Application guideline about disinfection-by-product precursor removal by different materials

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Report Author	POLIMI: Mattia Stefanoni, Laura Riva, Carlo Punta CAT: Andreu Fargas Marques, Josepa Fabregas Serra, Aleix Martorell EUT: Irene Jubany Güell, Leónidas Pérez Estrada, Laura Vinardell Magre UBA: Aki Sebastian Ruhl, Ehsan Ranjbar
Reviewed by	POLIMI: Manuela Antonelli, Beatrice Cantoni DVGW-TUHH: Mathias Ernst
Approved by	DVGW-TUHH: Anissa Grieb

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2	Politecnico di Milano	POLIMI
3	Berlin Centre of Competence for Water	KWB
4	BioDetection Systems B.V.	BDS
5	Centre Tecnológic de Catalunya (EURECAT)	EUT
6	German Environment Agency	UBA
7	Helmholtz-Centre for Environmental Research	UFZ
8	Consorci Concessionari d'Aigües per als Ajuntaments i Industries de Tarragona	CAT
9	Tutech Innovation GmbH	TUTECH
10	Metropolitana Milanese SPA	MM
11	Multisensor systems Ltd.	MSS
12	The National University of Water and Environmental Engineering	NUWEE

Abstract

This study focuses on the development of guidelines for the evaluation of conventional and advanced adsorbent materials to enhance water treatment processes, specifically ranking their ability to remove natural organic matter (NOM) as precursors to disinfection by-products (DBPs). A variety of experimental approaches were employed, including batch adsorption tests, rapid small-scale column tests (RSSCT), and pilot tests, enabling a comprehensive assessment of adsorbent performance across diverse water matrices. These matrices included synthetic waters spiked with specific NOM fractions (e.g., Suwannee River NOM, humic acid), tap water, and real groundwater samples from full-scale drinking water treatment plants. A key objective of this research was to provide guidelines, that are methodological procedure, to be followed to rank the adsorbent materials and operational configurations based on their performance in reducing NOM, which was measured using various methods, including absorbance, fluorescence, and total organic carbon (TOC) analysis. This ranking procedure aids in identifying the best-performing materials and strategies for full-scale applications. In particular, four guidelines are described for different scenarios: In this task an evaluation of different activated carbons and innovative materials for DBPs precursor reduction has been performed with the aim of developing guidelines for adsorbent materials selection and ranking in four different scenarios where the combination of adsorption and disinfection is crucial:

1) Conversion from non-disinfected to disinfected drinking water supply;
2) Upgrade of currently disinfected systems targeting precursors removal;
3) Development of innovative adsorbent materials;
4) Proposal of new treatment line scheme with pre-chlorination followed by adsorption.

All the procedures proposed in the guidelines were applied with experimental tests to show the step-by-step procedures and preliminary results obtained. The results provide valuable insights into optimizing adsorbent materials to minimize DBPs formation risks while maintaining effective water treatment processes. The findings could inform water utilities, adsorbent materials producers and decision makers and pave the way for the adoption of advanced water treatment solutions, contributing to global efforts to ensure safe drinking water in a climate change scenario. Future research in the next year before the end of this task (October 2025) will focus on enhancing material stability and expanding testing to a wider range of water sources. Moreover, new efforts will be made to combine not only technical performance evaluations of these adsorbents but also considers their sustainability, scalability and cost-effectiveness.

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Abbreviations

AC	Activated carbon
bPEI	Branched polyethyleneimine
CS1B	Case study n.1 Berlin
CS2M	Case study n.2 Milan
CS3T	Case study n.3 Tarragona
Cl_2eq	Equivalent chlorine
ClO_2	Chlorine Dioxide
CNS	Cellulose-based nanosponge
DBPFP	Disinfection by-products formation potential
DBPs	Disinfection by-products
DIW	Deionized Water
DPD	N,N-diethyl-p-phenylenediamine
DWTP	Drinking water treatment plant
EEM	Excitation-Emission Matrix
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
GC-MS	Gas chromatography/mass spectrometry
HAAs	Haloacetic Acids
IC	Ion Chromatography
LOD	Limit Of Detection
NaClO	Sodium Hypochlorite
NOM	Natural Organic Matter
pHPZC	pH Point of Zero Charge
SEM	Scanning Electron Microscopy
THMs	Trihalomethanes
THMFP	Trihalomethane formation potential
TTHMs	Total trihalomethanes
TEMPO	2,2,6,6-tetramethylpiperidin-1-yl)oxyl
TOCNF	TEMPO-oxidized cellulose nanofibers
TOC	Total Organic Carbon
UVA_{254}	UVA Absorbance at λ= 254 nm

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1 Introduction

1.1 Disinfection and adsorption processes: a short overview of the state of the art

The treatment of water for human consumption relies heavily on the application of both disinfection and adsorption processes to remove organic and inorganic contaