration, ultrafiltration, nanofiltration, reverse osmosis and electrodialysis. The membrane is, together with the driving force, the main factor determining the type of application in which it can be used. Microfiltration is used when the particle size to be retained is greater than 100 nm, combining a large pore size membrane (which has low hydrodynamic resistance and high permeability), together with low hydrostatic pressure gradients, which are sufficient to obtain a high flux. In ultrafiltration, macromolecules (molecular weight between $10^4$ and $10^6$ Da) are separated from an aqueous solution. Thus, the pore size of the membrane must be smaller, so the hydrodynamic resistance increases, and higher-pressure increments are necessary. If reduced molecular weight compounds of similar size should be separated, reverse osmosis is required. In this

---

[64] Guo, C., Fulp, J. W., Jiang, Y., Li, X., Chojnacki, J. E., Wu, J., & Zhang, S. (2017). Development and characterization of a hydroxyl-sulfonamide analogue, 5-chloro-N-[2-(4-hydroxysulfamoyl-phenyl)-ethyl]-2-methoxy-benzamide, as a novel NLRP3 inflammasome inhibitor for potential treatment of multiple sclerosis. ACS chemical neuroscience, 8(10), 2194-2201.

process, the membranes used have a very small pore size, reducing the permeability, where very high-pressure gradients must be applied. Typical pressure gradients and permeability values for these processes are given in Table *2*.

Table 2: Range of pressure gradients and permeabilities in various membrane processes where pressure is the driving force.

| Process | Permeabilities range ($L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$) (temperature 20˚C) | Pressures range (bar) |
|---|---|---|
| Microfiltration | >50 | 0.1-2.0 |
| Ultrafiltration | 10-50 | 1.0-5.0 |
| Nanofiltration | 1.4-12 | 1.0-20 |
| Reverse Osmosis | 0.05-1.4 | 10-120 |

Membrane technology is one of the most effective water treatment technologies that has been extensively used for micropollutant removal, according to Khan et al.[65]. Nanofiltration (NF) and reverse osmosis (RO) are the classical types of pressure-driven membrane processes used for the removal of micropollutants, including pesticides, as most of these organic micropollutants have molecular sizes close to 1 nm. Particularly, RO has demonstrated high removal efficiency of >90% for a wide spectrum of trace organic compounds, including those with low molecular weight of <200 g/mol [66]. Both pressure-driven processes (NF and RO) can treat pesticide-containing wastewater but principally NF offers higher specific water fluxes due to the structural variation in the membrane selective layer. Nevertheless, NF membranes always reject micropollutant at lower efficiency than their RO equivalents so may not be feasible as a standalone system for the treatment of trace organic compounds. In the case of NF, advantages are related to the no need for using chemicals or other inputs and the easiness of upscale and operation However, some considerations should be taken into account due to membrane fouling and the treatment of concentrates

---

[65] JUDD, S., JEFFERSON, B. Membranes for industrial wastewater recovery and re-use. Oxford: Elsevier Ltd, 2003.

[66] KHAN, F.S.A. et al. A comprehensive review on micropollutants removal using carbon nanotubes-based adsorbents and membranes. J. Environ. Chem. Eng., 9, Article 106647, 2021.

(retentate) and/or their final disposal[67,68]. For RO, limitations are the lower permeation flux, durability, fouling and high cost of membranes[69,70].

Emerging membrane technology such as forward osmosis (FO) and membrane distillation which features some attractive advantages such as low energy consumption and less fouling tendency have been increasingly used as alternative to pressure-driven membrane processes for water and wastewater treatment[71,72]. Interestingly, there has been a surge in applying FO as a tool for pesticide removal[73].

The transportation of solutes across a membrane is governed by their solubility in the membrane and diffusion through the membrane. As schematically presented in *Figure 14*, the interactions of solutes and membrane, which involve size exclusion, electrostatic repulsion and adsorption, are the main factors dictating the solution-diffusion phenomena.

---

[67] Shin, M. G. et al. Critical review and comprehensive analysis of trace organic compound (TOrC) removal with polyamide RO/NF membranes: Mechanisms and materials. Chemical Engineering Journal, 427, 130957, 2022. https://doi.org/10.1016/j.cej.2021.

[68] COUTO, C.F. et al. A critical review on membrane separation processes applied to remove pharmaceutically active compounds from water and wastewater. J. Water Process. Eng., 26, 156-175, 2018.

[69] Van der Bruggen, B., Vandecasteele, C. Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. Environ. Pollut., 122 (3), 435-445, 2003.

[70] Brovini, E.M., Moreira, F.D., Martucci, M.E.P., de Aquino, S.F. Water treatment technologies for removing priority pesticides Journal of Water Process Engineering, 53, 103730, 2023.

[71] Wenten, I.g. Reverse osmosis applications: prospect and challenges. Desalination, 391, 112-125, 2016.

[72] TIBI, F. et al. Fabrication of polymeric membranes for membrane distillation process and application for wastewater treatment: Critical review. Process Safety and Environmental Protection, 141, 190-201, 2020.

[73] Couto, C. F. et al. Assessing potential of nanofiltration, reverse osmosis and membrane distillation drinking water treatment for pharmaceutically active compounds (PhACs) removal. Journal of Water Process Engineering, 33, 101029, 2020.

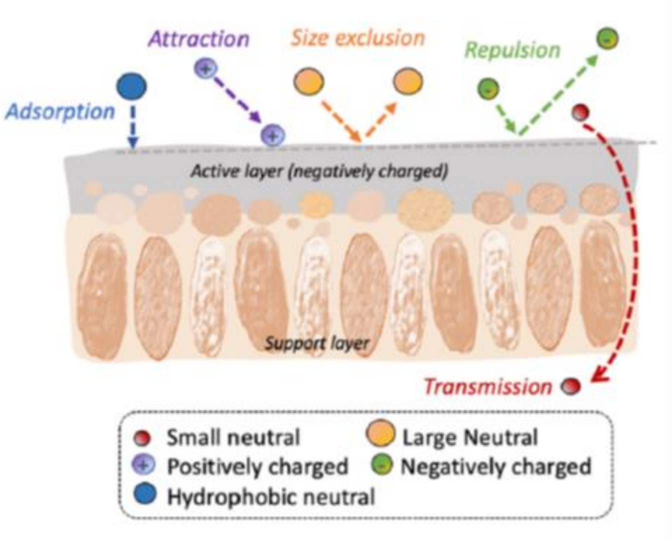


Figure 14: Schematic illustration of the possible interaction of pesticide compounds with the surface of TFC membranes (polamide-based membranes typically used in RO and NF) [73].

It has been generally agreed that size exclusion is one of the most important mechanisms responsible for the rejection of pesticides[74]. However, the separation performances of membranes are strongly governed by the physicochemical properties of both membranes and pesticide compounds. Therefore, the removal efficiency for specific types of pesticides can be greatly varied from one membrane to another. The characteristics of pesticides in terms of their molecular size, solubility, functional groups and charge should be carefully considered in a membrane filtration process. In the case where a particular type of membrane is inadequate to achieve the objective, multiple-stage filtration using different types of membranes can be considered to deal with the complex feedwater. Moreover, the operating conditions of a given membrane process have considerable effects on the separation performance and solute rejection mechanisms, so it could change the viability of the process.

Related to the removal of pharmaceutical residues, according to the literature[75], NF and RO are also efficacious methods. The membranes pore size range for NF and RO is approximately 0.001–0.002 µm and under 0.5 nm, respectively. Thus, the pharmaceutical compounds in µm particulate size are readily rejected using these membranes. Moreover, as specified by some works, some ultrafiltration (UF) processes are used in the removal of pharmaceuticals, although most of molecular sizes of pharmaceutical are smaller than their MWCO (UF typically has pores in the range of 0.002–0.10 µm), confirming that the physicochemical properties (e.g., hydrophobicity and polarity) of the pharmaceutical also play an important role in the wastewater treatment using UF membrane: hydrophobic compound absorbed onto

---

[74] GOH, P.S., AHMAD, N.A., WONG, T.W., YOGARATHINAM, L.T., ISMAIL, A.F. Membrane technology for pesticide removal from aquatic environment: Status quo and way forward. Chemosphere, 307, 136018, 2022.

[75] PLAKAS, K.V. et al. Removal of,pesticides from water by NF and RO membranes — A review. Desalination, 287, 255-265, 2012.

particulates or colloids that cannot pass through the membranes pore would be readily rejected. In conclusion, polarity of solute pharmaceutical also influences the electrostatic interaction of membrane rejection. Nevertheless, the use of membrane system as single operation is not capable to sustain all the contaminate pharmaceutical residue due to; (a) hydrophobic or absorptive mechanism on the membrane surface; (b) electrostatic interaction that contributes to the concentration polarization on membrane surface; and (c) potentially smaller size compound passing through the pore membrane.

Moreover, the fouling phenomena which generally happened when the cake formation on the membrane surface significantly reduced the permeability and the overall separation performance[76]. The chemical cleaning and membrane back-flushing were commonly used to overcome the fouling phenomena[77]. Finally, the disposal of concentrates after membrane separation processes become another problem issue which remains unsolved until now.

Owed to most suitable membrane processes to removal pesticides and pharmaceutical residues are NF and RO, and that ceramic membranes are usually in the range of microfiltration and ultrafiltration, practically all treatments found in the bibliography have been conducted with polymeric membranes.

The factors which most affect the removal of species by NF/RO membranes are listed below:

- Membrane characteristics:
    - Molecular weight cut-off (MWCO), expressed in Dalton, which indicates the molecular weight of a hypothetical non-charged solute that is 90% rejected. Membranes with a MWCO varying between 200 and 400 Da are considered appropriate for adequate removal of organic micropollutants (i.e., pesticides) from water.
    - Porosity.
    - Surface charge. Most of the commercial polymeric membranes are characterized by a negative charge which tends to minimize the adsorption of negatively charged compounds, enhancing the overall rejection performance.
    - Polymer composition, which defines the physico-chemical interactions in the system.
- Molecule properties: Molecular weight and size, polarity and hydrophobicity/hydrophilicity.
- Feed water composition: pH, ionic strength, and the presence of organic.
- Effect of the membrane fouling.
- Influence of the filtration system operating parameters: water permeation flux and feed-stream velocity in the crossflow mode of filtration.

---

[76] Rosman, N., Salleh, W.N.W., Mohamed, M.A., Ismail, A.F., Harun, Z. Hybrid membrane filtration-advanced oxidation processes for removal of pharmaceutical residue. Journal of Colloid and Interface Science, 532, 236–260, 2018.

[77] KOOPS, G.H. et al. Integrally skinned polysulfone hollow fiber membranes for pervaporation. J. Appl. Polym. Sci., 54, 385-404, 1994.

### 2.3.2 Membrane filtration of selected CoEC

In the next sections, studies related to the removal of selected contaminants of emerging concern are summarised in tables, where the most important factors are included.

#### Phenylurea pesticides

In this group, 3 types of pesticides have been selected: diuron, isoproturon and fenuron. Next, the different membrane filtration treatments found in the literature to remove them from water are discussed.

Diuron

The molecule of diuron presents a molecular weight of 233 Da, a size of 0.781 nm, with a linear molecular structure, and a high polarity (5.87 D)[78]. Because of the characteristics of this molecule, the interaction with the properties of the membrane could cause a low retention of diuron, owed to the dipole moment, which could make easier the transfer across the membrane due to electrostatic interactions, and the molecular structure (higher length and a lower width), providing a more linear form to the molecule, leading to a lower steric retention[79]. However, certain authors have pointed out that those molecules with a high dipole moment are much less restrained by the membranes and that this effect is independent of the membrane charge[80]. According to the literature revised, the low molecular size as well as relatively high polarity facilitates diuron to pass through the charged membranes.

Best results of the revised literature are shown in *Annex 2*, which present the NF variables of diuron removal by commercial membranes.

Isoproturon

The molecule of isoproturon presents a molecular weight of 207 Da, a size of 0.810 nm and a polarity lower than diuron (3.31 D). According to the literature, the isoproturon usually experiences better separation compared to diuron because of lower dipole moment, though it has a larger molecular size. *Annex 2* presents the NF variables of isoproturon removal by commercial membranes.

#### N-methyl carbamates

In this group, 2 types of pesticides have been selected: carbofuran and 3,4,5-Trimethacarb. Next, the different membrane filtration treatments found in the literature to remove them from water are discussed.

---

[78] Mehta, R., Brahmbhatt, H., Mukherjee, M., Bhattacharya, A. Tuning separation behavior of tailor-made thin film poly(piperazine-amide) composite membranes for pesticides and salts from water. Desalination 404, 280–290, 2017.

[79] Musbah, I., Cicéron, D., Saboni, A., Alexandrova, S. Retention of pesticides and metabolites by nanofiltration by effects of size and dipole moment, Desalination, 313, 51-56, 2013.

[80] Boussahel, R., Montiel, A., Baudu, M. Effects of organic and inorganic matter on pesticide rejection by nanofiltration. Desalination, 145, 109–114, 2002.

Carbofuran

The molecule of carbofuran presents a molecular weight of 221 Da and an intermediate polarity. The only results found in the revised literature are shown below. *Annex 2* presents the NF variables of carbofuran removal by polymeric commercial membranes and the variables of carbofuran removal of the only reference found related to ceramic membranes.

3,4,5-Trimethacarb

The molecule of 3,4,5-trimethacarb presents a molecular weight of 193 Da. The only result found in the revised literature is shown in *Annex 2*.

### Triazine pesticides

In this group, 4 types of pesticides have been selected: atrazine, cybutryne, simazine and terbutryn. Next, the different membrane filtration treatments found in the literature to remove them from water are discussed.

Atrazine

The molecule of atrazine presents a molecular weight of 215 Da (length 10.36 Å and width 8.02 Å) and polarity lower than diuron. Best results of the revised literature are shown in *Annex 2*, where it is presented the NF variables of atrazine removal by commercial membranes and the UF, RO and FO variables of atrazine removal. Finally, *Annex 2* shows the variables of atrazine removal of the only reference found related to ceramic membranes.

Cybutryne

A bibliographic search has been carried out in different search engines; no papers nor articles or PhD dissertations related to the membrane filtration of cybrutryne appeared. According to the literature, cybutryne could also be named as irgarol. *Annex 2* shows the variables of cybutryne removal of the only reference found combining the term “irgarol” with “membrane” or “filtration” in the different search engines used in this work.

Simazine

The molecule of simazine presents a molecular weight of 201 Da (length 10.34 Å and width 7.49 Å) and polarity lower than diuron. Best results of the revised literature are shown in Annex 2, which presents the NF variables of simazine removal by commercial membranes.

Terbutryn

The molecule of terbutryn presents a molecular weight of 241 Da. The only results found in the revised literature is shown in *Annex 2*.

### Dihydrofolate reductase inhibitor

Trimethoprim-d9 is the only compound selected from this class of CoEC. Thimethoprim presents a molecular weight of 290 Da. Next, best results of the different membrane filtration treatments found in the literature to remove it from water are shown in: *Annex 1* presents the NF variables of trimethoprim removal by commercial membranes and *Annex 2* displays the UF variables of trimethoprim removal, identified only with ceramic commercial membranes. Finally, *Annex 2* also shows the variables of trimethoprim removal by using RO and MBR treatments.

### Non-Steroidal Anti-Inflammatory Drugs (NSAIDs)

Ibuprofen is the only compound selected from this class of CoEC. Ibuprofen presents a molecular weight of 206 Da. Next, best results of the different membrane filtration treatments found in the literature to remove it from water are shown. *Annex 2* presents the NF variables of ibuprofen removal by commercial membranes. *Annex 2* displays the UF variables of ibuprofen removal, identified only with ceramic commercial membranes. Finally, it also shows the variables of ibuprofen removal by using RO and MBR treatment. It is remarkable that MBR treatment shows high degrees of removal, owed that ibuprofen is rapidly biodegraded.

### Benzamide

Amisulpride is the only compound selected from this class of CoEC. This compound is sold under different brand names (Barhemsys, Solian, Socian, Deniban, etc.), which have been included in the bibliographic search. However, no papers, articles or PhD dissertations related to the membrane filtration of amisulpride appeared.

In summary, according to the revised literature, membrane technology is an effective treatment to remove most of the selected pollutants included in this review. All of them, except 3,4,5-trimethacarb (N-methyl carbamate) and cybutryne (triazine pesticide), can be separated up to 90% by nanofiltration polymeric commercial membranes, depending on the selected membrane and the process parameters. Nevertheless, these 2 compounds can be eliminated by reverse osmosis, together with other compounds as atrazine (triazine pesticide), trimethoprim (dihydrofolate reductase inhibitor) or ibuprofen (non-steroidal anti-inflammatory drug), being the rejection higher than 90%. Other processes, as forward osmosis (FO) or membrane bioreactor (MBR), have been scarcely used with high rejections, being atrazine (FO) and ibuprofen (MBR) the analysed compounds.

Regarding to filtration with ceramic membranes, just 4 compounds have been studied using them. Carbofuran and atrazine have been separated by laboratory made or modified ceramic membranes with rejections up to 85%. Separation up to 60% of trimethoprim and ibuprofen has been obtained by means of commercial UF ceramic membranes.

# 3.0 Technical specifications of sensors

Detection and quantification of pollutants is the first step for an efficient remediation strategy. Of course, it would be desirable to eliminate the generation of pollutants or, at least, reduce it to the minimum. However, the generation of residues is a problem that needs to be addressed from all different perspectives.

As mentioned earlier, effective monitoring of pollutants is essential for an efficient remediation strategy. Firstly, accurate quantification of the pollutant is essential before and after any elimination treatment. Secondly, real-time, in-situ monitoring allows for timely adjustments to the remediation strategy.

Several sensors will be developed within the iMERMAID framework for an in situ and real time monitorization.

## *3.1 Electrochemical Sensor dedicated to organic micropollutants*

### *3.1.1 Sensor description*

The evaluation of the level of several organic micropollutants in aquatic media is reaching significant interest, particularly influent/effluent, which ends in seawater. The aim of this sensor is to monitor these contaminants before and after an effective treatment (WP3 and WP4 activities). This assessment involves employing advanced analytical techniques such as chromatography to check electrochemical sensors performances dedicated to on-site experiments. Traditionally, the evaluation of water source pollution, encompassing organic and micropollutants, relies on conventional laboratory analytical techniques, such as liquid or gas chromatography coupled to mass spectrometry (LC/MS, GC/MS). This approach could be supplemented by the development of customized electrochemistry to quantify water stream contamination and assess the efficiency of applied treatments in real time. As the demand for efficient, in-situ and real-time monitoring systems rises, electrochemical sensors emerge as versatile devices providing valuable insights into water quality (see *Figure 15*).

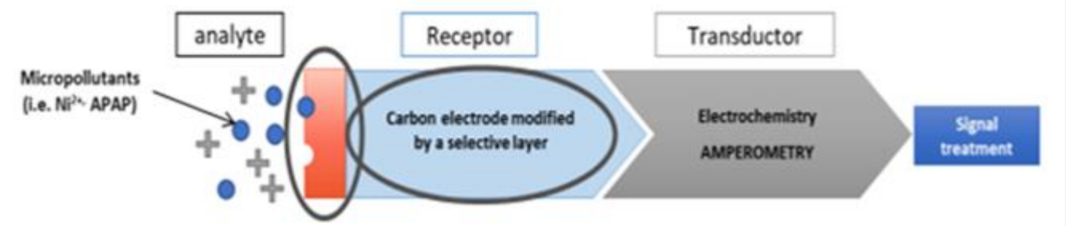


Figure 15: Scheme of electrochemical sensor for quantification of micropollutants.

Electrochemical sensors (ECS) enhance analytical performance by eliminating slow preparation and expensive reagents, providing affordable, portable, and easy-to-use tools. These sensors find applications in clinical diagnosis, food analysis and environmental monitoring. Operating on the principle of electrochemical reactions at a sensing electrode, these sensors offer sensitivity in sub-micromolar concentrations. Achieving reliability, low response time, simplicity, space-saving, and cost-effectiveness are crucial for sustainable micropollutant measurements. In challenging environments, the focus shifts to sensor regeneration and robustness for continuous analysis.

Among analytical techniques, electrochemical methods offer several advantages, making them advisable for water quality assessment in terms of cost, consistency, accuracy, response time, selectivity and sensitivity. Typically, these sensors exhibit a very high sensitivity, enabling the precise detection of trace amounts of pollutants. Additionally, the cost-effectiveness and ease of miniaturization of electrochemical sensors make them suitable for widespread deployment, facilitating a dense network for comprehensive water quality monitoring. The adaptability of electrochemical sensors to various environmental conditions enhances their reliability in diverse aquatic settings, allowing for in situ analyses and providing the opportunity to modify the electrode surface to assess micropollutants at trace levels. The selectivity of electrochemical sensors enables the discrimination of specific contaminants, contributing to a nuanced understanding of water composition. This selectivity is often achieved through the modification of sensor surfaces with tailored materials, enhancing the sensor's ability to target pollutants, even in very complex aqueous matrixes.

Despite their considerable advantages, electrochemical sensors are facing challenges like electrochemical interferences and limited long-term stability and they are not without limitations. The need for periodic calibration and maintenance to ensure accuracy also poses logistical challenges, particularly in remote or inaccessible locations. Additionally, the lifespan of certain sensor components may be limited, necessitating regular replacement and increasing operational costs.

Data will be stored in compliance with the formats and specifications detailed by the iMERMAID users.

Electrochemical sensors are currently undergoing testing to optimize the development of superior ECS tailored for a specific isolated organic micropollutant or a combination of micropollutants in mixtures. Fourth different types of ECS are being evaluated in this study:

Glassy Carbon Electrodes (GCEs):

Glassy carbon electrodes are commercially available glassy carbon substrates prepared through a meticulous polishing process involving successive slurries of 1 and 0.05 µm alumina powder under polishing cloth. The electrodes undergo sonication in deionized water for 5 minutes between slurries. GCEs serve as a benchmark material for carbon sensors in electrochemical research.

Carbon Paste Electrodes (CPEs):

Carbon paste electrodes consist of commercial Teflon tubes made of FEP resin, featuring a cylindrical cavity filled with a carefully blended mixture of carbon graphite powder and a binder, such as silicon oil. The electrode surface is easily renewable through polishing on a weighing paper. 20 analyses are possible with the quantity of carbon paste preparation done. The main default of such kind of sensor is its poor selectivity.

Homemade Ultramicroelectrodes (HUMEs):

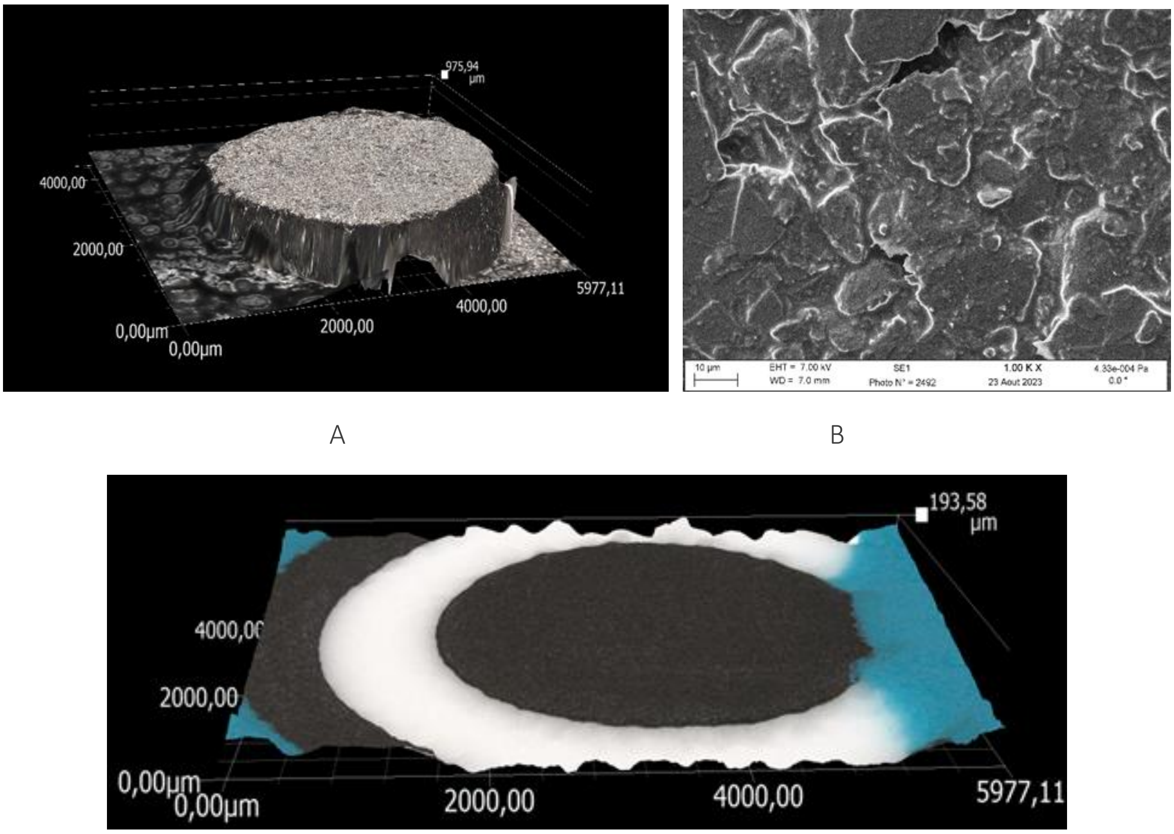
Homemade ultramicroelectrodes are one-micrometer-dimension electrodes, specifically carbon fibers with a diameter of 10 µm. The manufacture of HUMEs involves the assembling of a carbon fiber, a copper wire and a glass capillary tube by applying an adhesive. The assembly is meticulously arranged without damaging the carbon fiber (sensitive part of the sensor) and a quality control is systematically applied to improve the reproducibility. HUMEs prove beneficial when working with small volumes and in scenarios demanding low conductivity bulk (e.g., river water, tap water).

Screen printed electrode (SPEs):

SPEs are disposable, low-cost and portable devices that include a miniaturized display of the working, reference and counter electrodes; based on conductive substrates like carbon nano allotropes (e.g., graphite, graphene, carbon nanotube) and metals (e.g. Au, Ag, Pt). Furthermore, the volume of solution to be analysed decreased enormously from 40 mL to 50 mL. Its simplicity and robustness should engage us to develop such electrodes for the electrochemical sensors box conducting on-site experiments (see *Figure 16*).

The electrochemical sensors (GCE, CPE, HUME, SPE) have been tested previously to the iMERMAID project. In the current research, our focus is on developing carbon-based electrochemical sensors tailored for a specific pollutant or pollutant mixtures encountered on-site (i.e., Ibuprofen from pharmaceutical industry in Tunisia). During the sensor development process, modifications to the carbon surface will be implemented through techniques such as electrodeposition, electropolymerization, sorption, etc., aiming to enhance sensor performance parameters, including sensitivity, selectivity and sustainability (e.g., antifouling procedures), thereby aligning with specified regulatory requirements (e.g., EU regulation, WHO regulation) encountered to on-site experiments to be carried out. Our approach is based also on very recent knowledge by an exhaustive bibliography inspiring our research endeavours.

Although the analytical techniques operate quite well separately, it will be an opportunity to highlight their complementarities, since various types of micropollutant families (dyes, pesticides, drugs, and by-products) will be analysed. Assessing the level of those various micropollutants in water will be a good starting point in the water treatment/purification processes.



A B

C

Figure 16: A-B CPE-ECS images: 3D optical microscopy, B: 2D scanning electrochemical microscopy, C: SPE-ECS 3D image.

### 3.1.2 Contaminants to be monitored

Pharmaceutical compounds:

Electrochemical sensors play a pivotal role in the detection of pharmaceutical compounds such as Ibuprofen, Ketoprofen, Diclofenac, etc. (not exhaustive list). These sensors offer a sensitive and selective platform for quantifying these substances, leveraging electrochemical reactions at the sensing electrode. The application of electrochemical sensors provides advantages such as real-time monitoring, cost-effectiveness, and suitability for on-site analysis. Their ability to operate in complex matrices makes them valuable for pharmaceutical analysis, environmental monitoring, healthcare diagnostics and treated wastewater. Achieving reliable and rapid detection of these specific compounds underscores the importance of electrochemical sensors in advancing analytical methodologies.

Pesticides:

Electrochemical sensors serve as instrumental tools in detecting pesticides including Diuron, Fenitrothion, 3-Methyl-Paranitrophenol (not exhaustive list). Leveraging electrochemical reactions at the sensing electrode, these sensors offer a sensitive and selective means of quantifying these substances. Their aforementioned characteristics make them invaluable for environmental monitoring and agricultural practices. Electrochemical sensors play a pivotal role in advancing analytical methodologies, ensuring reliable and swift detection of specific pesticides and by-products.

PFAS:

PFAS contaminants is a big family of compounds (more than 15,000 molecules) with very different origin that can affect to environmental and human health. Those contaminants are included in both directives the Drinking Water Directive and the Water Framework Directive as a priority hazardous substance. That is the way, an electrochemical sensor will be developed to monitor PFAS (i.e., PFOS).

Others:

Further than pharmaceutical substances and pesticides, electrochemical sensors emerge as indispensable tools for the detection of various substances (the list of molecules must be determined in future analysis to be done on on-site experiments to be carried out). Operating through electrochemical reactions at the sensing electrode, these sensors provide a sensitive and selective approach to quantify these target substances. In the pool of analytical methodologies, electrochemical sensors contribute significantly to the reliable and swift detection of specific compounds, addressing diverse needs across industries.

Electrochemical sensor will be elaborated for each molecule isolated and/or for molecules in mixed solutions. Two papers were recently submitted in both *Chemosphere* and *Journal of Applied Electrochemistry*, respectively:

> *1) M. GORIN, S. MBOKOU, M. PONTIÉ et al. Application of fungal-based microbial fuel cells for biodegradation of pharmaceuticals: comparative study of individual vs. mixed contaminant solutions Chemosphere (in press, 2024) (example of recent work on GCE-ECS).*
>
> *2) H.T. BOUGNA, S. MBOKOU, M. PONTIÉ et al. Electrochemical determination of butylhydroxyanisol (BHA) using a carbon fiber microelectrode modified by electrodeposition of gold nanoparticles and poly-NiTSPc film J. Applied Electrochem. (in press, 2024) (example of recent work on HUME(ECS).*

### 3.1.3 Technical specifications

The electrochemical sensor has been developed attending to regulations and bibliography to select targeted molecules. Preparation and optimisation of the sensor for the desired application is the starting point for an appropriate definition of technical specifications.

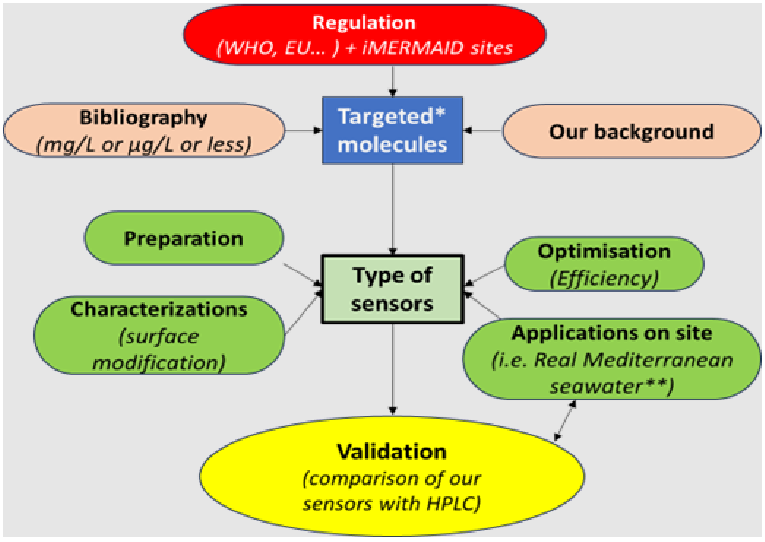


Figure 17: Methodology for electrochemical sensor development dedicated to organic micropollutants.

Table 3: Technical specifications of the ECS dedicated to organic pollutants (example of ibuprofen CPE-ECS-NFC Sensor).

| **Title** | Technical data | Comments | Confidential (Y or N) |
|---|---|---|---|
| TRL (at end of project) | 7 | M18 | N |
| Reliability | Y | Vs HPLC methods | N |
| Sensor dedicated to multicompounds (Y/N) | Y/N | Yes, if the compounds have different oxidation potentials | N |
| Repeatability | 95% | Test of 5 repetitions | N |
| Reproducibility | 96% | Test on 3 successive measurements | N |
| Sensitivity (slope)<br>(i.e., in µA. L mol$^{-1}$) | 24.72 x 10$^{-6}$ | Calibration | N |
| Limit of detection (mol.L$^{-1}$) | 11.1 x 10$^{-6}$ | S/N=3 | N |

| | | | |
|---|---|---|---|
| Limit of quantification (mol.L$^{-1}$) | 37.1 x 10$^{-6}$ | S/N=10 | N |
| Powered (Battery/main/both) | Y/N | Depends on potentiostat used | N |
| Size (L x W x H in mm) | (8 x 8 x 130) | | N |
| Weight (Kg) | 0.15 | | N |
| Operating range 1$^{*}$ | Current [µA - mA] | Range of current that could be measured when carrying out analyte measurement | N |
| Operating range 2$^{*}$ | Concentration [µM - mM] | Range of concentration to be measured with the CPE/CNF | N |
| Temperature range | [ambient temperature] | CPE-ECS-CNF works in aqueous media at ambient temperature; we mustmust check other temperatures if necessary | N |
| Type of waters (i.e. seawater, surface water, etc) | Seawater & PBS solution (0.1 M pH=7.4) | | N |
| Dedicated to which molecule(s) / application | Ibuprofen | oxidation | N |
| Data output<br>(Analog/digit) | Analog. | Curves I=f(E)<br>I= intensity; E= potential | N |
| Format (CSV; XLS,) | CSV, XLS | | N |
| Frequency | See on-site experiments | | N |
| Display (how data is displayed) | Current (A) | The measured current is linked to the analyte concentration | N |
| Reusability for few analysis Y/ N | Y | The sensor is usable for many analyses, and between two analyses, the sensor surface is renewed by polishing on the white paper | N |
| Sensor adapted to on-site measurements (Y/N) | Y/N | First developments started in lab. with the aim to adapt to on-site experiments | N |
| Protocol | Homemade sensor carbon -based (graphite) | | N |

| | | | |
|---|---|---|---|
| Interoperability with IoT | Y | | N |
| Indicative cost | 10 euros per analysis (estimation)** | | N |

**The operating range must be defined for each sensor. As an example, it could be the pH, salinity, molecular weight of the molecule, electric current of the sensor, etc.*

***as a comparison HPLC analysis cost is 100 euros/analysis*

### 3.1.4 Electrochemical sensor to organic micropollutants in iMERMAID

The electrochemical sensors dedicated to organic micropollutants (pesticides, pharmaceutical compounds, some PFAS and maybe some by-products) will be developed by the University of Angers.

The versatility of the sensor allows the detection of several contaminants. It will be deployed in three different Use Cases:

1- In Use Case 1, which consists of a WWTP located in San Esteban de Litera (Spain). The WWTP treats the waters resulting from the leachate and urban wastewaters mixture influent. The target molecule in this Use Case will be selected from those previously detected in the WWTP that is relevant from the point of view of the WFD and MSFD.

2- In Use Case 2, that consists in an influent produced in a pharmaceutical industry after synthesis of drugs and rinsing, cleaning operations applied to reactors and generating wastewaters. This company is in Tunis, (TUNISIA). Ibuprofen, Ketoprofen and Diclofenac are the most promising candidates for the study.

3- In Use Case 5, consisting in a leachates treatment plant that receives the leachate produced by the waste disposal and the sanitary landfill cells in Crete. Bisphenol A is one molecule candidate to electrochemical sensor development with the aim to assist on-site experiments. The target molecules in this Use Case will be selected from previously detected ones in the WWTP. Furthermore, PFAS compounds should be determined by electrochemical sensors if their presence is proven.

An option should be developed in Use Case 4. Use Case 4 corresponds to a buoy deployed in Cyprus with the purpose of monitoring environmental parameters and contaminants in the Mediterranean Sea (i.e., nitrite which is well known to be a coastal area anthropogenic pollutant). The target molecules in this Use Case will be selected from previously detected molecules at the coastal area of Limassol and/or around buoy.

## 3.2 Sensor OilSense

### 3.2.1 Sensor description

OilSense is a man-portable oil sensor based on membrane inlet mass spectrometry (MIMS). It will be developed for real-time monitoring of toxic petroleum hydrocarbons from crude oil and sunscreen agents including dissolved gases with the capability of being deployed in the field. Toxic petroleum hydrocarbons pose a great risk to water quality and aquatic biota, particularly after oil spills, while dissolved gases are indicators for relative rate of degradation of hydrocarbons in water.

BIOS has previously developed portable MIMS systems for identification of volatile organic compounds (VOCs) in air, breath, and water samples. Detection of VOCs in air using MIMS was successfully shown for simulants of drugs (e.g., cocaine, phencyclidine) and explosives (e.g., C4, TNT)[81]. During the H2020 PROTEIN EU project[82], a MIMS system was developed for detection of VOC concentrations (e.g., acetone, ethanol, isoprene, n-pentane) in exhaled human breath for food impact assessment[83]. During the oil-in-water project[84], MIMS was also used for identification of toxic hydrocarbons from crude oil in water.

Compared to GC/MS, MIMS-based oil sensor offers real-time monitoring, no sample preparation, analysis time within seconds and sensitivity down to parts per billion (ppb) in water and parts per trillion (ppt) in air. Also, the price of the portable MIMS system is at least three times less than that for well-known portable GC/MS systems such as Torion from PerkinElmer[85] and HAPSITE ER from Inficon[86].

A novel MIMS sample probe from BIOS will be simulated, designed, built, and tested for fast separation of a wide range of petroleum hydrocarbons and a custom membrane sample inlet will be built for detection and in-field monitoring of volatile organic compounds (VOCs) in seawater and will be temperature-controlled to provide greater sensitivity and maximize the number of detected VOCs from crude oil derivatives (e.g., BTX) and sunscreen agents (e.g., butyl methoxydibenzoyl-methane, benzophenone-3). To provide greater resolving power, a miniature temperature-programmed desorption (TPD) device will be built for enhanced identification of VOCs in complex mixtures such as diluted oil in water. Identified compounds of interest and their concentrations will be uploaded to the iMERMAID platform.

BIOS's oil sensor will be initially calibrated and tested for the most common toxic hydrocarbons from oil traces (e.g., BTX) and dissolved gases (e.g., $O_2$ and $CO_2$) to assess its functionality. It will also be tested with samples from the monitoring platform in the Mediterranean Sea basin to assess its capability. The developed sensor will have the full functionality of a lab-scale instrument.

---

[81] B. Brkić, N. France, S. Giannoukos and S. Taylor, An optimised quadrupole mass spectrometer with a dual filter analyser for in-field chemical sniffing of volatile organic compounds, Analyst 143, 3722-3728 (2018).

[82] Personalized nutrition for healthy living (PROTEIN), Horizon 2020, Innovation Action, GA 817732, (2018-2022), https://www.protein-h2020.eu/.

[83] M. Jakšić, A. Mihajlović, Đ. Vujić, S. Giannoukos, B. Brkić, Membrane inlet mass spectrometry method for food impact assessment on specific volatile organic compounds in exhaled breath, Analytical and Bioanalytical Chemistry 414, 6077-6091 (2022).

[84] B. Brkić, N. France, S. Taylor, Oil-in-Water Monitoring Using Membrane Inlet Mass Spectrometry, Analytical Chemistry 83, 6230-6236 (2011).

[85] Torion T-9 Portable GC/MS, Perkin Elmer, https://www.perkinelmer.com/product/torion-t-9-portable-gc-ms-instrument-ntsst090500.

[86] HAPSITE ER, Inficon, https://www.inficon.com/en/products/chemical-detection-and-utility-monitoring/hapsite-er.

During the project, the oil sensor will be used for project pilots as part of Use Case 4 and Task 4.3. Multi-component mass spectra obtained during the pilots will be resolved and quantified using a suitable in-house built data processing software. Project research will be carried out together with lab-based GC/MS to identify a list of key VOCs emitted by crude oil derivatives and sunscreen agents. This will enable in-field monitoring of trends of target VOCs related to different pilot locations.

### 3.2.2 Contaminants to be monitored

iMERMAID will deliver innovative solution for in-field identification of industrial crude oil derivatives and sunscreen agents defined in the Directive 2008/105/EC as part of the Watch List for environmental quality standards. The list of selected compounds to be monitoring using oil sensor is given below:

- Oil compounds (source: industries, sea traffic): Anthracene, Benzene, Toluene, Xylene, 1,2-Dichloroethane, Dichloromethane, Benzo(A)Pyrene, Trichlorobenzenes, Bisphenol-A, Tetrachloroethylene, Benzo(A)anthracene.
- Sunscreen agents (source: tourism): Butyl methoxydibenzoyl-methane, Benzophenone-3.

### 3.2.3 Technical specifications

The sampling and data acquisition will be performed on site. Output data generated by the oil sensor will be both quantitative and qualitative for target compounds. Processing of the data will be done using in-house software developed by BIOS. The data collection sampling diagram is provided in *Figure 18*, while the technical specification of the oil sensor is in Table *4*.

- Diagram:

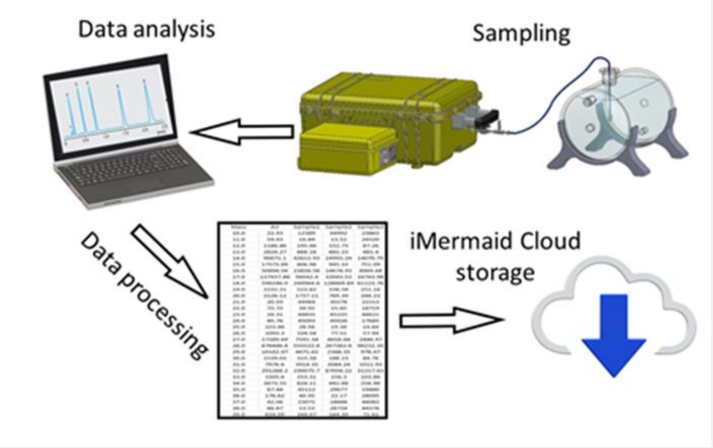


Figure 18: Scheme of data collection from BIOS sensor.

Table 4: Technical specification of the oil sensor.

| **Title** | Technical data | Comments | Confidential (Y or N) |
|---|---|---|---|
| TRL (at end of project) | 6 | Current TRL level is 4. | N |
| Reliability | Y | Reliable in controlled environment. | N |
| Sensor dedicated to multicompounds (Y/N) | Y | Compounds that can be detected include residual gases, volatile and semivolatile organic compounds (VOCs/SVOC/s). | N |
| Repeatability | Y | To be specified in detail upon completion of project pilots (due to in-field conditions). | N |
| Reproducibility | Y | To be specified in detail upon completion of project pilots (due to in-field conditions). | N |
| Sensitivity (slope)<br>(i.e., in $\mu$A. L mol$^{-1}$) | 1 to 4 × $10^{-4}$ A mbar$^{-1}$ | Depends on the type of compound. | N |
| Limit of detection | 1 to 10 ppb | Depends on the type of compound. | N |
| Limit of quantification | 5 to 50 ppb | Depends on the type of compound. | N |
| Powered (Battery/main/both) | Mains/battery | Battery operation up to 8h. | N |
| Size (L x W x H in mm) | 616 x 220 x 433 mm | Size of the final system may change due to demands of Use Case 4 for buoy operation. | N |
| Weight (Kg) | 23 kg | Weight of the final system may change due to demands of Use Case 4 for buoy operation. | N |
| Operating range 1$^{*}$ | 1 to 300 Da | Molecular weight range, where 1 Da = 1 g/mol. | N |
| Operating range 2$^{*}$ | N/A | N/A | N/A |
| Temperature range | 20 to 90 C | Temperature range for the sample probe. | N |
| Type of waters (i.e. seawater, surface water, etc) | Any type of water | | N |

| | | | |
|---|---|---|---|
| Dedicated to which molecule(s) / application | Molecules: Residual gases, all non-polar and limited number of polar VOCs/SVOCs<br>Applications: environmental, healthcare, agriculture, food safety, security, space exploration | | N |
| Data output<br>(Analog/digit) | Analogue or digital | Depends on the scan type. | N |
| Format (CSV; XLS,) | .csv | | N |
| Frequency | 1.8 to 2.2 MHz | Autotuning in frequency range. | N |
| Display (how data is displayed) | Laptop screen | - Mass spectra (raw data)<br>- Target compounds concentrations (processed data) | N |
| Reusability for few analysis Y/ N | Y | To be specified in detail upon completion of project pilots (due to in-field conditions). | N |
| Sensor adapted to on-site | Y | To be adapted for coastal and buoy operation. | N |
| Protocol | Sampling, ionisation, mass scanning, detection, data storage and processing | | N |
| Interoperability with IoT | Y | | N |
| Indicative cost | 40.000,00 EUR | | Y |

### 3.2.4 Sensor OilSense in iMERMAID

The Oilsense sensor has been developed by BioSense Institute (BIOS). It is planned to use the oil sensor in the buoy deployed in Limassol, Cyprus, which corresponds to Use Case 4.

The Oilsense will be added to the monitoring together with **satellite data: Monitoring** an extensive maritime area is a logistical and economic challenge, particularly, for small countries with limited resources, and low investment in environmental practices. Remote sensing offers the opportunity to assess a large amount of data with both a high spatial and temporal resolution.

Satellite data play an important role in detecting oil spills and monitoring water quality, leveraging advanced technologies and specialized models[87]. Copernicus Marine Environment Monitoring Service (CMEMS) provides oil spill models, but with coarse geospatial resolution. European satellites like Sentinel-1, part of the Copernicus Programme, are powerful instruments in this domain. Sentinel-1 Synthetic Aperture Radar (SAR) data can be used for detecting of oil spills even under cloud cover or at night, offering reliable tool for the large maritime regions monitoring. Sentinel-3 with its Ocean and Land Colour Instrument (OLCI) and Sea and Land Surface Temperature Radiometer (SLSTR) delivers data on sea surface temperature and colour, indicative of phytoplankton abundance and water quality estimations. These satellite capabilities are bolstered by products like the European Space Agency's (ESA) Water Colour Climate Change Initiative (CCI), which synthesizes satellite data to provide long-term, consistent records of water quality parameters, aiding in environmental monitoring and policy-making.

While satellite-based water quality products offer invaluable insights, a notable limitation is their relatively low spatial resolution. For instance, the Copernicus Sentinel-3's OLCI provides a resolution of up to 300 meters, which can be insufficient for detailed analysis in smaller water bodies or near coastlines. Similarly, the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Aqua and Terra satellites delivers water quality data at the resolution from 250 to 1000 meters, which may not capture finer-scale variations.

Addressing these limitations, the iMERMAID project aims to enhance water quality monitoring by integrating available satellite data with higher-resolution Sentinel-2 and Sentinel-1 data and sensor data collected at pilot sites. By visualizing this combined information on a dedicated dashboard, the project might improve the spatial resolution and accuracy of water quality assessment[88]. Additionally, the iMERMAID project is focused on refining machine learning models for oil spill detection using high-resolution Sentinel-1 SAR data. This adaptation will be provided for the project's pilot sites, potentially offering a more precise and reliable method for identifying and tracking oil spills. The synergy between satellite data, ground sensor measurements, and advanced machine learning techniques in iMERMAID represents a significant step towards more effective and detailed environmental monitoring and management.

## 3.3 Sensor METALSENS

### 3.3.1 Sensor description

Heavy-metal (HM) sensor: electrochemical sensor for trace heavy metals monitoring in aqueous samples.

---

[87] Adjovu GE, Stephen H, James D, Ahmad S. Overview of the Application of Remote Sensing in Effective Monitoring of Water Quality Parameters. Remote Sensing. 2023; 15(7):1938.

[88] M. Lavreniuk, L. Shumilo and A. Lavreniuk, "Generative Adversarial Networks for the Satellite Data Super Resolution Based on the Transformers with Attention," IGARSS 2023 - 2023 IEEE International Geoscience and Remote Sensing Symposium, Pasadena, CA, USA, 2023, pp. 6294-6297.

On-site HM detection in a body of water, avoiding any pre-treatment and maintaining the most original characteristics of HMs, has shown the advantages compared to the traditional approaches for heavy metals distribution assessment in waters, which usually involve manual sampling, off-site detection, and possible contamination. However, the on-site detection using electrochemical measurement approaches still suffer from the low portability caused by the large size and lack of remote operation and automation, requiring human presence to control the operation of sensing probes between different testing sites, which induces high costs. Thus, until now, a fully autonomous sensing tool for on-site HM measurements in natural waters has rarely been reported. iMERMAID will be focused on the development of an electrochemical tool for the continuous monitoring of heavy metals ($Cd^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Hg^{2+}$) in water samples.

Electrochemical devices arise as a possible solution in this sense. They are largely used for trace HM detection, since they require simple procedures: screen-printed electrodes are miniaturised devices, based on different layers of inks printed on an inert plastic or ceramic substrate. Moreover, since they are mass-produced at low cost, they can be used as disposable. They are also well-suited for miniaturisation and automatic in situ measurements with minimal sample changes.

Stripping analysis is considered to be the most sensitive electroanalytical technique and to be highly suitable for the task of field monitoring of toxic metals. The sensitivity of stripping analysis is attributed to its preconcentration step, in which trace metals are accumulated onto the working electrode surface. This is then followed by the measurement step, in which the metals are stripped away from the electrode during an appropriate potential scan. Stripping analysis can provide useful information on the total metal content, as well as characterisation of its chemical forms[89],[90].Portable and compact (hand-held) battery operated stripping analysers are currently being commercialised for controlling these field-deployable devices. Thus, contamination by reagents or losses by adsorption on containers are drastically decreased. Electrochemical systems also allow quite fast analyses with experimental data obtained mostly in real time or in a few minutes. Hence, on-line monitoring of water samples becomes possible, providing dynamic data of relevance for biogeochemical survey. Nevertheless, specific developments are still required for such applications, particularly to improve automation.

Electrochemical stripping voltammetry should be the predominant technique used for the analysis of these heavy metal pollutants in the next few years. The electrochemical measurement of heavy metals presents many inherent characteristics which facilitate compatibility with decentralised real-time measurements in different kinds of water bodies including WWTP and seawater. As already mentioned, these characteristics include a possible miniaturisation of the device, multiplexed analysis, autonomy, low power consumption, and cost-effective analysis.

Measurements of any analyte in real samples are theoretically possible only providing that the analytical performances of the sensors (LoD, response time, stability, robustness) are sufficient. To reach the goals

---

[89] J. Wang, Analytical Electrochemistry, VCH, USA, 1994, pp. 44–49.

[90] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Application, 2nd ed., Wiley, New York, 2001, pp. 459– 462.

of the project, the final sensors should possess a simplified maintenance as well as a controlled signal stability due to chemical fouling and biofouling, effect of changes in environmental conditions. The integration of the analytical sensors in a (micro)fluidic tool will allow increasing the number of operations needed to reach the sensitivity and stability required (sample treatment, calibration check, sensor cleaning steps) in an easy and automatic way. Analytical validation, first at the laboratory scale (ICP/MS ICP/OES analysis on the same samples to validate the electrochemical data) and then in the field, will bring electrochemical sensors to reach reliable sensing tools for ion monitoring in seawater.

### 3.3.2 Contaminants to be monitored

The target compounds that electrochemical sensors could detect in the waters of the Mediterranean Sea basins include various heavy metals, such as $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$ and others (on the base of analytical needs). These heavy metals are often present in water due to human activities and natural processes. Their sources include industrial discharges, agricultural runoff, atmospheric deposition, and leaching from geological formations.

Cadmium ($Cd^{2+}$):

Sources: Industrial processes (e.g., metal plating, battery manufacturing), mining activities, and fertilizers. Cadmium is toxic to aquatic life and can accumulate in the food chain, posing risks to human health.

Lead ($Pb^{2+}$):

Sources: Lead-based paints, industrial discharges, plumbing systems (lead pipes), and atmospheric deposition from past gasoline use. Lead is a neurotoxin that can harm both aquatic ecosystems and human health.

Nickel ($Ni^{2+}$):

Sources: Industrial discharges (e.g., metal processing, electroplating), mining, and natural weathering of nickel-containing rocks. Nickel can be toxic to aquatic organisms and may cause water quality issues.

Mercury ($Hg^{2+}$):

Sources: Coal combustion, industrial processes, and natural sources (e.g., volcanic activity). Mercury transforms into methylmercury in water, a highly toxic form that bioaccumulates in aquatic organisms, posing risks to ecosystems and human health.

Monitoring these heavy metals is crucial due to their potential ecological and public health impacts, and understanding their sources helps implement effective pollution control measures.

### 3.3.3 Technical specifications

The analytical procedure is based on the determination of a certain group of heavy metals using stripping voltammetry, thanks to a suitable electrode surface modification able to accumulate these metals in a selective way.

The sensitivity of the applied electrochemical technique, together with the specificity given by the surface modification, allow to obtain a highly sensitive system with detection limits for the investigated analytes at sub-ppb levels, with a reproducibility of around 6% (reported as RSD).

In addition to its exceptional sensitivity and specificity, the sensor's manufacturing technology employs established and standardized procedures. This not only ensures the reproducibility across different batches but also monitors the repeatability of the surface modification process, thereby establishing a reliable and robust system. This approach is crucial for maintaining consistency in sensor performance and data accuracy over time, contributing to the overall dependability of the analytical system.

The results can be returned directly as analyte concentration, through the use of an internal calibration curve or by using the standard addition method and related calculation.

The measurement protocol consists of the following phases: conditioning, metal accumulation, stripping and cleaning. All these steps are performed by keeping the sensor in a suitable flow cell for continuous on-site monitoring purpose. The sample inlet, as well as the measurement management solutions, are managed by a suitable pump. The complete measurement cycle requires between 5 and 10 minutes as execution time, depending on the sensitivity that must be achieved. The cleaning process includes a final check to evaluate the reusability of the sensor.

Interoperability with IoT: Similarly, data interpolation is given by a simple mathematical function; these that can be easily transmitted and shared, for example via cloud, in order to be integrated with the parameters coming from the other analysis systems.

Once the monitoring is completed, the data collected can be graphed in order to evaluate the trend over time of the concentration of the metal under examination. This allows to identify an average value to be established, which can constitute a threshold value that must not be exceeded (alarm bell).

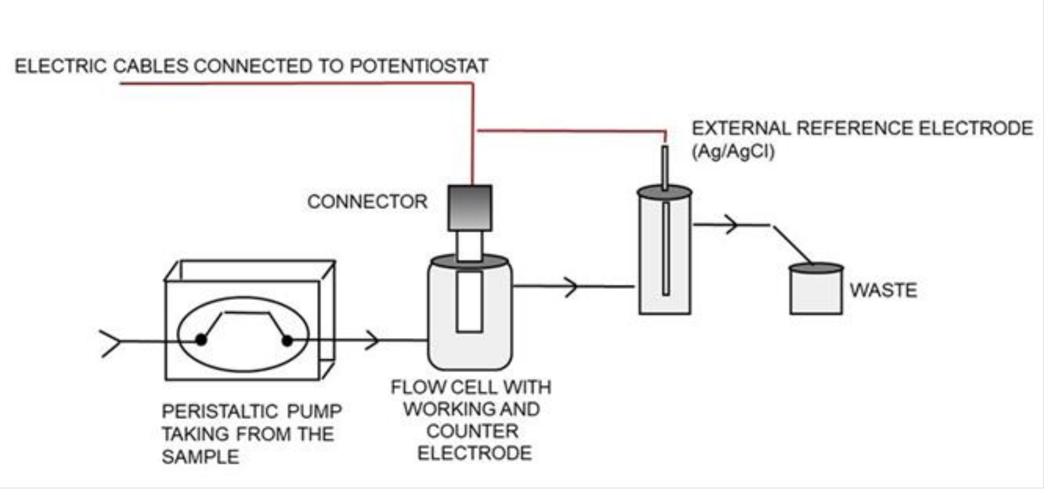


Figure 19: Electrochemical sensor scheme for monitoring of heavy metals in aqueous samples.

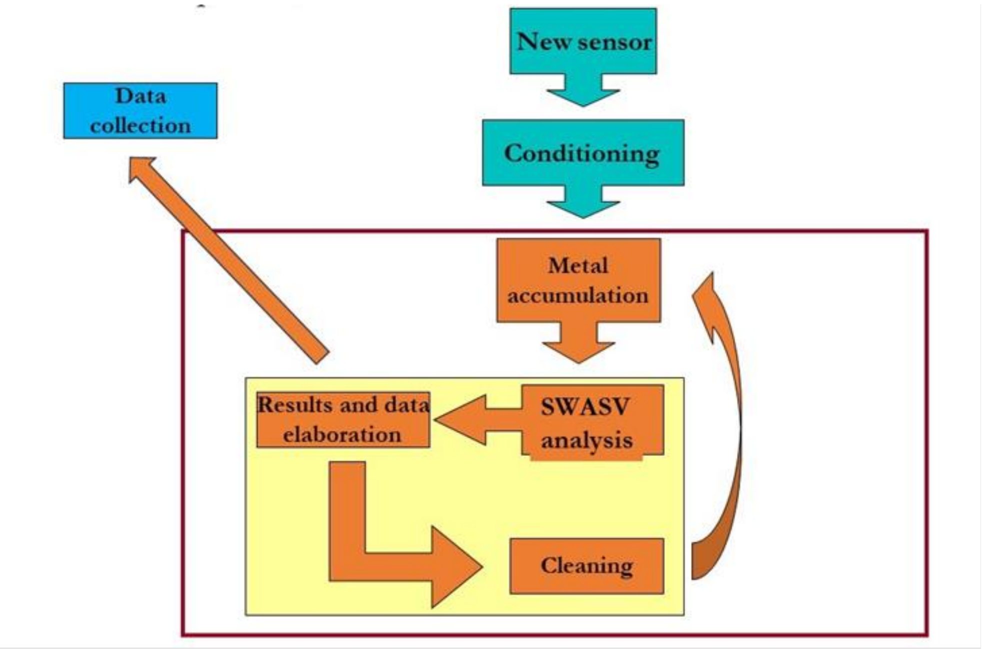


Figure 20: Electrochemical sensor diagram for detection of traces of heavy metals in aqueous samples.

Table 5: Technical specifications of sensor METALSENS.

| **Sensor for heavy metal detection** | Technical data | Comments | Confidential (Y or N) |
|---|---|---|---|
| TRL (at end of project) | 6 | | Y |
| Operation process | Fluidic system | | N |
| Quality requirements (of the water to be treated) | Solids need to be prefiltered;<br>sample pretreatment (e.g., acidification) could be necessary | Suitable solid filtration system needs to be included in the pilot equipment | N |
| Target contaminants | Heavy metals (Cd2+, Pb2+, Ni2+) | | N |
| Reliability | TBD. | Reliability for long-term measurements must be estimated. | Y |
| Repeatability | CV= 5% | Calculated on n=10 different unmodified sensors. For modified sensors must be estimated. | Y |
| Reproducibility | CV= 3% | Calculated on n=10 different unmodified sensors. For modified sensors must be estimated. | Y |
| Limit of detection | Sub-ppb levels | Depending on the heavy metal (Cd2+, Pb2+, Ni2+) | Y |
| Limit of quantification | Ppb levels | Depending on the heavy metal (Cd2+, Pb2+, Ni2+) | Y |

| | | | |
|---|---|---|---|
| Operating range 1$^{*}$ | Acidic medium (for example acetate buffer pH 4.75) | Sample needs to be acidified, so a suitable fluidic system must be implemented | Y |
| Operating range 2$^{*}$ | | | |
| Temperature range | Room temperature | Should be between 20-30 °C | Y |
| Power supply | 5 V (potentiostat, stirrer), 220 V for pumps and accessories | | N |
| Data output (Analog/digit) | Digit | | Y |
| Format (CSV; XLS,) | CSV, XLS | | Y |
| Frequency | TBD. | | Y |
| Protocol | SWASV measurement | Analytical parameters depending on the used transducer | Y |
| Raw material supply | TBD. | Depending on the frequency of measurement | N |
| Disposable | Sensor will have to be replaced after a certain number of measurement cycles | | N |
| Waste | Used sensors, measured sample | TBD. | |
| Maintenance | Sensor regeneration protocol; flow-cell cleaning protocol | To be defined on the base of the Use Case | y |
| Interoperability with IoT | Interaction of the embedded potentiostat with a data elaboration system to send data to cloud | | Y |
| Indicative cost | 5 000€ | Estimate for this specific pilot equipment. Does not include work. | |

### 3.3.4 Sensor METALSENS in iMERMAID

The sensor has been developed by the University of Florence (UNIFI). The sensor will be installed in two different Use Cases. Firstly, it will be deployed in Use Case 3, Turin area in the facilities of a WWTP that treats both urban and industrial effluents. On the other hand, the sensor will be also installed in the Use Case 5 (Crete). Installation on Use Case 4 (Cyprus) will also be evaluated, but after the verification of the limits of detection required for the analytes to be monitored and then check the feasibility of those analysis in seawater media.

# 4.0 Technical specifications of technologies

Remediation technologies play a crucial role in water remediation strategies. Addressing pollutant that inevitably find their way into water effluents is imperative. The iMERMAID project will develop four distinct remediation technologies, targeting contaminants outlines in various water directives. Moreover, these technologies are at the forefront of innovation, characterized by low energy consumption and a chemical-free process.

## 4.1 Technology AKVO

### 4.1.1 Technology description

AKVO is an innovative, compact, and energy-efficient microfluidic water treatment system with a specific focus on addressing micropollutants. It is designed for tertiary water treatment applications, including potable water production, water reuse and pre-discharge sanitation. The core of the AKVO system consists of filtration discs, roughly the size of a standard CD, which can be stacked in groups of 10s or 100s, tailored to the needs of individual clients.

These discs feature intricate networks of microchannels organized into intelligent energy-efficient microfluidic grids, closely resembling the vascular systems found in the human body. AKVO offers a variety of disc types optimized for treating water of varying quality. When combined with different configuration, AKVO proves to be an exceptionally adaptable solution for advanced water treatment, promoting sustainability and accessibility.

The ingenuity of microfluidic water treatment lies in its remarkable benefits. By processing water within these precisely controlled microenvironments, AKVO significantly reduces the consumption of reagents and raw materials, minimizes thermal losses and accelerates essential reactions via process intensification. Additionally, it is designed to operate at low pressures of ~ 1bar. This unique approach positions AKVO as the epitome of energy efficiency and compactness, surpassing existing solutions.

The current system operates based on the principles of photocatalysis, utilizing a specialized photocatalyst-coated glass that is affixed to a microfluidic CD. This arrangement is exposed to UV light to trigger the photocatalytic reactions required for the system's functionality. However, a potential issue arises when we consider the application of this technology in the context of AKVO. The challenge stems from the fact that as the multiple CDs are stacked on top of each other, UV light diffusion becomes a limiting factor. To overcome this limitation and ensure efficient photocatalysis across all the stacked CDs, it is imperative to optimize various optical components within the system. These components include the UV light source itself, ensuring it emits a uniform and intense UV light spectrum. Additionally, reflective surfaces or coatings can be strategically placed to direct and distribute the UV light more effectively, thereby enhancing the photocatalytic reactions within each CD stack.

By fine-tuning and optimizing these optical elements, we can ensure consistent and efficient UV light exposure throughout the entire AKVO system, enabling it to function optimally even when multiple CD stacks are involved. This optimization is crucial for achieving the desired performance and reliability of the photocatalytic processes in the overall system.

The adoption of AKVO perfectly aligns with the objectives outlined in the Zero Pollution Action Plan, a key component of the European Green Deal. This groundbreaking technology promises to play a pivotal role in achieving cleaner, more sustainable water treatment practices while contributing to the environmental goals set forth by the European Commission.

### 4.1.2 Contaminants to be treated

Non-steroidal anti-inflammatory drug (NSAID):

The microfluidic water treatment system aims to effectively remove three commonly found pharmaceutical compounds in water: Ibuprofen, Ketoprofen, and Diclofenac. These pharmaceuticals, belonging to the non-steroidal anti-inflammatory drug (NSAID) class, are frequently detected as micropollutants in water sources. Ibuprofen is a propionic acid derivative widely used as an over-the-counter pain reliever and anti-inflammatory medication. It is commonly detected in water bodies due to its common usage and it is known to have adverse effects on aquatic organisms. Ketoprofen is a propionic acid NSAID primarily prescribed for pain relief and inflammation. It is found in water sources due to human excretion and improper disposal; poses ecological risks. Diclofenac is an acetic acid NSAID used to alleviate pain and inflammation; prescribed for various medical conditions. It is known to be persistent in aquatic environments; has been associated with adverse effects on aquatic organisms.

Pesticides:

The microfluidic water treatment system will be engineered to efficaciously eliminate pesticides from water sources, focusing on enhancing the removal efficiency of these agrochemical contaminants. Glyphosate, atrazine and chlorpyrifos are some of the pesticides most frequently found, widely used in agricultural and weed control and a pre-harvest desiccant. Glyphosate is detectable in water bodies due to runoff and leaching, posing concerns for aquatic ecosystems. Atrazine is persistence in water, leading to its detection in surface and groundwater sources, associated with adverse effects on aquatic life. Chlorpyrifos are detected in water due to runoff, posing risks to aquatic organisms and ecosystems.

Other contaminants:

Bisphenol A (well encountered in Crete) (Use Case 5).

### 4.1.3 Technical specifications

The implementation of the prototype will be done downstream of the existing prefiltration setup, as part of the tertiary remediation system. This prototype will be designed to treat around 1 cubic meter of water. An analysis of water inflow and outflow will be carried out to assess its efficiency, with the possibility of implementing system improvements during a redesign phase if necessary. The determination of CAPEX and OPEX will be done at a later stage.

The AKVO microfluidic water treatment system, in its prototype implementation, is seamlessly integrated downstream of the existing prefiltration setup, constituting a vital component of the tertiary remediation system. This prototype is meticulously designed to treat approximately 1 cubic meter of water, offering a compact yet powerful solution for targeted water treatment.

Residual materials or spent components from the prototype's microfluidic water treatment process are subject to a comprehensive waste management strategy. Recycling, reclamation or safe disposal methods are employed based on the nature of by-products during the prototype's analysis. The prototype phase underscores environmentally conscious waste management practices, considering the lifecycle of materials and components, the prototype reflects a commitment to sustainable water treatment practices.

Determination of CAPEX and OPEX, although slated for a later stage, will further contribute to the comprehensive evaluation of the prototype's viability and sustainability.

The disposal process in the prototype phase underscores a commitment to minimizing the generation of by-products. The microfluidic treatment's controlled environments and efficient reactions aim to reduce any undesirable secondary substances. Any residual by-products will be meticulously managed and assessed during the prototype's analysis phase. The prototype maintains aligning with the commitment to minimal energy consumption during water treatment. Microfluidic grids continue to optimize thermal and optical losses, contributing to the prototype's overall energy efficiency. Energy recovery strategies may be explored during the analysis phase to further enhance sustainability. Construction of the prototype's filtration discs, akin to standard CDs in size, prioritizes sustainability and efficiency. Raw material selection emphasizes responsible sourcing and recyclability, reflecting a commitment to environmental stewardship. The disposal process considers the recyclability and responsible sourcing of materials to minimize environmental impact during the prototype phase.

As the reaction involved is nonselective, it will lead to the degradation of all organic micropollutants and their resultant by-products. Nevertheless, there could be some by-products present in the effluent. To verify this, the effluent water will undergo examination using conventional techniques.

The microfluidic discs will be constructed using recyclable polymers to facilitate recycling. Equipment maintenance will involve rejuvenating the photocatalytic layer, a process achievable by circulating an extremely diluted acidic solution through the channels.

Table 6: Technical specifications of AKVO technology.

| **Title** | Technical data | Comments | Confidential (Y or N) |
|---|---|---|---|
| TRL (at end of project) | 6-7 | | N |
| Operation process | Microfluidics + Photocatalysis | | N |
| Implementation point (secondary, tertiary?) | Tertiary | | N |
| Target contaminants | Ibuprofen, Ketoprofen, Diclofenac (pesticides not identified yet) | Pesticide analysis ongoing in ESDAK Use Case | N |

| | | | |
|---|---|---|---|
| Quality requirements (of the water to be treated) | No suspended particles and pretreated. | | N |
| Capacity ($m^3$/day) | 1 | | N |
| Temperature range | 50-60 °C | | Y |
| Energy consumption | <0.1 kWh/m3 | | Y |
| Raw material supply | | | |
| Disposable | Recyclable material | | Y |
| Maintenance 1 | Regeneration of the catalyst | | y |
| Maintenance 2 | Purging to remove any clogging | | Y |
| Interoperability with IoT | Planned | | Y |
| CAPEX | ~65000€ | | Y |
| OPEX | ~10k€/year | | Y |
| MAPEX | | | |

### 4.1.4 Technology in iMERMAID

The technology has been developed by EDEN. This technology will be implemented in Use Cases 2 and 5. Use Case 2 corresponds with a pharmaceutical industry located in Tunisia. Meanwhile Use Case 5 is a leachates treatment plant located in Crete.

## 4.2 Technology PDP

### 4.2.1 Technology description

Pulsed Discharge Plasma (PDP) is an Advanced Oxidation Technology capable of completely breaking down toxic organic compounds, including pharmaceuticals, hormones, pesticides, and PFAS frequently present in wastewater. One of the primary advantages of this innovative PDP technology compared to the State of the Art is that it operates without the need for additional chemicals; the reactive agents are generated by the plasma itself.

Pulse discharge plasma systems often require a significant amount of electrical energy to generate and sustain the plasma. High energy consumption can lead to increased operational costs and may not be suitable for applications with limited access to energy resources. Some pulse discharge plasma systems may face challenges when it comes to scaling up for large-scale water treatment applications. Ensuring the technology can be effectively scaled while maintaining efficiency is a critical consideration. The electrodes in plasma systems can experience erosion over time due to the intense conditions within the discharge chamber. This can lead to reduced efficiency and may require frequent maintenance or replacement of electrodes.

Plasma discharge can generate by-products and secondary pollutants, such as ozone and nitrogen oxides, which may need to be carefully managed. These by-products could have their own environmental or health implications, and the overall environmental impact of the treatment process should be assessed. The effectiveness of pulse discharge plasma can be influenced by the composition of the water being treated. Some contaminants may be more resistant to plasma treatment, and the technology may be more effective for certain types of pollutants than others.

Plasma discharge generates heat, and this rise in temperature can affect the treated water. It is important to monitor and control the temperature to prevent undesirable effects on the water quality or the formation of undesired by-products. Pulse discharge plasma systems can be complex to operate and require skilled personnel for maintenance and troubleshooting. Adequate training and ongoing support are crucial for successful implementation.

Thereby, while pulse discharge plasma shows promise, there might still be a need for more research and demonstration projects to validate its efficacy under different conditions and applications. Before implementing pulse discharge plasma technology for water treatment, a thorough assessment of these limitations and potential mitigations should be conducted to ensure the feasibility and sustainability of the chosen approach.

The device is compact and portable, ideal for punctual treatment of water from Persistent organic pollutants (particularly pharmaceuticals and hormones), pesticides and biocides, per- and polyfluorinated alkyl substances – PFAS.

Furthermore, IRIS has patented an innovative nano-PDP system that delivers significantly shorter pulses than existing devices, resulting in a substantial reduction in energy consumption (a 30% decrease compared to existing technologies). Combining PDP with a catalyst and graphene oxide (GO) can significantly enhance its performance by efficiently utilizing the reactive species produced by the plasma.

### 4.2.2 Contaminants to be treated

Pesticides:

- Carbofuran (CAS: 1563-66-2).
- Fenuron (CAS:101-42-8).
- 3,4,5-Trimethacarb (CAS: 2686-99-9).

Drugs:

- Trimetoprim-d9 (CAS: 1582-09-8), included in the Watch List.
- Ibuprofen (CAS: 53949-53-4), included in the WFD, and in the Use Case 1.
- Amisulpride (CAS: 71675-85-9), included in the new proposal for wastewater Directive.

Others:

- Bisphenol A (CAS: 84-17-3). Endocrine disruptor. Included in the WFD.
- Benzotriazole (CAS: 95-14-7).

### 4.2.3 Technical specifications

The disposal process within the context of plasma technology for water treatment involves a meticulous examination of the generated by-products, the sourcing of energy or raw materials, and the ultimate achievement of complete the treatment process. In this regard, degradation products resulting from the plasma treatment are subjected to comprehensive treatment procedures, ensuring their effective neutralization or elimination.

An integral aspect of the plasma water treatment technology is the absence of a requirement for the supply of raw materials. Unlike certain water treatment methodologies that necessitate the introduction of specific chemicals or substances for effective treatment, plasma technology relies on the inherent properties of the water contaminants and the plasma-generated reactive species to drive the degradation processes. This characteristic not only simplifies the operational logistics but also aligns with principles of sustainability by minimizing external inputs.

In terms of energy consumption, a noteworthy parameter at the laboratory scale testing (Technology Readiness Level 5 - TRL5) is reported. The energy consumption is quantified at 0.3 kWh per litter of treated water, with the total organic carbon (TOC) levels set at 30 mg/L. This metric provides insights into the efficiency of the plasma-based water treatment process, demonstrating its potential as an energy-efficient technology. It is essential to recognize that these laboratory-scale findings serve as a foundational reference point, and further optimization and scale-up may be required for practical implementation in larger-scale water treatment applications.

In summary, the disposal process in plasma water treatment involves a meticulous consideration of by-products, the absence of raw material supply requirements, and efficient energy utilization, as exemplified by the low energy consumption observed at the laboratory scale. These features collectively contribute to the attractiveness of plasma technology as a sustainable and effective approach for water treatment applications.

Table 7: Technical specifications of PDP technology.

| **Title** | Technical data | Comments | Confidential (Y or N) |
|---|---|---|---|
| TRL (at end of project) | 7 | | N |
| Operation process | Semi-continuous | | Y |
| Implementation point (secondary, tertiary?) | Tertiary / quaternary treatment | | N |
| Target contaminants | Carbofuran (CAS: 1563-66-2) | | N |

| | | | |
|---|---|---|---|
| | Fenuron (CAS:101-42-8)<br>3,4,5-Trimethacarb (CAS: 2686-99-9)<br>Trimetoprim-d9 (CAS: 1582-09-8)<br>Ibuprofen (CAS: 53949-53-4)<br>Amisulpride (CAS: 71675-85-9) | | |
| Quality requirements (of the water to be treated) | Suspended solids, high TOC and high conductivity can affect the performance | | N |
| Capacity ($m^3$/day) | 0.1 - 1 | At TRL5 we are testing many different reactors, it will change by the end of the project | N |
| Temperature range | 10-50 °C | | N |
| Energy consumption | *0.3kWh/L* | *At TOC levels of 30mg/L* | N |
| Raw material supply | No | | N |
| Disposable | | | N |
| Maintenance 1 | | | N |
| Maintenance 2 | | | N |
| Interoperability with IoT | Yes | Water quality sensors | N |
| CAPEX | 6.5 | CAPEX and OPEX at lab scale (TRL5). Will be improved throughout the project. | Y |
| OPEX | 0.86 | CAPEX and OPEX at lab scale (TRL5). Will be improved throughout the project. | Y |
| MAEX | | | N |

### 4.2.4 Technology in iMERMAID

The testing will be initially performed at IRIS at the lab scale with wastewaters coming from the Use Case and will be propaedeutic to the scale up of the technology. The scaled-up technology will then be deployed in San Esteban de Litera (Use Case 1), where will be implemented to treat contaminants that are recalcitrant to biological treatment. San Esteban de Litera (Huesca, Spain) is a town located in the North-East Spain, where SOCAMEX manages the wastewater treatment at the wastewater treatment plant.

## 4.3 Technology 4D Scavenger

### 4.3.1 Technology description

4D Scavenger (4DS) is an innovative technology for selective recovery of dissolved metals. It is chemically active porous filter that can target specific metals from different liquid streams. During this project the focus is on heavy metal removal. The scavengers are made by 3D printing chemically functional materials. By altering the printing parameters and the used materials the 4DS is very scalable and customizable.

This technology employs a chemically active porous filter designed to target and capture predetermined metals, with a particular focus on heavy metals within the scope of this project. The unique feature of the 4DS lies in its adaptability and effectiveness in addressing diverse liquid streams containing dissolved metals. The 4DS operates as efficient filter for dissolved elements, leveraging its distinctive structure to selectively capture and recover dissolved metals from liquid sources. This porous filter is characterized by its customizable and scalable nature. The tailored design enables the 4DS to exhibit a high degree of selectivity, focusing on specific metals of interest, particularly heavy metals, amidst complex and varied liquid compositions.

Central to the scalability and adaptability of the 4DS is its fabrication through 3D printing. This manufacturing method facilitates precision in the creation of the porous filter, allowing for the customization of its properties based on the targeted metals and the specific characteristics of the liquid streams to be treated. The scalability of the 4DS is particularly advantageous, enabling its seamless integration into various water treatment scenarios, ranging from laboratory-scale applications to large-scale industrial processes. The 4DS technology presents several advantages, including its selective recovery capability, scalability, and ease of customization. By specifically targeting heavy metals, it addresses a critical aspect of water treatment associated with environmental contamination. The scalability of the technology ensures its applicability across a spectrum of liquid streams, making it versatile for deployment in diverse industrial and environmental contexts.

It's important to note that the effectiveness of 4DS in these applications will depend on factors such as the type of metals targeted, the concentration of metals in the water and the overall water chemistry. While the specific applications of 4DS may vary based on the targeted metals and the composition of liquid streams, here are some general applications for 4DS in water treatment: A primary application involves the selective removal of heavy metals from water streams. This is especially crucial in industrial wastewater treatment, where heavy metal contamination is a prevalent issue. 4DS can effectively be employed in treating industrial effluents to selectively recover specific metals present in the discharge from diverse manufacturing processes. 4DS can play a role in selectively extracting these metals from wastewater streams for subsequent reuse or recycling. As new contaminants emerge in water sources, 4DS can be customized to selectively target and remove these contaminants, providing a versatile solution for evolving water treatment challenges.

The 4DS technology is employed in the Mediterranean Sea for the tailored treatment of emerging contaminants in water. This innovative technology selectively extracts and retrieves heavy metals from the water stream, effectively preventing their entry into the Mediterranean Sea. Unlike existing state-of-the-art water treatment solutions, which exhibit limited cost-efficient recovery of heavy metal pollutants, 4DS technology overcomes these challenges.

The adaptability of 4DS extends to tailoring it for specific processes, ensuring optimal performance. The chemical composition of 4DS is modified through material combination choices, allowing fine-tuning of metal recovery characteristics, kinetics and selectivity. Traditional water treatment methods often result in hazardous sludges deposited in landfills, posing potential risks. Commercially available materials like ion exchange resins, chelating agents or adsorbents used in heavy metal recovery face limitations such as low selectivity and slow chemical kinetics. In contrast, 4DS technology excels by enabling faster reaction kinetics, more efficient washing steps and reduced equipment costs.

During the manufacturing process, controlled sintering of the powder imparts predictable and customizable flow properties to 4DS. This affords virtually infinite control and customization to meet diverse demands. Beyond complete removal of heavy metals, 4DS facilitates the recovery of metals in their high-purity form. Single 4DS units can achieve the complete removal of small concentration contaminants, while close to 100% removal of larger concentrations typically requires a sequential arrangement of two or more 4DS units. The technology is characterized by high scalability, customization and integrability, making it a versatile and effective solution for water treatment in the Mediterranean Sea.

### 4.3.2 Contaminants to be treated

When applying 4DS technology to address emerging contaminants in the water of the Mediterranean region, it's crucial to consider various parameters to ensure its effectiveness and suitability. The target compounds suitable for treatment using 4DS encompass heavy metals present in water streams. It is essential to identify and characterize specific contaminants in the Mediterranean Sea, understanding their chemical nature, concentration levels, and potential impacts on the environment and human health. The technology is specifically designed for the selective recovery of heavy metals, including lead, cadmium, mercury, copper, zinc, arsenic, nickel, and hexavalent chromium. The selection of target compounds depends on the specific requirements of the piloting site water.

The performance of 4DS is influenced by factors such as pH, salinity, and the presence of ions in the complex chemistry of the Mediterranean Sea. Adapting the technology to accommodate variations in these parameters is crucial for optimal function across diverse environmental settings. Ensuring compliance with local and international regulations governing water quality and contaminant levels in the Mediterranean is imperative. This not only meets regulatory standards but also establishes a foundation for responsible and effective water treatment practices.

The integration of 4DS technology into existing water treatment infrastructure in the Mediterranean requires a careful assessment of compatibility with other treatment methods and processes. This comprehensive evaluation is essential for the seamless incorporation of 4DS into established water treatment systems. Implementing monitoring systems is necessary to assess the real-time efficiency of 4DS. Developing methods for the detection and quantification of target contaminants levels, both before and after treatment, contributes to a robust water treatment strategy. Addressing concerns related to the management and disposal of spent or saturated 4DS is a critical aspect of responsible technology application. Establishing proper disposal protocols is paramount for sustainable and environmentally conscious water treatment practices.

Evaluating the cost-effectiveness of implementing 4DS technology in the Mediterranean context considers economic feasibility and potential benefits relative to other water treatment methods. This assessment informs decision-making processes to ensure efficient resource allocation in water treatment initiatives. Public acceptance of the technology is crucial, necessitating engagement with local communities, authorities, and stakeholders. Addressing concerns, fostering open communication and effectively communicating the benefits of utilizing 4DS for water treatment are pivotal for successful adoption and integration. By considering these parameters, the iMERMAID project can enhance the likelihood of the successful implementation of 4DS for treating emerging contaminants in the water of the Mediterranean geographical area.

### 4.3.3 Technical specifications

The technology has undergone laboratory testing, and specific applications have been piloted. However, for this application, customization and optimization in laboratory scale are necessary before piloting. Scaling up 4DS technology for treating emerging contaminants and heavy metals in water presents challenges and considerations that must be carefully addressed. Consistent and reproducible manufacturing on a larger scale is challenging, and maintaining uniformity in material properties and structural characteristics is crucial for reliable performance.

Scaling up may require larger quantities of materials, emphasizing the need for a consistent, high-quality supply of suitable materials. Parameters in the 3D printing or manufacturing process may need optimization for larger-scale production, aiming for efficiency, speed and cost-effectiveness while preserving efficacy. In addition, understanding and addressing the hydrodynamics of larger treatment systems is crucial. Ensuring that 4DS can handle increased flow rates and maintain sufficient contact time with water contaminants poses a significant challenge.

Integrating 4DS technology into larger water treatment infrastructure necessitates careful planning, considering compatibility with other treatment methods and seamless integration into established systems. Implementing robust real-time monitoring and control systems for larger treatment facilities can be complex. The technology will be initially tested, developed and customized on laboratory scale. After laboratory tests, the technology will be piloted on-site to treat larger water streams and optimize the process under real-life conditions. Post-piloting, optimization and process design, the Technology Readiness Level (TRL) will be 7. The objective is to develop an effective method for heavy metal removal that is user-friendly on-site. Recovery rate targets will be determined in collaboration with piloting side provider, aiming to reduce metal concentrations below environmental limits.

The piloting equipment can treat water at rates ranging from 500 L/h to 5 $m^3$/h, and a pre-filtration system will be integrated to remove suspended solids. Implementation requires water inlet and outlet, as well as an electricity supply. Capital expenditures (CAPEX) include pilot equipment components and assembly, testing, and automation. Operating expenditures (OPEX) encompass electricity, chemical consumption, and manual work during the piloting period.

During the metal recovery process, a metal concentrate is produced. Regeneration of 4DS involves using dilute acid to remove metals and prepare it for reuse. An eluent with a high concentration of removed metals is generated using a suitable chemical, such as sulfuric acid or hydrochloric acid. The equipment requires 100 L to 1 $m^3$ of eluent during piloting, with an electricity consumption of approximately 2-4 kWh.

The equipment itself has a lifespan of approximately 5-10 years. The core, the 4DS, needs replacement annually. The equipment is automated, requiring no continuous operation. In case of issues, the equipment sends alerts for necessary actions. Ideally, the 4DS can be ground to powder and printed again for a new scavenger; alternatively, in the worst case, the used 4DS will have to be incinerated.

Table 8: Technical specifications of 4D Scavenger technology.

| **Title** | Technical data | Comments | Confidential (Y or N) |
|---|---|---|---|
| TRL (at end of project) | TRL7 | | N |
| Operation process | Selective recovery of dissolved heavy metals | Water will be pumped through 4D Scavenger for the recovery of targeted metals. As the 4DS capacity is spent, elution cycle will be performed. | N |
| Implementation point (secondary, tertiary?) | Secondary | Water from wastewater treatment plant will be treated to remove heavy metals | N |
| Target contaminants | Zn, Cu, Al | These metals were found in the Use Case's water and thus are the target. | N |
| Quality requirements (of the water to be treated) | Solids need to be prefiltered | Suitable solid filtration system will be included in the pilot equipment | N |
| Capacity ($m^3$/day) | 20-40 m3/d | Maximum flowrate for the pilot equipment is 5 m3/h | N |
| Temperature range | 5-40 °C | | N |
| Energy consumption | 10-20 kWh/d | Consists mostly of the energy consumption of the pump | N |

| | | | |
|---|---|---|---|
| Raw material supply | Sulfuric acid weekly and sodium hydroxide | Sulfuric acid and sodium hydroxide will be diluted to 5% solution. | N |
| Disposable | Metal sulphate elution solution that is possible to utilize by some actor or it can be disposed of. | Only liquids are generated during the process. | N |
| Maintenance 1 | 4DS is eluted regularly approximately once a week. Sufficient supply of sulphuric acid will be ensured. | | N |
| Maintenance 2 | | | |
| Interoperability with IoT | The equipment can be automatic and remote controllable. Sensors can be integrated in the equipment. | Level of automation will be determined later | N |
| CAPEX | 50 000€ | Estimate for this specific pilot equipment. | N |
| OPEX | 300-600€/week | Estimate for this specific pilot equipment. Does not include work. | N |
| MAEX | 0 € | Is included in OPEX | N |

### 4.3.4 Technology in iMERMAID

The technology is being developed by Weeefiner Oy. The Use Case where the technology will be implemented is the Use Case 3, in Turin at a wastewater treatment plant. The Società Metropolitana Acque di Torino (SMAT) will provide piloting site for the demonstration of the technology. This technology will be combined with the sensor developed by the University of Florence (UNIFI) that is designed for measuring the metal concentrations.

## 4.4 Technology RROM

### 4.4.1 Technology description

The aim of this technology is to convert reclaimed Reverse Osmosis (RO) membranes to Nano-Filtration (NF) and/or Ultra-Filtration (UF) pre filtration membranes (M1-M24) under the leading of ENIG with the collaboration of University of Angers.

The idea of this task is to investigate valorisation of end-of-life modules as ultrafiltration/microfiltration membranes to be used as prefiltration system for tertiary solution systems developed in iMERMAID. This will allow keeping all the benefits of membrane processes for warranting the best performances of micro-pollutant processing technologies developed in the project. The intended work will focus on characterization of yield and separation performances of treated and untreated end-of-life RO membrane modules for providing the best wastewater stream for the developed iMERMAID technologies. Both experimental and simulation approaches will be implemented in close coordination with technologies' providers of pollutant treatment technologies providers.

The conversion of reclaimed RO membranes into NF membranes for use as prefiltration systems involves a strategic process with the goal of repurposing end-of-life RO modules. This approach seeks to capitalize on the existing infrastructure and materials to enhance the sustainability and efficiency of water treatment systems. There are various techniques that could be employed to modify the structure and characteristics of reclaimed RO membranes. These may include surface modifications, alterations in membrane morphology, or changes in membrane chemistry to optimize their performance for prefiltration applications. The reclaimed membranes are customized to align with the requirements of prefiltration systems. This may involve adjustments in pore size, porosity, and surface properties to enhance their effectiveness in capturing particulate matter, colloids, or other impurities commonly encountered in water sources.

Rigorous characterization should be conducted to assess the properties of the converted membranes. This includes evaluating factors such as membrane permeability, selectivity, and structural integrity. Consideration is given to the compatibility of the converted membranes with pre-existing water treatment infrastructure. The integration process involves evaluating how well the modified membranes align with the overall system requirements and mesh with other treatment technologies. The technology accounts for the variable nature of water sources, especially in regions like the Mediterranean basin. The converted membranes should be designed to accommodate fluctuations in water chemistry, temperature and the presence of different ions, ensuring robust and consistent prefiltration performances.

The economic feasibility of converting RO membranes for prefiltration is a key consideration. This involves assessing the cost-effectiveness of the conversion process compared to alternative prefiltration methods, considering factors such as materials, labour and maintenance. The environmental impact of the conversion process is evaluated. This includes considering the sustainability of the materials used, waste management protocols for spent membranes and the overall eco-friendliness of the technology.

Thereby, the conversion of reclaimed RO membranes into prefiltration membranes is a multifaceted process that involves modifying membrane properties, ensuring compatibility, optimizing performances, and addressing environmental and economic considerations. This scientific-technical approach aims to repurpose existing resources for sustainable and efficient water treatment solutions.

The Membrane Modules Characterization and Treatment Pilot Unit is intended for characterization of used membrane modules. The characterization is mainly a non-destructive technique based on flow hydrodynamic assessment in modules through Residence Time Distribution (RTD) patterns of a tracer as demonstrated in *Figure 21*.

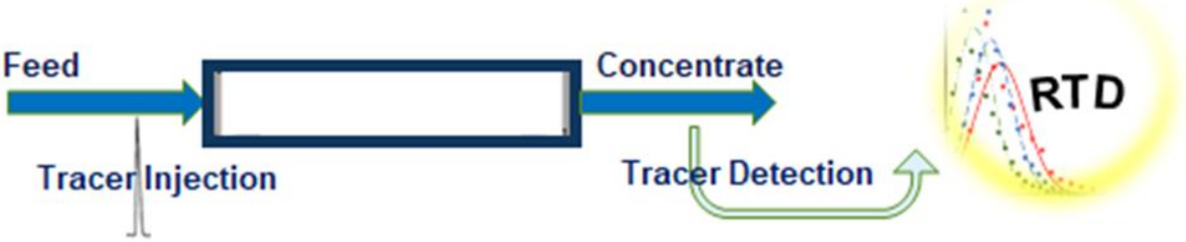


Figure 21. Schematic representation of RTD flow characterization procedure.

The test will be complemented by the assessment of overall properties such as the recovery and rejection rates. Module treatment protocols will be defined based on recovering initial or pristine modules characteristics or targeted separation objectives of the treated module allowing it to perform more moderate and less demanding separation operations such as when converting RO modules into NF or UF ones.

The study involves the examination of two distinct types of End-of-Life RO membranes: brackish water membranes and seawater membranes. Brackish water membranes are specifically designed for treating less salty waters, featuring lower membrane density. They find optimal use in environments where salinity is moderate, such as groundwater, rivers or estuaries. These membranes are suitable for freshwater production from sources with lower salinity levels. On the other hand, seawater membranes are engineered for the desalination of seawater, characterized by higher salinity.

With denser membranes, these modules can withstand relatively high pressures, making them ideal for coastal areas and regions facing water scarcity with abundant seawater. However, the desalination process using seawater membranes is generally more energy-intensive and the choice between the two types depends on the specific water source salinity, energy considerations and the intended application for the treated water. It is noteworthy that both types have a lifecycle and considerations about their End-of-Life characteristics are pivotal, particularly in the context of potential repurposing or conversion into filtration membranes as part of the study's objectives.

As modules are exploited, they gradually lose their performances. The damage could be minute and just a cleaning could allow retrieve initial performances. In some cases, fouled membranes need additional chemical treatments allowing acquiring new properties fit for less demanding separation operations. In such case end-of-life Seawater Reverse Osmosis (SWRO) module will be converted to Brackish Water Reverse Osmosis (BWRO) or NF or even to UF modules. Membrane autopsies should be done also for an evaluation of the end-of-life RO membranes to diagnose (bio)fouling and/or scaling presence. Autopsies will be done in the University of Angers.

### 4.4.2 Contaminants to be treated

Given the utilization of waste membrane modules from various membrane-based separations, including SWRO, BWRO, and NF, the target compounds for this technology in water treatment span a range of contaminants commonly encountered in these diverse water sources. The technology is well-suited for addressing both inorganic and organic pollutants present in different water matrices.

Inorganic Pollutants:

Salt Ions: Given the origin of the waste membrane modules from SWRO and BWRO, the technology is effective in removing salt ions, including sodium, chloride and other dissolved salts.

Heavy Metals: The technology is adept at capturing heavy metals such as lead, cadmium and mercury, commonly found in brackish water and seawater.

Organic Pollutants:

Micro-Pollutants: The technology is designed to target micro-pollutants, including organic compounds like pesticides, pharmaceuticals and personal care products.

Dissolved Organic Matter: Waste membrane modules can effectively address dissolved organic matter, improving water quality by reducing the concentration of organic substances.

Colloids and Particulate Matter:

The technology can remove colloidal and particulate matter present in water sources, contributing to enhanced clarity and quality.

Microorganisms:

The technology may also contribute to the removal of microorganisms, depending on the nature of the waste membrane modules and the specific design considerations for prefiltration.

The versatility of the technology lies in its ability to be customized for various contaminants commonly associated with brackish water, seawater and other water sources subjected to membrane-based separations. The target compounds encompass a broad spectrum of contaminants, making the technology applicable to diverse water treatment scenarios.

### 4.4.3 Technical specifications

The reutilization of RO membranes as NF and/or UF membranes entails certain scientific limitations. Pore size disparities may emerge, given that RO membranes possess smaller pores compared to NF and UF counterparts, potentially impacting filtration efficacy and solute selectivity. Persistent fouling and scaling tendencies inherent in RO membranes may persist during repurposing, potentially compromising membrane longevity and operational efficiency.

Structural integrity may be compromised due to wear and tear from prior RO use, potentially diminishing mechanical strength essential for sustained filtration. Energy efficiency may be suboptimal, as RO membranes, originally designed for high-pressure operations, may not align optimally with the lower pressure characteristic of NF or UF applications. Repurposing may also challenge the selective permeability of RO membranes, impacting permeation characteristics and the achievement of desired separation efficiency.

Compatibility issues may arise as materials optimized for RO processes may encounter challenges under different NF or UF filtration conditions, influencing performance and structural integrity. Challenges in adapting RO membrane cleaning protocols to NF or UF conditions may necessitate the development of novel, effective cleaning strategies. The limited applicability of repurposed RO membranes for specific contaminants underscores the importance of tailored membrane characteristics for diverse filtration scenarios.

In addressing these limitations, innovative engineering solutions and comprehensive performance assessments during repurposing become imperative to ensure effective, reliable technology deployment. The most crucial challenge resides in securing adequate funding for implementing a pilot unit with the requisite size and capabilities. Managing substantial treatment solution volumes during scaling up necessitates intensive pre- and post-filtration procedures, coupled with closed-circuit (CC) operations. Additionally, real-time tracer concentration readings are imperative for overcoming operational challenges and ensuring optimal performance during repurposing efforts.

A high-pressure pump is needed. Online tracer monitoring is also needed. Estimated CAPEX is around 50k€. The OPEX is difficult to estimate & depends on the fouling extend and nature for used modules and the targeted second use. Since chemicals will be used for treatment, the OPEX will vary from few €s to 100€ per treated module. These figures need to be further cheeked and updated.

End-of-Life modules and some non-harmful chemicals will be used. There will be some water footprints. As for OPEX, energy, water and chemical consumptions depend on the site of the used membrane module. However, great efforts will be deployed to limit water and chemical consumptions with CC operations and recycling. In addition, filters will be treated and regenerated to prolong their lifespan. Energy consumption will be a bit higher than in desalination, but we will make some effort to seek renewable supply of energy. Modules that cannot be treated for any reason will be returned to the provider. Some of these modules will undergo autopsies to gather useful information on how to prevent such extreme modules fouling events for end-of-life modules' provider but also for not spoiling the chance of reusing the modules.

Additional characterization procedures, perhaps destructive one as Autopsies, will be used to help unfolding best treatment and cleaning protocols. Such characterization techniques are extremely important when end-of-life modules are damaged to the point where reuse is out of option. Such procedures will generate some waste that need to be handled. Very important information on operational history of RO modules will be collected from waste RO modules providers.

Table 9: Technical specifications of RROM technology.

| **Title** | Technical data | Comments | Confidential (Y or N) |
|---|---|---|---|
| TRL (at end of project) | 5-6 | The technique has been performed on 0.5m2 modules (TRL 2-3) | Y |
| Operation process | Batch / Semi-batch | Could operate in continuous mode such of for the Use Cases | Y |
| Implementation point (secondary, tertiary?) | Secondary & possibly tertiary | Depends on the Use Case, it could be beneficial to conceive it as a tertiary treatment | Y |

| | | | |
|---|---|---|---|
| Target contaminants | M2P is designed for reusing End-of-Life modules | Reclaimed End-of-Life modules can be used for enhancing Use Case contaminants treatment | Y |
| Quality requirements (of the water to be treated) | To be defined later | Depending on the Use Case configuration | Y |
| Capacity ($m^3$/day) | Not applicable | Depends on the capacity of the Use Case pilot | N |
| Temperature range | Ambient range | - | N |
| Energy consumption | Not available | To be defined later | Y |
| Raw material supply | Chemicals | To be defined later | Y |
| Disposable | Wastewater | Limited quantities, much of it will be recycled | Y |
| Maintenance 1 | Not available | To be defined later | Y |
| Maintenance 2 | Not available | To be defined later | Y |
| Interoperability with IoT | Might be | To be defined later | Y |
| CAPEX | 50 k€ | - | N |
| OPEX | 5-100 € | To be defined later | Y |
| MAEX | 500-1000 € | To be tuned later | Y |

### 4.4.4 Technology in iMERMAID

The technology will be developed by ENIG. It will be implemented in the Use Case 2, which consists of the treatment of pharmaceutical industry effluents. For the Use Cases a smaller unit will be used since Eden's microfluidic pilot to be tested has a much smaller capacity than the targeted one. However, similar approach will be used. This will allow providing an additional test for scale-up limitations for the RROM unit.

# 5.0 Use Cases

Sensor and treatment technologies will be combined to make a comprehensive study about the detection of contaminants and the strategies for water remediation. By focusing on the kind of contaminated effluents, the best combinations have been selected to obtain reliable data for further implementation of water remediation strategies derived from iMERMAID project. Together with technologies, an innovative data lifecycle philosophy will be developed.

Within the project, five different Use Cases will be implemented. The studies will be carried out in three different wastewater treatment plants (WWTP) with contaminants of diverse nature, one pharmaceutical industry, and a monitoring buoy located in the Mediterranean Sea basin that will allow to monitor the efficiency of the upstream technologies.

## *5.1 Use Case 1*

This Use Case will be implemented in San Esteban de Litera (Huesca) a town located in north-east of Spain, where SOCAMEX manages the wastewater treatment plant.

The WWTP receives and treats jointly wastewater coming from different sources, including household water and water from industries. Derived from both types of wastewaters, a variety of micropollutants are expected in the input and even in the output of the WWTP due to the recalcitrant behaviour of these compounds. These contaminants include pharmaceuticals and personal care products, hormones, endocrine disruptors as well and disinfection products and contaminants contained in toxic spills coming from industry. In an area like the province of Huesca, with strong water restrictions during drought periods, opportunities for water recycling should be explored. In addition, the high importance of agricultural activities in the area favours the presence of pesticides in the wastewater effluent, posing a problem for the quality of water.

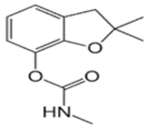
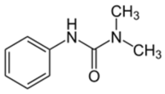
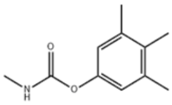
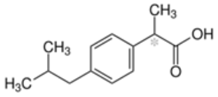
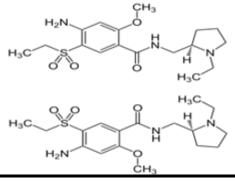
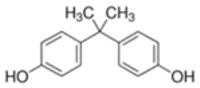
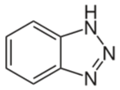
Considering the iMERMAID's objectives, particular attention will be given to pesticides, recognizing their significance among COEC's list. In this specific Use Case, emphasis will be placed on both sensor and treatment technologies, specifically targeting pesticides such as carbofuran, fenuron and 3,4,5-Trimethacarb. Other contaminants detected on the effluent, to consider, are the drugs Ibuprofen and Amisulpride and other general compounds like Bisphenol A and Benzotriazole.

Therefore, the sensor that has been selected to be implemented in this Use Case is the electrochemical sensor for organic pollutants described in *Section 3.1*. For the remediation treatment, the process based on pulse discharge plasma described in *Section 4.2* will be implemented.

The WWTP of San Esteban de Litera is designed for a population of around 1042 inhabitants, equivalent to a medium volume of 250 $m^3$ per day. The surface covered in this Use Case is approximately 71.9 $km^2$.

As an innovation technology that is in a TRL between 5 and 7, it is planned to treat around 1 $m^3$ per day in the treatment process, which corresponds to 4% of the total effluent.

Table 10: Feasibility of electrochemical analysis SOCAMEX's molecules (Dec. 2023)

| Compounds | Electrochemical analysis feasibility (YES/NO) |
|---|---|
| Carbofuran<br> | YES |
| Fenuron<br> | YES |
| 3,4,5-trimethacarb<br> | YES |
| Ibuprofen<br> | YES |
| Amisulpride<br> | YES |
| Bisphenol A<br> | YES |
| Benzotriazole<br> | YES |

*NB: Molecules for electrochemical sensors analysis not defined depending on quantitative analysis occurring in SOCAMEX in January 2024.*

## 5.2 Use Case 2

Use Case 2 involves the monitoring and treatment of a pharmaceutical industry effluent. The industry is based in Kalaat Al Andalouss, in Tunisia. The produced pollution is removed by a conventional Activated Sludge Process. Active pharmaceutical ingredients maybe discharged in tiny amounts into the environment. Although the concentration of contaminants is quite diluted, it is true that due to the nature of contaminants, it may have a notable impact. Many pharmaceuticals used for treating both humans and animals, have been discovered in water and soil and their presence may contribute to hastening the emergence and spread of drug resistant bacteria and fungi. Furthermore, some of them are also commonly found in urban WWTP. That is why, this Use Case is very important and relevant to the project.

The sensor selected for this application is the electrochemical sensor for organic pollutants described in *Section 3.1* as well as the remediation technology for the treatment of the residual effluent based on the microfluidic system described in *Section 4.1*, with a capacity of treating 1 $m^3$ per day.

## 5.3 Use Case 3

Use Case 3 is a WWTP based in Turin (Italy), which is located in north-western Italy. SMAT manages the integrated water service in about 290 municipalities of the surrounded area. The WWTP treats both domestic and industrial effluents. The WWTP is designed for a population of 9000 inhabitants.

The WWTP consists of an initial screening of gross solids, skimming of fats, oils and grease. This is followed by a denitrification process in an anoxic environment and a primary oxidation. The process continues with a secondary oxidation and sedimentation. Finally, the disinfectant is dosed into the outlet channel of the secondary sedimenters. This WWTP has been selected to study the case of heavy metals monitoring and decontamination. As Zinc is found at the inlet of the wastewater treatment plant in a high concentration of around 0.34 mg/L, it was chosen for the study, together with aluminium, copper and nickel.

The sensor assigned to this Use Case is the METALSENS described in *Section 3.3* that is an electrochemical sensor based on voltammetry and especially designed for the detection of heavy metals. In combination with the heavy metal sensor, the 4D Scavenger technology for the elimination of heavy metals will be implemented. As described in *Section 4.3*, this piloting equipment can treat from 500 l/h to 5 $m^3$/h of water, which corresponds, at most, to 6% of the total volume of effluent.

Use Case 3 can contribute with data coming from Turin area served by SMAT of about 6,500 $km^2$, included in the Mediterranean basin.

The historical data of the plant for the input water to the 4D Scavenger technology presents the following average physicochemical values: COD (mg/L) = 768, BOD5 (mg /L) = 415, SST (mg/L) = 272.

## 5.4 Use Case 4

This Use Case will be implemented to demonstrate the monitoring of chemical pollutants of emerging concern at Sea. The Cyprus Marine and Maritime Institute (CMMI), in collaboration with seven partners, has developed a scientific buoy for the observation of metocean parameters. The primary aim is to contribute to the marine observation and marine data exchange (open source) but also to develop expertise for the benefit of National and European goals, as well as for the scientific community. The buoy has been already deployed off the coast of Cyprus near the city of Limassol. The main structure has a wooden frame with fibreglass coating in a cylindrical shape with three meters diameter and 1.10 meters height. It incorporates both the batteries and the electrical panel with the necessary wiring for the installed sensors. The battery capacity, which is recharged by four PV panels, supports an additional electrical load.

The electrical panel has been specifically designed to accommodate two additional 12 V sensors and two additional 24 V sensors, which can be placed within the surplus internal space of the buoy. Therefore, the buoy's floatation, balancing weight, and mooring system are also designed to allow the incorporation of additional equipment. The internal PC of the buoy is connected to the datalogger and of additional instruments connection through USB connectors. The buoy's datalogger is designed with more input slots allowing the integration of additional sensors through network cable pins. Data collected by these sensors are transmitted via 4G to the cloud system of CMMI. This project complies with open source, and FAIR data principles, and CMMI offers an online dashboard to present the information.

Currently, the facility measures a range of parameters, including chlorophyll-a, fluorescence, dissolved organic matter, pH, nutrients, conductivity, pressure, salinity, seawater temperature, current speed and direction, dissolved oxygen, acoustic, and meteorological information.

During the iMERMAID project, the involved partners will explore the perspective of monitoring organic pollutants and heavy metals within Use Case 4. For this reason, four iMERMAID sensors will be incorporated into the buoy:

- BIOS - Development of oil sensor for contaminants (e.g., crude oil derivatives and sunscreen oils) as part of a pilot testing.
- UA - Organic micropollutants electrochemical sensor box.
- ZEN – PFAS monitoring platform.
- UNIFI - Heavy metals electrochemical sensor box.

In the Use Case, the iMERMAID's consortium will also employ the technology developed by NTUU KPI for monitoring Water bodies using satellite data. The satellite data will be employed to assimilate the data from in-situ sensors, incorporate innovations and provide a cross-assessment, comparing satellite data recognition with data available from sensors. This assimilation, which has proven to be the most viable approach to determine the best estimates of the ocean state, is the combination of in-situ data with all available information from numerical models describing the ocean dynamics, observations, and prior information.

## 5.5 Use Case 5

Use Case 5 will be installed in the Leachate Treatment Plant (LTP) of Pera Galini Sanitary Landfill, Crete (Greece). The LTP is a tertiary treatment plant that receives the leachate produced by the waste disposal sites and the Sanitary landfill cells of Pera Galini. The Municipal Sanitary Landfill of Pera Galini is the largest landfill of the island and is located 40 km west of Heraklion city in an area of 45 acres. It receives around 130,000 tons/year of municipal solid waste from the majority of Heraklion prefecture.

The LTP Treatment consist of three stages: a) a physical/chemical process including coagulation, flocculation, and Dissolved Air Flotation (DAF); b), a physical/biological treatment based on a Membrane BioReactor (MBR); and c) a purification process with Reverse Osmosis technology. The effluent after degasification and chlorination can be used for recirculation to the landfill for enhancing its performance and/or irrigation of the plants on the surface of the restored landfill cells.

Through the utilization of cutting-edge innovations such as microfluidic systems described in *Section 4.1* within wastewater treatment plants together with an efficient and real-time monitoring of the pollutants with the electrochemical sensor described in *Section 3.1* we aim to successfully lower the concentration of micropollutants in the effluent. As a result, this reduction plays a crucial role in mitigating the flow of these contaminants into the Mediterranean Sea. Additionally, an electrochemical sensor that is described in *Section 3.3* for heavy metals monitoring in the effluent will also be applied. The target compounds that electrochemical sensors could detect include various heavy metals, such as $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$ and others.

The average raw leachate flow rate entering the plant is 110 $m^3$/day and includes physicochemical and biochemical treatment stages. However, the remediation technology that will be applied here has the capacity to treat 1 $m^3$ per day, corresponding to around 1% of the total effluent flow. Although it seems a small percentage, it is needed to assess the development stage of the technology. The flow treated should be enough to evaluate the efficiency of the technology.

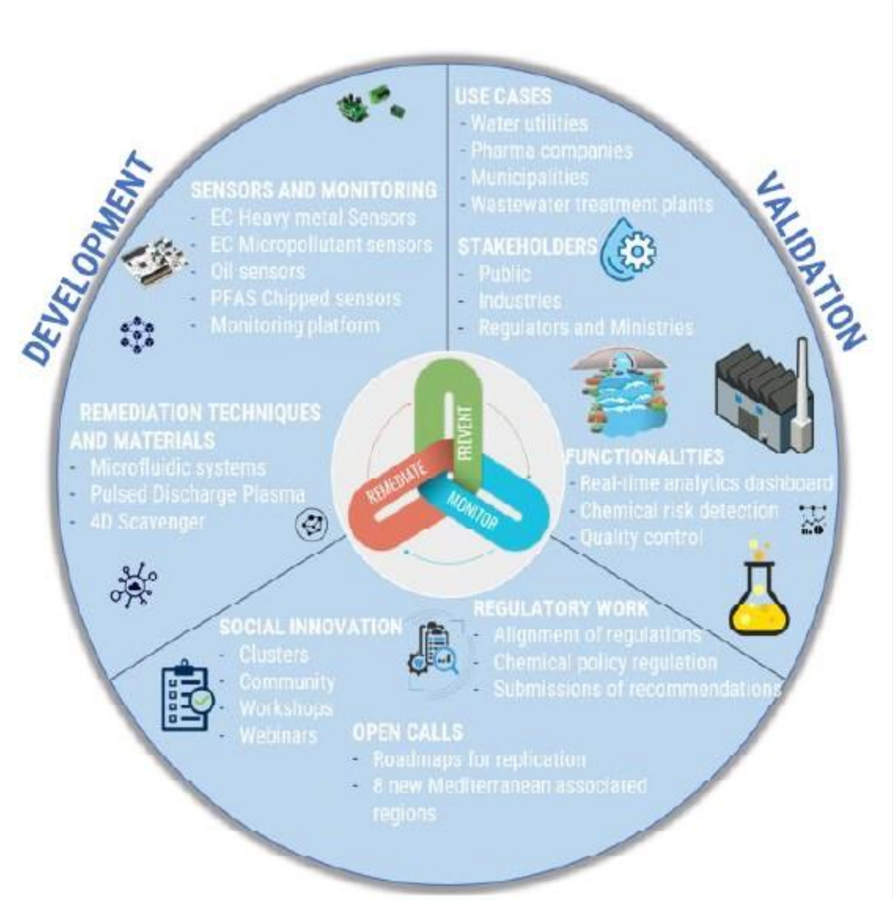


Figure 22: iMERMAID Concept.

# 6.0 Contaminants

Contaminants in water cover a wide range of substances, from solids in suspension, heavy metals, cleaning products to pharmacological substances or pesticides. Therefore, in wastewater it is possible to find thousands of molecules that can be considered as pollutants.

The WFD has served as the primary water protection legislation in Europe since 2000. It encompasses inland superficial water, transitional water and coastal superficial water, all regulated by a daughter directive focusing on surface water quality. Additionally, the WFD extends its application to groundwater, which is subject to another daughter directive addressing both groundwater quality and quantity. These directives collectively contribute to a comprehensive framework for safeguarding various water sources.

The main objective of the directive is to protect and restore the good status of the water from ecological and chemical point of view as well as prevent deterioration. The most important point from the project perspective is that WFD includes in its Annex X the list of priority substances that Member States must monitor in surface waters.

## *6.1 CoEC*

Contaminants of Emerging Concern can be defined as those contaminants not subject to a specific regulation but that they have been detected and could become a problem for human health or the environment. In general, they are found in a small concentration, but due to their nature, they can cause environmental and health effects by long term or chronic exposure.

There are different families of compounds included in the CoEC, such as pharmaceuticals, pesticides, food additives, flame retardants, cosmetics and so on.

Under the WFD, the Watch List strategy has been developed with particular focus on the monitoring of a series of emerging contaminants that could be a risk for human health and the environment. Currently, there is not enough data to determine the associated risks. Every three years, the List is reviewed to incorporate new contaminants or withdraw some of the existing. The List (see *Table* 11) is limited to a small number of contaminants due to the limited resources available, therefore, the contaminants of the highest concern are selected in each revision.

Table 11: Substances in the Wacht List of the WFD in 2022.

| Substance name | CAS number | Family |
|---|---|---|
| Sulfamethoxazole | 723-46-6 | Drug |
| Trimethoprim | 738-70-5 | Drug |
| Venlafaxine | 93413-69-5 | Drug |
| O-desmethylvenlafaxine | 93413-62-8 | Drug |
| Clotrimazole | 23593-75-1 | Drug |

| | | |
|---|---|---|
| Fluconazole | 86386-73-4 | Drug |
| Imazalil | 35554-44-0 | Pesticide |
| Ipconazole | 125225-28-7 | Pesticide |
| Metconazole | 125116-23-6 | Pesticide |
| Miconazole | 22916-47-8 | Drug |
| Penconazole | 66246-88-6 | Pesticide |
| Prochloraz | 67747-09-5 | Pesticide |
| Tebuconazole | 107534-96-3 | Pesticide |
| Tetraconazole | 112281-77-3 | Pesticide |
| Dimoxystrobin | 149961-52-4 | Pesticide |
| Azoxystrobin | 131860-33-8 | Pesticide |
| Famoxadone | 131807-57-3 | Pesticide |
| Diflufenican | 83164-33-4 | Pesticide |
| Fipronil | 120068-37-3 | Pesticide |
| Clindamycin | 18323-44-9 | Drug |
| Ofloxacin | 82419-36-1 | Drug |
| Metformin | 657-24-9 | Drug |
| Guanylurea | 141-83-3 | Drug |
| Butyl methoxydibenzoylmethane | 70356-09-1 | Sunscreen agent |
| Octocrylene | 6197-30-4 | Sunscreen agent |
| Benzophenone-3 | 131-57-7 | Sunscreen agent |

## 6.2 Contaminants in iMERMAID

The compounds to be studied within the iMERMAID project will be selected depending on several factors and not only because they are in the Wacht List. As a research project, there are several limitations coming from the maturity of the technologies. Therefore, to carry out an appropriate development in the laboratory it is necessary to work intensively with the molecules to be monitored or treated. In that sense, it is important both the availability of standard for good quality of results but also the chemical structure of the compound that should be close to those of higher interest.

Besides that, other crucial factors to determine the contaminants to be studied include the specificities of each Use Cases. So, for each Use Case there are some specific contaminants and no other. That is why, the compound to be selected must be found, previously, in the Use Case where the sensor and the remediation technology will be implemented.

Therefore, in Use Case 1, coordinated by SOCAMEX, the involved pollutants are related to pesticides and drugs because the main industry in the place where the WWTP is located is the agriculture and sewage water which contain residues of the intake drugs by the region’s inhabitants.

Use Case 2 is the monitoring and treatment of the effluents of a pharmaceutical industry, so in particular Diclofenac, Ibuprofen and Ketoprofen will be the target compounds.

In the WWTP of Use Case 3, metals such as Ni, Cu, Zn and Al will be chosen as target compounds. Although other types of contaminants can be present, the focus is made on heavy metals as because other Use Cases will deal with other contaminants.

In the buoy of Use Case 4, four of the project's sensors will be deployed to monitor the contaminants in the Mediterranean Sea.

Finally, the leachates of Use Case 5 that contain most types of contaminants will be studied with a different combination of sensor and remediation technology where the molecule to be monitored is defined by both the used sensor and technology.

# 7.0 Technological platforms and tools

In the constant struggle to preserve water quality, Data Life Cycle management is fundamental for both the planning and execution of processes for the Elimination of Pollutants in Water and for the work of dissemination, awareness, and training in these areas.

In today's industrial context dominated by digital transformation, effective data management has become essential. The data lifecycle, which spans from acquisition to visualization, plays a crucial role in removing pollutants and protecting our water resources. We will then explore the different phases of this cycle and apply them in the context of removing pollutants from water.

## *7.1 Data Life Cycle*

The data life cycle is a concept that describes the different stages that a piece of data goes through from its creation to its eventual disposal. These phases are essential to understanding how to efficiently manage and leverage information in any system or process. The main phases of the data lifecycle are detailed below:

- **Data Generation or Creation**: In this phase, the data originates. It can be generated by a person, a machine, a sensor, or any other device or system capable of collecting information (e.g., a sensor in a water treatment plant that measures the concentration of pollutants).
- **Data Capture**: The newly created data is captured and recorded in a structured format. It may involve converting unstructured data into formats that allow an efficient storage and processing (the information measured by the sensor is transformed into an understandable format and sent to a database).
- **Data Storage**: The captured data is stored in a repository, which can be a file system, database, or any other storage medium (the results of the sensor's measurements are usually stored in a centralized database).
- **Data Processing and Transformation**: Stored data can be processed and transformed to obtain information or generate additional knowledge. This can include calculations, aggregations, or combining data from multiple sources (an analysis of trends in pollutant concentrations over time is conducted).
- **Data Exploitation**: The processed data is used for specific purposes, such as reporting, analysis, decision-making, or feeding systems and applications (the results of the analysis are used to evaluate the effectiveness of the pollutant control measures implemented).
- **Sharing or Distributing Data**: Relevant data is shared with other people, systems, or applications that may benefit from that information (water quality reports can be shared with government authorities, scientists, or the general public).
- **Data Retention**: It is decided how long the data will be retained. Some data may have long-term value, while others may be deleted after a certain amount of time (water quality data can be retained for years, for long-term studies).

- **Data Deletion**: In this phase, data that is no longer needed or relevant is securely deleted to free up space and ensure privacy (obsolete or irrelevant data on water quality may be deleted after an agreed specified period).

Understanding and managing these phases effectively is critical to ensuring the integrity, security, and usefulness of data throughout its lifecycle. In addition, these phases are applicable in a variety of contexts, from water management to data management in enterprise environments.

### 7.1.1 Data Lifecycle Applicability in the Context of CoEC Elimination

Therefore, the data lifecycle is significantly applicable in the context of the removal of CoECs in water from the perspective and specific objectives of the iMERMAID project. The following paragraphs detail the key applications of the data lifecycle that are of interest for the valorisation of results presented in this deliverable. These considerations should be taken into account as objectives or guidelines when designing the systems or functionalities of the project that are involved in these stages of the cycle.

Data Acquisition: Sensors as perpetual and automatic water watchers

The first phase of the data lifecycle begins with the acquisition of information. In the field of water management, sensors have become autonomous inspection elements. Equipped with advanced technology, such as those featured in the iMERMAID project, these devices can measure a variety of contaminants, from chemical to biological, providing accurate, real-time data.

Data Storage and Processing: The Basis of Decision Making

Once collected, data needs to be stored and processed in a common and standardized environment that is compatible with all possible processing and exploitation needs. In this phase, the definition of storage infrastructure and processing technologies play a crucial role. In addition, the application of advanced digital technologies makes it possible to provide systems with the ability to analyse large data sets to identify patterns and trends, providing valuable information for informed decision-making.

Pollutant Removal: Innovative Technologies in Action

With information in hand, the door is open to being able to design, evaluate, and implement the best innovative pollutant removal technologies. The effectiveness of many of these technologies will depend largely on the quality and accuracy of the data collected. A well-managed data lifecycle ensures efficient implementation of these solutions and correct measurement of their impact on improving water quality.

Data Visualization: Platforms for Awareness and Management

Data visualization is the culmination of the cycle, transforming information into accessible knowledge. Intuitive visualization platforms allow managers and the general public to understand water quality clearly and effectively. This not only raises awareness, but also boosts citizen participation and responsibility in water preservation.

In short, the data lifecycle stands as an essential enabler in the removal of contaminants in water. From acquiring data using advanced sensors to visualizing meaningful information, each phase plays a key role in the effective management of water resources. In this process, collaboration between technologies and public awareness becomes the key to a sustainable and healthy future for our water bodies.

### 7.1.2 Requirements for Data Lifecycle Applicability

In order to translate all these work philosophies into the applied context of the iMERMAID project, which is reproducible and extended to any work environment with different solution providers and heterogeneous sources of data, a prior process of collection of needs and standardization is necessary, a process from which a data architecture must be obtained as a result. The following are the considerations needed to develop a proper data architecture.

An adequate data capture architecture must be the result of the search for the optimal solution for automatic data collection in industrial environments, based on principles of versatility and reliability, and whose result will be reflected both in the capture of data in pilot cases (through adaptation motivated by the particular circumstances of each company), as well as the exploitation platform as a support element in tasks of diagnosis, validation or dissemination of existing results.

The objective of the generic architecture is the real-time collection and storage of historical data of those process variables that are considered critical or object of study from the perspective of the project's objectives. For the development of this task, a series of technical objectives are proposed to be covered:

- Development of sensors appropriate to the project in charge of collecting the physical magnitudes under study.
- Definition of capture architecture to be implemented.
- Selection of equipment (such as programmable logic controllers - PLCs) in charge of collecting time information from sensors.
- Selection of the communication elements responsible for providing connectivity to those elements.
- Design of the database (DB) in charge of storing the information collected by the control element for its subsequent exploitation.
- Design of an exploitation layer for the visualization of information and indicators.
- Implementation of architecture in pilot cases.

For the development of the data capture architecture, we will be based on the principles of IoT (Internet of Things) and on the creation of a set of connection alternatives for the sensor/technology/platform connection, working on gathering information to define the necessary requirements of all its components. To achieve this, the following steps have been followed:

Identification of information sources:

First of all, the different sources of information that may coexist within the field of application (facilities with different sensors and/or technologies) must be studied at the level of measurement points, controllers or automated systems that make up a source of information. To do this, the nature of the different transducers, controllers and buses they incorporate must be analysed. This study will serve as a starting point for the approach to the technical needs that may arise for the collection of information from these different sources.

Identification of technical needs, types of signal and protocols:
Based on the identification of the different sources of information, the identification of the technical needs that the capture layer may require is proposed in order to enable the acquisition of information in real time:

- Signal Type: analog or digital.
- Interface Type: Characteristic of the data bus in the case of wired or wireless communication.
- Protocol Type: Characteristics of communication protocols.

Definition of the specification booklet, database, capture service and exploitation layer:

Once the possible sources of information and their needs have been defined, the specification booklet must be carried out to be considered in the capture layer and in its architecture to ensure the collection and storage of the data:

- Modular architecture depending on the nature of the information.
- Sample cycles adaptable to the type of signal.
- Pre-processing required prior to storage.

The applicability of relational databases should be checked to verify that they are correctly adapted to the type of application by analysing their characteristics and functionalities. In reference to the exploitation layer, work must also be done on the definition of graphs and indicators that allow both real-time monitoring and historical consultation of the information stored in the database.

### *7.1.3 Implementation of the architecture in pilot cases:*

Lastly, the final work will be the functional implementation in the pilot cases, i.e., the installation of the controllers and sensors in an electrical panel that allows the measurements of the variables to be made and stored for exploitation and analysis, as well as to consult them remotely.

Within this methodology, it is worth highlighting the duality between technology providers and the entities responsible for the pilot cases, since, based on the same base architecture, two theoretically opposed implementations must be carried out; on the one hand, a specific functional implementation for the pilot cases, given certain intrinsic particularities and, on the other hand, the development of a scalable generic protocol that is capable of measuring any type of facility. This is possible thanks to the detailed study of existing IoT technologies and the selection of those that provide greater versatility and the development of a range of solutions that can be adapted to the typical cases of restrictions that appear in this type of installation.

On the side of the **entities responsible for the pilot cases**, their work consists mainly of providing specific information about the facility, which helps to define the generic architecture. Once the architecture has been defined, it will be shared with the companies to make the necessary modifications/updates to adapt to it and host the data capture system. In general, the architecture must be versatile enough not to involve major modifications to the entity's existing communications infrastructure, so that the main modifications are mainly the installation of sensors necessary to capture parameters with which to correctly characterize the facility. Despite this, and as expected, each data collection solution in each entity will be unique.

On the **technology provider** side, the work should be aimed at designing the communications alternatives based on all the lessons learned through the implementation of the architecture in the pilot cases, so that it is applicable to all of them. To do this, they must select and acquire the equipment and sensors that provide the greatest versatility when it comes to data capture. In general, this means having more complex equipment with greater communication capacity, which is not usually found in industrial facilities, but which is undoubtedly necessary to adapt to the different casuistry that can be found when having to place it in companies of different nature (sector, activity, type of technology, etc.).

## 7.2 Architecture for Data Capture for the iMERMAID Project

The data collection architecture is therefore a set of alternatives in terms of procedures and protocols that manage to build an automated database record (DB) for the collection of data in real time through the capture of values of measurable physical magnitudes, all that through a combination of hardware and software elements. The aim is to make a series of key data available for further exploitation, in this case through the platform developed in WP5.

Based on the criteria of simplicity and versatility, a classic hierarchical architecture of the following type has been chosen (*Figure 23*).

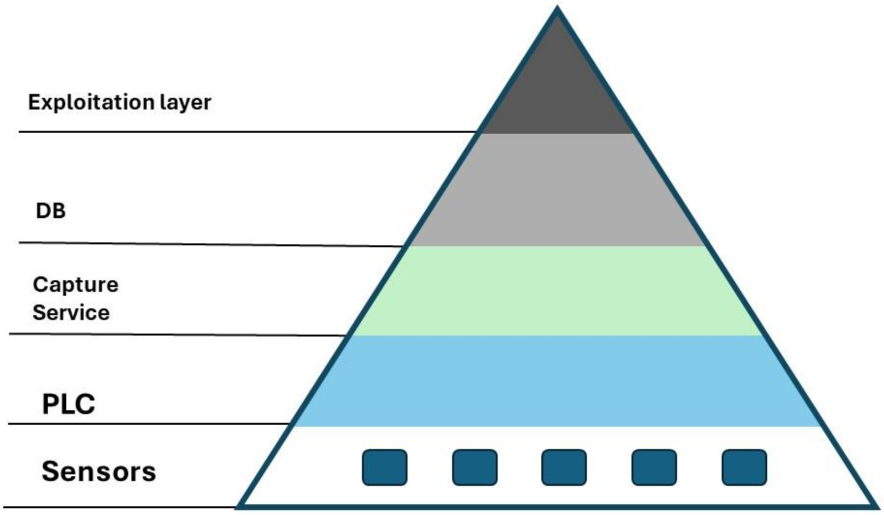


Figure 23: Traditional data architecture.

In general, the architecture will consist of two clearly distinguishable layers, a **physical** one, made up of the installed hardware elements (sensors, PLC, PC/Server, etc.) and a programming layer**,** responsible for capturing, transmitting and storing the data, mainly made up of software (communication protocols, database, capture service, etc.). These layers are integrated within the architecture as follows:

- **Measuring equipment [SENSOR]**: is a sensor or transducer (hardware) that extracts data directly from the source of information, converting a physical magnitude into an electrical signal that is transmitted over a certain channel.
- **Signal concentration and transmission elements [PLCs]:** these are elements that combine hardware (they are equipment that collect a signal and transmit and/or transform it so that it is understandable by the terminal elements) and software (specific communication protocols that make such transmission possible).
- **Data capture, storage and exploitation system:** consisting mainly of software, the physical support of these elements is a PC or server where all programmed procedures, databases and other services are hosted. It can be divided into three elements:
    - [Capture service]: through the programming of different reading and writing services, functionalities are developed that range from the capture of a signal in a certain element (generally a PLC or signal concentrator), the transformation of the electrical signal into numerical data (corresponding to the measured physical magnitude), and its storage in a database.
    - [DB]: This is the key element where all captured information is stored, it must have enough versatility to host any type of data that can be generated, and enough capacity to store data in real time and manage it quickly.
    - [Exploitation layer]: it is the terminal element where the interface with which a user interacts with the stored data is programmed, composed of different functionalities, which will be reflected in the tools developed in WP5 (iMERMAID platform), being the consultation of real-time and historical data the most relevant in relation to the data capture objective.

To define architecture, each of its main components must therefore be defined:

- Measuring equipment or transducers (hardware).
- Concentration and signal transmission elements.
- Data capture, storage and exploitation system.

### *7.2.1 Measuring equipment (hardware)*

Within the industrial field, specifically in the elimination of pollutants, the following sensors are considered:

Traditional sensors, mainly related to basic analytical parameters (pH, conductivity, turbidity, DOC, TOC), are today not sufficient. This is a relatively simple enumeration of traditional sensor typologies, i.e., those that perform a measurement of a physical quantity and after a stage integrated into the transducer it is converted to a signal. To address the iMERMAID challenge, selective sensors must be developed in the context of the iMERMAID project. In this sense, the following will also be considered:

- Electrochemical sensor for organic compounds.
- Oil sensor based on mass spectrometry.
- Electrochemical sensor for heavy metals.
- Electrochemical sensor for PFAs.

The signal emitted by a sensor is an electrical variable that can be given digitally (oscillates between two states of information, 0 or 1), or in analogue format. In either case, it is a conversion to an electric variable. Within iMERMAID project, the innovation work devoted to sensors will be focalized on targeted molecules and not as usual on global parameters (i.e., phenol index, TOC, DOC).

For a **digital signal**, the information is represented in two discrete states (0V and 24V). These signals will make it possible to discriminate the information referring to two states, such as the detection of the presence of a metallic object, or a plastic object, or the arrival of a certain pressure or temperature threshold, but in any case, we always speak of differentiation of two states (0 or 1).

In the case of an **analogue signal**, the information can travel through different values over a continuous range, with voltage output (0 – 10V) and current output (0 – 20 mA / 4 – 20 mA). In this case, live systems are intended to work at shorter distances from the sensor to the capture system (such as a PLC). Systems that are currently working make it possible to cover greater distances between the sensor and the receiving element, since the losses are lower, and they are more immune to noise (signal disturbances).

In either case, these sensors, which could be called traditional sensors or sources of information, do not incorporate any pre-processing of the information and the sending of the same is done in a wired way and without associated protocol.

In recent years, the reduction in the cost of this type of device, the reduction in its size and the incorporation of new measurement technologies based on optics and electronics have led to an evolution of these sources of information. In this case, elements for the measurement of electrical variables such as voltage, current can be found integrated in elements such as analysers that offer information through the MODBUS protocol.

MODBUS (Modular Digital Bus) is a widely used industrial communication protocol, which was developed by Modicon (now part of Schneider Electric) in 1979. Its popularity is due to its simplicity, versatility and wide adoption. It allows data transmission between master and slave devices through various media such as RS-232, RS-485 or TCP/IP. The flexibility of MODBUS facilitates its implementation in wired and wireless systems, while its interoperability with devices from different manufacturers makes it a cost-effective option. Its success lies in its ability to simplify communication in industrial environments, ensuring efficiency and effective integration of equipment from different sources. At present, MODBUS has become a widely used standard in industrial automation, and its name is commonly associated with efficient communication between devices in industrial environments.

In conclusion, in the physical part of data capture we will have two types of sensors, on the one hand sensors without data pre-processing that give as output an electrical signal (analog or digital) proportional to a single physical quantity, and on the other hand more complex and advanced equipment with communication through MODBUS protocol where it is possible to extract more than one parameter, generally related to the measurement of electrical magnitudes.

Based on this knowledge, several devices have been identified to aid in the information capturing. These devices are explained below:

- Analogue sensors: They are characterized by their simplicity and are responsible for measuring basic parameters such as temperature or pressure, they have analogue output signals of 4 – 20 mA and it is necessary to integrate them into a PLC to capture their information.
- Advanced sensors (flowmeters, network analysers): These are complementary equipment to improve the quality of the data collected, which can have different types of digital outputs, on the one hand requiring integration into a PLC with reading capacity or on the other hand through protocols such as the MODBUS type.
- Communication-capable communication cards: The controller of a machine or process is the most complete source of information, but access is often restricted by the equipment manufacturer. Generally, each manufacturer has its own product to make this information accessible, offered under different protocols, with the MODBUS option being available. This allows access to machine parameters (status, pressure, temperature, hours, on, off, control, etc.) However, not all of them are sensor-based, there are some parameters such as where the equipment can offer an estimate based on the manufacturer's software. Therefore, this information is suitable when there are no other sources available, but for the real-time data capture of the iMERMAID project, priority will be given to the installation of sensors that capture real magnitudes of the facility itself.

### 7.2.2 Concentration and signal transmission elements

Since the terminal element is a PC/Server, the last leg of the communications network will always be **Ethernet**, so the rest of the network elements will have to adapt with different protocol changes throughout the transmission of the signal. This offers a large number of advantages, the main ones being the integration of the data capture system into the IoT and the wireless transmission of information.

For the transmission of signals from the source of the data (sensor) to the point of storage and subsequent exploitation (PC/Server), we can find three options, which are shown in *Figure 24*:

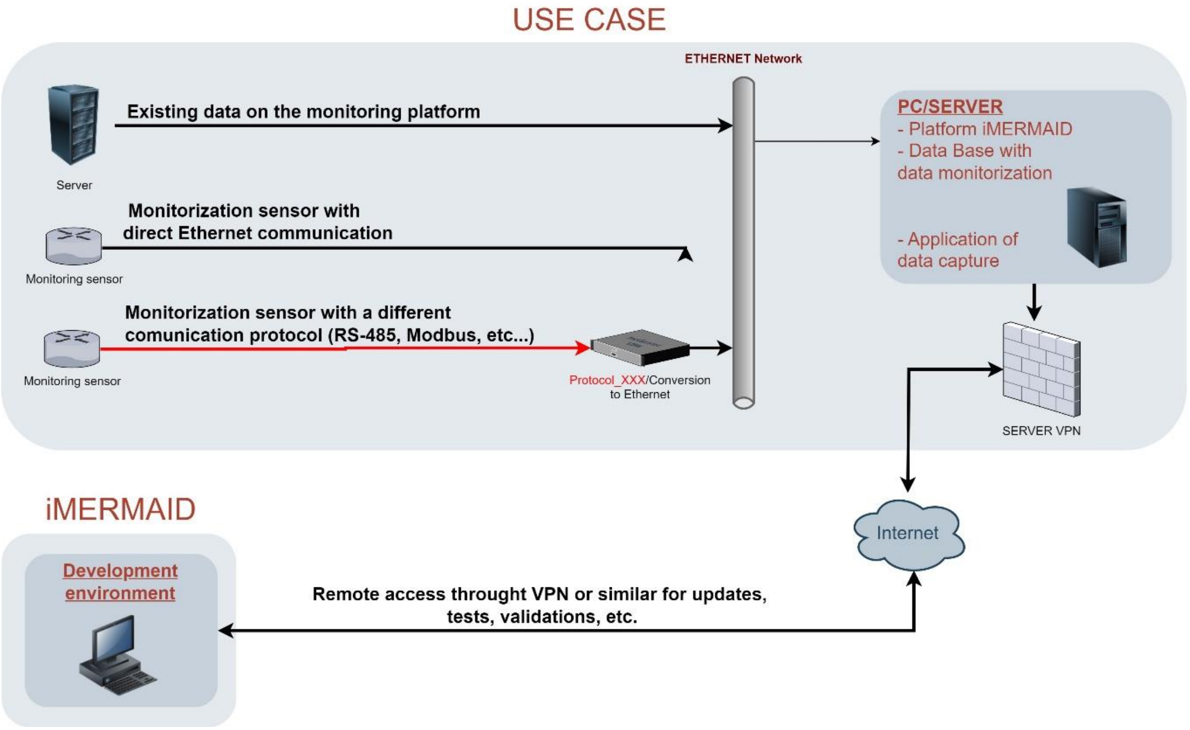


Figure 24: Basic Communications Outline.

First, the simplest way will be the transmission via Ethernet of data that already **exists in the network itself,** collected by other capture systems that the company already has. In this case, only a data migration service (software programming) from the company's database to the iMERMAID database will be required.

Secondly, sensors can be available **with direct communication through Ethernet,** this allows IoT techniques to be applied, as the sensor is another node in the company's network, and to be able to connect it directly with the capture and storage service, without the need for intermediate protocols or additional hardware.

Thirdly, **sensors with a protocol other than** Ethernet may be available, in this case, it will be necessary to install a converter (hardware) from that protocol to Ethernet (typically, these devices will be PLCs or communication gateways specific to that protocol). In this case, the converter or PLC is actually the node in the network where IoT techniques will be applied for data capture and, depending on its nature, it may house one or more sensors.

Therefore, PLCs and Gateways are key elements of the architecture to facilitate the integration and communication of sensors. For the capture architecture developed, the integration of a PLC that performs the function of FRONT END has been considered, so that the wired sensors are connected to this PLC, and it is the PLC that serves the data to the database.

Based on the previous section where the sensor layer has been defined, in this section the traditional hierarchical architecture has been analysed, obtaining a set of possible transmission methods that, depending on the nature of the information sources, can be divided into different equipment and protocols.

In the **hardware part,** the element that must concentrate all the captured signals has been defined, which is a **Programmable Logic Controller (PLC).** In this layer, the type of controllers found are going to be more related to systems such as programmable controllers, network analysers, industrial controllers, vacuum measuring systems, etc. In this sense, the information will certainly be processed, and will be accessible through industrial protocols such as Industrial Ethernet, PROFINET, PROFIBUS, etc.

In the part of protocols (software), protocols capable of working within the proposed architecture have been identified, described below:

- **PROFIBUS.** (Process Field Bus) International standard for high-speed fieldbus for process control standardized in Europe by EN 50170.
- **MODBUS** is a transmission protocol for process control and supervision systems (SCADA) with centralized control, it can communicate with one or more Remote Stations (RTUs) in order to obtain field data for the supervision and control of the process. Physical Layer Interfaces can be configured in: RS-232, RS-422, RS-485. In MODBUS, data can be exchanged in two transmission modes.
- **DeviceNet.** Low-level network suitable for connecting simple devices such as photoelectric sensors, magnetic sensors, pushbuttons, etc., and high-level devices (PLCs, controllers, computers, HMIs, among others). It provides additional information about the status of the network, the data of which will be displayed in the user interface.

### *7.2.3 Data capture, storage and exploitation system:*

The data capture service is a software development in charge of collecting information from different controllers such as sensors, PLCs or network analysers connected to the company's Ethernet network. This service collects the information through the indicated protocol (MODBUS, Profibus, etc.) and registers the information on the variables in the database.

Based on the analysis of the different sources of information, a series of needs are identified that the information collection infrastructure must have.

- On the one hand, the **real-time feature** is a factor to be taken into account, the need to have updated and synchronized information is a key factor in its analysis and exploitation. For this reason, it is necessary that the read cycles of the different capture systems of each element minimize the latency time between reads in order for the information to be sampled as quickly as possible and that in turn allows stable reading cycles that do not corrupt the information.
- **Synchronization** is another factor to take into account, since the information will come from different points of origin, it is convenient that the storage is carried out in a synchronized way, that is, that the values read have the same timestamp in a way that facilitates their analysis and correlation between data. In the same way, this synchronization must be accompanied by a fixed insertion frequency, i.e., in those types of numerical variables where the value of a set of related variables is to be recorded periodically, it will be important that the recording frequency remains unchanged. For those variables that are state changes such as alarms or operating modes, the

record should not be periodic but what will be sought is a record in the event of an event change, in this way the storage size will be optimized since it will only be recorded when there is a change of state.

The capture service must be considered to work on a continuous execution, which allows reading the sensor variables through the protocol with which they operate and inserting the information read in the database in a synchronized way (same 'timestamp') and with a high sampling rate, which makes it possible to insert the information every minute in the database.

The inserted value can be pre-processed in such a way that an average of the values read in that minute is actually inserted in the database according to a series of imposed rules, in such a way that the saved data is as real as possible and that avoids any disturbance due to unrealistic peaks or null values due to a failure in the capture.

On the other hand, the capture service must have a space where all captured information can be stored, a role played by the database, with sufficient versatility and capacity to face the challenges of capture in real time.

The data capture service is also supported by the specifications of the variables from the database, so that each variable can be characterized from one of the tables created in the database. This allows you to determine a series of maximum and minimum values per variable in such a way that it does not take into account any values captured outside that range for that variable. This can restrict variables to positive values or avoid unwanted spikes.

Given that the database is the common element of data communication with the rest of the platform, in addition to the particularities of the data to be captured, its design must follow the guidelines set out in WP5, to ensure compatibility with the rest of the information present in the iMERMAID platform, which will also be stored in a database.

To this end, relational databases are based on the model of the same name and are currently the most widespread. These databases are based on an ***RDBMS (or database management system)*** *and use* the SQL (*Structured Query Language)* for the administration and retrieval of information in this type of database. This type of database consists of:

- Fully structured tables with a defined schema.
- Relationships between tables by using:
    - A set of primary keys, which identify the table itself by being unique to each record.
    - Foreign keys that allow the identification of a table's record (by using its primary key) from another table's records.

The transactions of this type of database are of the type called ***ACID,*** which has a series of characteristics that must be complied with and are managed by the *DBMS* or ***RDBMS.*** These features are:

- Atomicity: Transactions in these databases must be complete. In other words, when a transaction requires a succession of steps to carry it out, either all of them are carried out or none will be carried out.

- Consistency: Implies that any transaction that is carried out in the database will take it from one valid state to another valid state.
- Isolation: Ensures that different transactions on the same information are totally independent and do not interfere with each other. Therefore, several operations on the same information cannot generate error or affect each other.
- Durability: This feature guarantees that any transaction made on the database will be persistent and will not disappear, even if there is a failure in the system.

PostgreSQL has been chosen as the main database structure because it is open source and has a large support community behind its development. In addition, it offers a large number of possibilities in terms of programming and automation through the development of triggers and stored procedures that can be carried out by using different programming languages. For data capture, a table has been created for the real-time collection of information and other tables for historical data where the information of all the variables is collected synchronically.

Finally, the data exploitation layer, formed by the interface with which a user interacts with the stored data, and also following the already known WP5 guidelines, has been designed to be in a web environment, i.e., accessible by browser and accessed by each user through LOGIN and PASSWORD credentials.

This layer has a dashboard (according to Task 2.5) where the user can observe the data captured in real time of the variables, consult historical data and access all the tools developed.

### 7.2.4 iMERMAID platform conceptual architecture

The iMERMAID platform (*Figure 25*) represents an innovative digital solution designed to safeguard the Mediterranean Sea basin from chemical contamination scenarios. At its core, the architecture is a synergistic combination of user-centric interfaces, robust data processing mechanisms, and secure, immutable data storage methodologies.

The platform is structured into multiple layers, starting with the user-friendly dashboard that serves as the nexus for interactive visualization and storytelling, aimed at engaging stakeholders in effective decision-making processes. Below this, the platform is fortified by a suite of APIs that ensure fluid communication between the front-end and the diverse backend services. A resilient database acts as the central repository for all collected data, with a sophisticated data processor that handles the active pipeline of multimodal data. Ensuring the integrity and trustworthiness of this data is the blockchain connector, leveraging cutting-edge distributed ledger technology to maintain data veracity. On the ground level, a network of IoT sensors, categorized into groups X, Y, and Z, continuously gathers critical environmental data, which is then channelled through a cloud connector and gateway, ensuring secure and efficient transmission to the platform's central systems. This hierarchical yet interdependent structure is designed to be both scalable and adaptable, capable of integrating with emerging technologies and responding to evolving environmental monitoring needs.

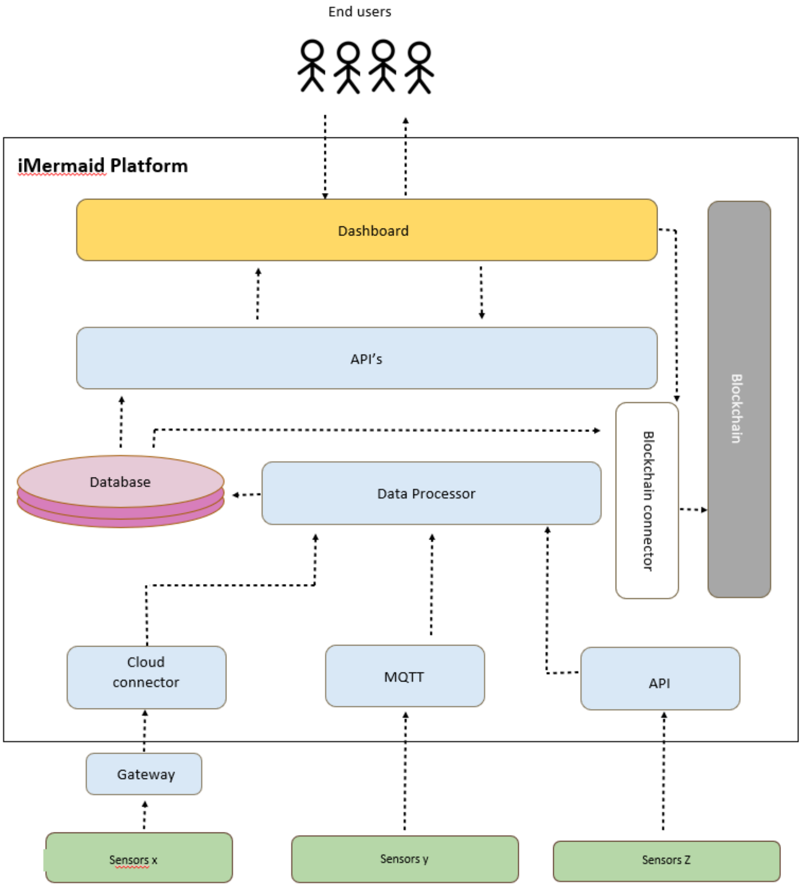


Figure 25: iMERMAID platform architecture.

The main actors and components of the platform are:

- **End Users:** The end users are the primary stakeholders of the iMERMAID platform. They interact with the platform through a visual toolbox that offers interactive dashboards and storytelling elements. These features are designed to engage various stakeholders, such as policymakers and environmentalists, in decision-making activities related to the Mediterranean Sea basin protection.
- **iMERMAID Platform Dashboard:** The dashboard is the user interface of the iMERMAID platform. It serves as a visual toolbox that provides end users with interactive dashboards, aiding in storytelling and the interpretation of data. This is where stakeholders can visualize data from IoT devices and modelling tools in a user-friendly manner, facilitating informed decision-making and policy development.
- **Application Programming Interfaces (APIs):** are the conduits through which different software components communicate. In the iMERMAID platform, APIs serve as bridges between the dashboard, data processor, and the blockchain connector. They enable the retrieval, manipulation, and storage of data, ensuring seamless interaction between the platform's frontend and backend systems. The APIs are also used to collect data from specific types of sensor data or external services that need to

integrate with the platform. They could be tailored to handle specific data formats or communication protocols.

- **Database:** The database is the centralized repository for all data within the iMERMAID platform. It stores information collected from various sources, including IoT devices. This database is essential for data consolidation and provides the necessary infrastructure for effective data management and retrieval.
- **Data Processor:** The data processor is a critical component responsible for the active processing pipeline of multimodal and heterogeneous data. It receives data from the database and IoT devices, processes it, and sends it to the dashboard and the blockchain connector. It is a crucial part of the unified cloud-data infrastructure, ensuring secure and efficient data handling.
- **Blockchain Connector:** This component ensures the trustworthiness of information by utilizing distributed ledger technology. It writes data hashes into the blockchain, guaranteeing the immutability and integrity of the collected data. By using scalable, open-source blockchain protocols, the platform ensures that the data is tamper-proof and verifiable.
- **Cloud Connector:** The cloud connector provides middleware services that enable the platform to interact with cloud-based resources. It facilitates the secure collection and storage of data from IoT devices and ensures that the platform's services are scalable and resilient.
- **MQTT:** MQTT (Message Queuing Telemetry Transport) is a lightweight messaging protocol used for the efficient transmission of telemetry data from sensors (IoT devices). It facilitates real-time data exchange between sensors and the iMERMAID platform, ensuring timely and reliable communication.
- **Gateway**: The gateway acts as the intermediary between the sensors (IoT devices) and the cloud connector. It is responsible for data aggregation, protocol translation, and ensuring secure data transmission to the cloud.
- **Sensors:** These are the IoT devices deployed in the field to collect various data points related to the Mediterranean Sea basin. Sensors have been explained in more detail in *Section 3.0* of the present document.

# 8.0 Upstream technologies and reusable work

Within the iMERMAID project, different contaminant's sensors as well as remediation technologies will be developed. Although most of the Use Cases combine a sensor with a remediation technology, it is important to point out that sensors and technologies can be used separately. In fact, in the Use Case 4, which consists of a buoy located in the sea close to Limassol, only sensors are deployed, furthermore, that buoy is monitoring other complementary parameters such as salinity, pH, temperature and so on.

On the other hand, during the project, the bioaccumulation and biomagnification of pollutants in biota of different trophic levels will be studied. When contaminants of water are delivered into the environment, they will travel from effluents and rivers until they reach the Sea. Finally, the contaminants enter the life organisms where they can accumulate and propagate arriving to humans through the food chain. For this reason, it is not only important to assess the direct effect of these pollutants on the water quality of the Mediterranean Sea basin, but also their indirect influence through food intake. In this regard, it is important to note that marine products collected in the Mediterranean basin are consumed globally. Therefore, an improvement in the ecosystem's quality will have a positive impact, to a greater or lesser extent, on the quality of life of the world's population.

Methodology for assessing **bioaccumulation-biomagnification of contaminants** in the marine environment: Collection of seawater, phyto- and zooplankton, benthos and fish samples will be conducted using HCMR research vessel 'FILIA' equipped with appropriate oceanographic instrumentation (Ninskin bottles, CTD, Zooplankton nets, filtration systems). The vessel is also equipped with fisheries gear and fish and benthic organisms will be collected during experimental trawling. The aim is to obtain a well-defined food web from seawater, Phyto and zooplankton and up to 6 species of fish and pelagic invertebrates. Stable isotopes analysis nitrogen (δ15N) and carbon (δ13C) in zooplankton and animals' tissues will be done in a dedicated isotopes' laboratory and will be used to identify the trophic position of the organism. Contaminants analyses in samples/tissues will be determined using standard analytical techniques (Hg Fluorescence Analyzer, ICP/MS, LC/MS/MS). For organic contaminants, the solid-liquid extraction method will be customised according to the requirements of the targeted substances, which will be identified and quantified through advanced chromatography techniques. iMERMAID solutions for chemical pollution remediation.

Monitoring the quality of the sea water and identifying those contaminants that produce effects in environment and human health is of high importance. Quantifying the contaminants in the Mediterranean Sea is very important to determine the existing contaminants, however, it is impossible at this stage to act over the sea water for remediation. That is why, together with the monitoring in the sea, it is necessary to monitor those contaminants upstream in the rivers reaching the source of the contaminants. Meanwhile, the concentration of contaminants in the sea is notably low, making it impractical to treat the entire water mass. On the contrary, in sources of contaminants such as water treatment plants, industries, and similar sites, the concentration is higher, and the water flow is smaller. Therefore, this becomes a critical juncture for introducing remediation technologies tailored to address various pollutants. Furthermore, it is at these locations where the concentration of pollutants is typically higher, and therefore, more dangerous for the ecosystem. Thus, remediation technologies will have a greater impact the closer they are to the original sources of aquatic contamination.

Summing up, the life of contaminants, in the source of contamination the concentration is higher, and the flow water is smaller, then, in the river the contaminants start to dilute until they arrive in the sea where the concentration is much lower than in the source of contamination. However, iMERMAID project will act in a previous stage. The use of high concern compounds is something that is always under regulation. From scientific results, the project also aims to direct the policies to avoid or restrict those contaminants that represent the highest concern for environment and human health. The iMERMAID project will provide relevant information to regulatory authorities, indicating the typology of pollutants and their concentration. Additionally, it will enable the mapping of the distribution of these contaminants, allowing for local intervention if necessary and reducing the risk posed to the ecosystem of the region.

Another important aspect of the project is the data management. In general, the WWTP work as independent units, however, iMERMAID aims to treat data in a holistic way, from monitoring contaminants in the sea and the accumulation in life organism together with the data obtained in the source points. All those data will allow to track contaminants from the origin to the final effects in the environmental and human health. Furthermore, the joint processing of data through new computational methods will allow us to extract more robust and global conclusions. It will enable the observation of the influence of different parameters and its correlation, which could be lost if treated independently and in isolation.

So, from iMERMAID project not only sensors or technologies will be developed to be reused in the future but a more comprehensive water remediation strategy from monitoring, data treatment and policy making that will be the product of the project to be used for coming challenges on water remediation in the Mediterranean basin.

# 9.0 Conclusions

Deliverable ‘D4.2 Benchmarking and analysis of current aspects, requirements, specifications and conceptual architecture’ completes Task 4.2 ‘Technical Specifications’, covering all the relevant aspects and activities described in the Task.

*Section 2.0* involves the benchmarking of water remediation technologies, with a specific focus on treatment methods designed to eliminate recalcitrant contaminant that persist after primary and secondary wastewater treatment. Additionally, the chosen technologies do not introduce any additional chemicals into the process.

The technical specifications for various sensors and technologies have been outlined in *Section 3.0* and *Section 4.0* respectively. To ensure thorough development, detailed specifications have been provided taking into account the Technology Readiness Level for each development. Both sensors and treatment are at the forefront of innovation, emphasizing a cutting-edge approach for a comprehensive integration into the wastewater remediation process.

Both sensors and technologies will be applied in real-world scenarios. *Section 5.0* describes five distinct Use Cases incorporated into the project, each with its unique characteristics. The cases involve various wastewater effluents, and the nature and composition of contaminants vary across them. In addition to addressing wastewater effluents, the project incorporates a monitoring buoy to enhance the detection of contaminants in the Mediterranean Sea basin.

*Section 6.0* sets out that the selection of contaminants for the iMERMAID project adheres to the most pertinent European Directives, both the ‘Water Framework Directive’ and the ‘Marine Strategy Framework Directive’. However, additional considerations encompass parameters like the likelihood of occurrence in the studied Use Cases, along with results derived from laboratory testing of various technologies and chemical families.

*Section 7.0* is devoted to defining technological platforms and tools. The data lifecycle and data architecture have been established, underscoring their paramount importance in effectively managing the remediation strategy. The significance of the data lifecycle extends beyond the efficient elimination of pollutants through water treatment, also by playing a vital role in understanding the origin of contaminants and their implications for the environment and for the human health.

Lastly, *Section 8.0* provides a summary of the upstream technologies and reviews the reusable work that will be generated throughout the iMERMAID project’s lifespan.

This comprehensive deliverable corresponds to the starting point that will bring together the technical concepts that can be used in the iMERMAID’s Use Cases and will mark the focus of the subsequent work, regarding the tasks of investigation, modelling, monitoring, control and verification of the water remediation.

# 10.0 References

1. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal Legislation 327, 22/12/2000, P. 0001 – 0073.
2. Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a framework for community action in the field of marine environmental policy. Official Journal Legislation 164, 25/6/2008, p. 19 – 40.
3. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. Official Journal Legislation 435, 23/12/2020, p. 1 – 62.
4. Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. Official Journal Legislation 135, 30/5/1991, p. 40 – 52.
5. Hasan, H. A., & Muhammad, M. H. (2020). A review of biological drinking water treatment technologies for contaminants removal from polluted water resources. Journal of Water Process Engineering, 33, 101035.
6. Peiró, A.M. Nuevas aportaciones al desarrollo de metodologías en química verde: Eliminación fotocatalítica de contaminantes fenólicos y preparación de fotocatalizadores mediante procesos químicos suaves. Barcelona: Universitat Autónoma de Barcelona, 2003. Doctoral dissertation.
7. Fox, M. A.; Dulay, M. T. Heterogeneous Photocatalysis. Chem. Rev., 93, 341-357, 1993.
8. Wold, A. Photocatalytic properties of TiO2. Chem. Mater., 5, 280-283, 1993.
9. Houas, A.; Lachleb, H.; Ksibi, M.; Elaloui, E.; Guillard, C.; Hherrmann, J.M. Photocatalytic degradation pathway of methylene blue in water. Applied Catalysis B: Environmental, 31, 145-157, 2001.
10. Frazer, L. Titanium dioxide: environmental white knight? Environmental health perspectives 109, 174-177, 2001.
11. Fujishima, A.; Zhang, X.; Tryk, D.A. TiO2 photocatalysis and related surface phenomena. Surface Science Reports 63, 515-582, 2008.
12. Isopencu, G.O., Mocanu, A., Deleanu, I.M. A Brief Review of Photocatalytic Reactors Used for Persistent Pesticides Degradation. ChemEngineering 6, 89, 2022.
13. Puma, G.L., Machuca-Martínez, F., Mueses, M., Colina-Márquez, J., Bustillo-Lecompte, C. Scale-Up and Optimization for Slurry Photoreactors. In Advanced Oxidation Processes; IntechOpen: London, UK, 1–22, 2020.
14. Ahmed, S., Rasul, M.G., Brown, R., Hashib, M.A. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. Journal of Environmental Management, 92, 311–330, 2011.
15. Blanco Gálvez, J. et al. Descontaminación y desinfección de agua y aire mediante procesos solares de oxidación avanzada. Madrid: CIEMAT, 2009.
16. Al-Nuaim, M.A., Alwasti, A.A., Shnain, Z.Y. The photocatalytic process in the treatment of polluted water. Chemical Papers, 77, 677–701, 2023.
17. Ahmed, S., Rasul, M.G., Brown, R., Hashib, M.A. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. Journal of Environmental Management, 92, 311–330, 2011.

18. Fenoll, J., Martínez-Menchón, M., Navarro, G., Vela, N., Navarro, S. Photocatalytic degradation of substituted phenylurea herbicides in aqueous semiconductor suspensions exposed to solar energy. Chemosphere, 91(5), pp. 571–578, 2013.
19. Fenoll, J., Sabater, P., Navarro, G., Pérez-Lucas, G., Navarro, S. Photocatalytic transformation of sixteen substituted phenylurea herbicides in aqueous semiconductor suspensions: Intermediates and degradation pathways. Journal of Hazardous Materials, 244-245, 370–379, 2013.
20. Gambín, M., Pérez-Lucas, G., Navarro, S. Removal Kinetics of Four Leacher Herbicides Through Solar Heterogeneous Photocatalysis as Influenced by Water Matrix Components. Bulletin of Environmental Contamination and Toxicology, 106, 989–995, 2021.
21. Mahmoodi, N.M., Arami M., Limaee, N.Y., Gharanghij, K. Photocatalytic degradation of agricultural N-heterocyclic organic pollutants using immobilized nanoparticles of titania. Journal of Hazardous Materials, 145, 65-71, 2007.
22. Haque, M.M., Muneer, M. Heterogeneous photocatalysed degradation of a herbicide derivative, isoproturon in aqueous suspension of titanium dioxide. Journal of Environmental Management, 69(2), 69–176, 2003.
23. Parra, S., Olivero, J., Pulgarin, C. Relationships between physicochemical properties and photoreactivity of four biorecalcitrant phenylurea herbicides in aqueous TiO2 suspensions. Appl. Catal. B: Environ. 36, 75–85, 2002.
24. Maldonado, M.I., Passarinho, P.C., Oller, I., Gernjiak, W., Fernández, P., Blanco, J., Malato, S. Photocatalytic degradation of EU priority substances: a comparison between TiO2 and Fenton plus photo-Fenton in a solar pilot plant. J. Photochem. Photobiol. A: Chem. 185, 354-363, 2007.
25. FENOLL, J., HELLÍN, P., FLORES, P., MARTÍNEZ, C.M., NAVARRO, S. Degradation intermediates and reaction pathway of carbofuran in leaching water using TiO2 and ZnO as photocatalyst under natural sunlight. Journal of Photochemistry and Photobiology A: Chemistry, 251, 33-40, 2013.
26. TOMAŠEVIC, A. MIJIN, D. MARINKOVIC, A., CVIJETIC, GAŠIC, S. Photocatalytic degradation of carbamate insecticides: effect of different parameters. Pestic. Phytomed. (Belgrade), 34, 193-200, 2019.
27. MAHALAKSHMI, M., ARABINDOO, B., PALANICHAMY, M., MURUGESAN, V. Photocatalytic degradation of carbofuran using semiconductor oxides. Journal of Hazardous Materials, 143, 240-245, 2007.
28. CHU, W., RAO, Y., HUI, W.Y. Removal of simazine in a UV/TiO2 heterogeneous system. Journal of Agricultural and Food Chemistry, 57, 6944-6949, 2009.
29. SIRTORI, C., AGÜERA, A., GERNJAK, W., MALATO, S. Effect of water-matrix composition on Trimethoprim solar photodegradation kinetics and pathways. Water Research, 44, 2735–2744, 2010.
30. JALLOULI, N., PASTRANA-MARTÍNEZ, L.M., RIBEIRO, A.R., MOREIRA, N.F.F., FARIA, J.L., HENTATI, O., SILVA, A.M.T., KSIBI, M. Heterogeneous photocatalytic degradation of ibuprofen in ultrapure water, municipal and pharmaceutical industry wastewaters using a TiO2/UV-LED system. Chemical Engineering Journal, 334, 976–984, 2018.
31. Harry, J. E. (2013). Introduction to plasma technology: science, engineering, and applications. John Wiley & Sons.
32. Zheng, C., Xu, Y., Huang, H., Zhang, Z., Liu, Z., Yan, K., & Zhu, A. (2013). Water disinfection by pulsed atmospheric air plasma along water surface. Aiche journal, 59(5), 1458-1467.

33. Rashmei, Z., Bornasi, H., & Ghoranneviss, M. (2016). Evaluation of treatment and disinfection of water using cold atmospheric plasma. Journal of water and health, 14(4), 609-616.
34. Singh, R. K., Philip, L., & Ramanujam, S. (2016). Disinfection of water by pulsed power technique: a mechanistic perspective. RSC advances, 6(15), 11980-11990.
35. Abramov, V. O., Abramova, A. V., Cravotto, G., Nikonov, R. V., Fedulov, I. S., & Ivanov, V. K. (2021). Flow-mode water treatment under simultaneous hydrodynamic cavitation and plasma. Ultrasonics Sonochemistry, 70, 105323.
36. Hijosa-Valsero, M., Molina, R., Schikora, H., Müller, M., & Bayona, J. M. (2013). Removal of priority pollutants from water by means of dielectric barrier discharge atmospheric plasma. Journal of hazardous materials, 262, 664-673.
37. Sarangapani, C., Misra, N. N., Milosavljevic, V., Bourke, P., O'Regan, F., & Cullen, P. J. (2016). Pesticide degradation in water using atmospheric air cold plasma. Journal of Water Process Engineering, 9, 225-232.
38. Magureanu, M., Piroi, D., Mandache, N. B., David, V., Medvedovici, A., & Parvulescu, V. I. (2010). Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment. Water research, 44(11), 3445-3453.
39. Li, Z., Wang, Y., Guo, H., Pan, S., Puyang, C., Su, Y., & Han, J. (2021). Insights into water film DBD plasma driven by pulse power for ibuprofen elimination in water: performance, mechanism and degradation route. Separation and Purification Technology, 277, 119415.
40. Zhou, R., Zhou, R., Alam, D., Zhang, T., Li, W., Xia, Y., Mai-Prochnow, A., An, H., Lovell, E.C., Massod, H., Amal, R., Ostrikov, K.K., & Cullen, P. J. (2021). Plasmacatalytic bubbles using CeO2 for organic pollutant degradation. Chemical Engineering Journal, 403, 126413.
41. National Center for Biotechnology Information (2023). PubChem Compound Summary for CID 7560, Fenuron. Retrieved October 2, 2023.
42. EU Pesticides Database. Fenuron. Reg. (EC) No 1107/2009. Retrieved October 2, 2023.
43. Feng, J., Zheng, Z., Sun, Y., Luan, J., Wang, Z., Wang, L., & Feng, J. (2008). Degradation of diuron in aqueous solution by dielectric barrier discharge. Journal of hazardous materials, 154(1-3), 1081-1089.
44. Li, Z., Wang, Y., Guo, H., Pan, S., Puyang, C., Su, Y., ... & Han, J. (2021). Insights into water film DBD plasma driven by pulse power for ibuprofen elimination in water: performance, mechanism and degradation route. Separation and Purification Technology, 277, 119415.
45. Magureanu, M., Bradu, C., & Parvulescu, V. I. (2018). Plasma processes for the treatment of water contaminated with harmful organic compounds. Journal of Physics D: Applied Physics, 51(31), 313002.
46. Oturan, M. A., Edelahi, M. C., Oturan, N., & Aaron, J. J. (2010). Kinetics of oxidative degradation/mineralization pathways of the phenylurea herbicides diuron, monuron and fenuron in water during application of the electro-Fenton process. Applied Catalysis B: Environmental, 97(1-2), 82-89.
47. Kovács, K., Farkas, J., Veréb, G., Arany, E., Simon, G., Schrantz, K., ... & Alapi, T. (2016). Comparison of various advanced oxidation processes for the degradation of phenylurea herbicides. Journal of Environmental Science and Health, Part B, 51(4), 205-214.
48. National Center for Biotechnology Information (2023). PubChem Compound LCSS for CID 2566, Carbofuran. Retrieved September 28, 2023.

49. Lumei, P., Jinzhang, G., Yusen, H., Huiguang, L., Wen, X., & Xingmin, W. (2008). Oxidation degradation of aqueous carbofuran induced by low temperature plasma. Plasma Science and Technology, 10(3), 348.
50. Singh, R. K., Philip, L., & Ramanujam, S. (2016). Rapid removal of carbofuran from aqueous solution by pulsed corona discharge treatment: kinetic study, oxidative, reductive degradation pathway, and toxicity assay. Industrial & Engineering Chemistry Research, 55(26), 7201-7209.
51. Moutiq, R., Pankaj, S. K., Wan, Z., Mendonca, A., Keener, K., & Misra, N. N. (2020). Atmospheric pressure cold plasma as a potential technology to degrade carbamate residues in water. Plasma Chemistry and Plasma Processing, 40, 1291-1309.
52. Kumar, R., Kumar, N., Roy, R. K., & Singh, A. (2017). Triazines—A comprehensive review of their synthesis and diverse biological importance. Curr. Med. Drug Res, 1(1), 173.
53. Mededovic, S., & Locke, B. R. (2007). Side-chain degradation of atrazine by pulsed electrical discharge in water. Industrial & engineering chemistry research, 46(9), 2702-2709.
54. Vanraes, P., Willems, G., Daels, N., Van Hulle, S. W., De Clerck, K., Surmont, P., & Leys, C. (2015). Decomposition of atrazine traces in water by combination of non-thermal electrical discharge and adsorption on nanofiber membrane. Water Research, 72, 361-371.
55. Feng, J., Jiang, L., Zhu, D., Su, K., Zhao, D., Zhang, J., & Zheng, Z. (2016). Dielectric barrier discharge plasma induced degradation of aqueous atrazine. Environmental Science and Pollution Research, 23, 9204-9214.
56. Wang, Q., Zhang, A., Li, P., Héroux, P., Zhang, H., Yu, X., & Liu, Y. (2021). Degradation of aqueous atrazine using persulfate activated by electrochemical plasma coupling with microbubbles: removal mechanisms and potential applications. Journal of Hazardous Materials, 403, 124087.
57. Giardina, A., Tampieri, F., Marotta, E., & Paradisi, C. (2018). Air non-thermal plasma treatment of Irgarol 1051 deposited on TiO2. Chemosphere, 210, 653-661.
58. Vanraes, P., Willems, G., Nikiforov, A., Surmont, P., Lynen, F., Vandamme, J., ... & Leys, C. (2015). Removal of atrazine in water by combination of activated carbon and dielectric barrier discharge. Journal of hazardous materials, 299, 647-655.
59. Roccamante, M., Salmeron, I., Ruiz, A., Oller, I., & Malato, S. (2020). New approaches to solar Advanced Oxidation Processes for elimination of priority substances based on electrooxidation and ozonation at pilot plant scale. Catalysis Today, 355, 844-850.
60. Ruíz-Delgado, A., Roccamante, M. A., Oller, I., Agüera, A., & Malato, S. (2019). Natural chelating agents from olive mill wastewater to enable photo-Fenton-like reactions at natural pH. Catalysis Today, 328, 281-285.
61. Schweitzer, B. I., Dicker, A. P., & Bertino, J. R. (1990). Dihydrofolate reductase as a therapeutic target. The FASEB Journal, 4(8), 2441-2452.
62. Gangjee, A., Shi, J., Queener, S. F., Barrows, L. R., & Kisliuk, R. L. (1993). Synthesis of 5-methyl-5-deaza nonclassical antifolates as inhibitors of dihydrofolate reductases and as potential antipneumocystis, antitoxoplasma, and antitumor agents. Journal of medicinal chemistry, 36(22), 3437-3443.
63. Li, Z., Wang, Y., Guo, H., Pan, S., Puyang, C., Su, Y., & Han, J. (2021). Insights into water film DBD plasma driven by pulse power for ibuprofen elimination in water: performance, mechanism and degradation route. Separation and Purification Technology, 277, 119415.

64. Guo, C., Fulp, J. W., Jiang, Y., Li, X., Chojnacki, J. E., Wu, J., & Zhang, S. (2017). Development and characterization of a hydroxyl-sulfonamide analogue, 5-chloro-N-[2-(4-hydroxysulfamoyl-phenyl)-ethyl]-2-methoxy-benzamide, as a novel NLRP3 inflammasome inhibitor for potential treatment of multiple sclerosis. ACS chemical neuroscience, 8(10), 2194-2201.
65. JUDD, S., JEFFERSON, B. Membranes for industrial wastewater recovery and re-use. Oxford: Elsevier Ltd, 2003.
66. KHAN, F.S.A. et al. A comprehensive review on micropollutants removal using carbon nanotubes-based adsorbents and membranes. J. Environ. Chem. Eng., 9, Article 106647, 2021.
67. Shin, M. G. et al. Critical review and comprehensive analysis of trace organic compound (TOrC) removal with polyamide RO/NF membranes: Mechanisms and materials. Chemical Engineering Journal, 427, 130957, 2022. https://doi.org/10.1016/j.cej.2021.
68. COUTO, C.F. et al. A critical review on membrane separation processes applied to remove pharmaceutically active compounds from water and wastewater. J. Water Process. Eng., 26, 156-175, 2018.
69. Van der Bruggen, B., Vandecasteele, C. Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. Environ. Pollut., 122 (3), 435-445, 2003.
70. Brovini, E.M., Moreira, F.D., Martucci, M.E.P., de Aquino, S.F. Water treatment technologies for removing priority pesticides Journal of Water Process Engineering, 53, 103730, 2023.
71. Wenten, I.g. Reverse osmosis applications: prospect and challenges. Desalination, 391, 112-125, 2016.
72. TIBI, F. et al. Fabrication of polymeric membranes for membrane distillation process and application for wastewater treatment: Critical review. Process Safety and Environmental Protection, 141, 190-201, 2020.
73. Couto, C. F. et al. Assessing potential of nanofiltration, reverse osmosis and membrane distillation drinking water treatment for pharmaceutically active compounds (PhACs) removal. Journal of Water Process Engineering, 33, 101029, 2020.
74. Couto, C. F. et al. Assessing potential of nanofiltration, reverse osmosis and membrane distillation drinking water treatment for pharmaceutically active compounds (PhACs) removal. Journal of Water Process Engineering, 33, 101029, 2020.
75. GOH, P.S., AHMAD, N.A., WONG, T.W., YOGARATHINAM, L.T., ISMAIL, A.F. Membrane technology for pesticide removal from aquatic environment: Status quo and way forward. Chemosphere, 307, 136018, 2022.
76. PLAKAS, K.V. et al. Removal of,pesticides from water by NF and RO membranes — A review. Desalination, 287, 255-265, 2012.
77. Rosman, N., Salleh, W.N.W., Mohamed, M.A., Ismail, A.F., Harun, Z. Hybrid membrane filtration-advanced oxidation processes for removal of pharmaceutical residue. Journal of Colloid and Interface Science, 532, 236–260, 2018.
78. KOOPS, G.H. et al. Integrally skinned polysulfone hollow fiber membranes for pervaporation. J. Appl. Polym. Sci., 54, 385-404, 1994.
79. Mehta, R., Brahmbhatt, H., Mukherjee, M., Bhattacharya, A. Tuning separation behavior of tailor-made thin film poly(piperazine-amide) composite membranes for pesticides and salts from water. Desalination 404, 280–290, 2017.

80. Musbah, I., Cicéron, D., Saboni, A., Alexandrova, S. Retention of pesticides and metabolites by nanofiltration by effects of size and dipole moment, Desalination, 313, 51-56, 2013.
81. Boussahel, R., Montiel, A., Baudu, M. Effects of organic and inorganic matter on pesticide rejection by nanofiltration. Desalination, 145, 109–114, 2002.
82. B. Brkić, N. France, S. Giannoukos and S. Taylor, An optimised quadrupole mass spectrometer with a dual filter analyser for in-field chemical sniffing of volatile organic compounds, Analyst 143, 3722-3728 (2018).
83. Personalized nutrition for healthy living (PROTEIN), Horizon 2020, Innovation Action, GA 817732, (2018-2022), https://www.protein-h2020.eu/.
84. M. Jakšić, A. Mihajlović, Đ. Vujić, S. Giannoukos, B. Brkić, Membrane inlet mass spectrometry method for food impact assessment on specific volatile organic compounds in exhaled breath, Analytical and Bioanalytical Chemistry 414, 6077-6091 (2022).
85. B. Brkić, N. France, S. Taylor, Oil-in-Water Monitoring Using Membrane Inlet Mass Spectrometry, Analytical Chemistry 83, 6230-6236 (2011).
86. Torion T-9 Portable GC/MS, Perkin Elmer, https://www.perkinelmer.com/product/torion-t-9-portable-gc-ms-instrument-ntsst090500.
87. HAPSITE ER, Inficon, https://www.inficon.com/en/products/chemical-detection-and-utility-monitoring/hapsite-er.
88. Adjovu GE, Stephen H, James D, Ahmad S. Overview of the Application of Remote Sensing in Effective Monitoring of Water Quality Parameters. Remote Sensing. 2023; 15(7):1938.
89. M. Lavreniuk, L. Shumilo and A. Lavreniuk, "Generative Adversarial Networks for the Satellite Data Super Resolution Based on the Transformers with Attention," IGARSS 2023 - 2023 IEEE International Geoscience and Remote Sensing Symposium, Pasadena, CA, USA, 2023, pp. 6294-6297.
90. J. Wang, Analytical Electrochemistry, VCH, USA, 1994, pp. 44–49.
91. A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Application, 2nd ed., Wiley, New York, 2001, pp. 459– 462.

# 11.0 Annex

During the realization of the present deliverable D4.2, two extra documents have been generated that have been included as annexes in order to create a more readable document with the most relevant information but keeping the extra data obtained.

*Annex 1.* Reactors type and photocatalytic conditions for degradation of contaminants.

*Annex 2.* Variables of removal of contaminants by filtration systems.

The Mediterranean Sea and its surrounding regions support a diverse variety of essential socioeconomic activities. It is one of the highly exploited water ways and the influence of anthropogenic activities on its marine habitats and ecosystems has grown significantly since the industrial revolution. Because of this, the Mediterranean Sea basin is very vulnerable to chemical contamination and build-up. To safeguard the Mediterranean Sea basin from contaminants for emerging concerns (CoEC), iMERMAID will integrate, coordinate, and synergize innovative preventive, monitoring, and remediation solutions. iMERMAID will build an evidence-based multidimensional framework that will guide policymaking and transform societal perceptions to reduce CoEC usage, emissions, and pollution. Furthermore, next generation sensor and remediation solutions will be developed within iMERMAID to monitor and remove prioritized chemicals from its source while reducing upstream pollution. iMERMAID builds an ideal interdisciplinary team by bringing together prominent SMEs, researchers, regulators, and innovation professionals who have been essential in improving the knowledge and awareness of CoEC. Beyond state-of-the-art techniques, iMERMAID will strive to strengthen regulations against CoEC, expand economic possibilities and competitiveness, improve the standard of living for EU residents, while preventing the accumulation of chemical pollution in the Mediterranean Sea basin. iMERMAID will empower the efforts to create a zero pollution, contaminant free waters by enabling the Chemical Strategy's goals to become a practical reality.

iMERMAID

Funded by
the European Union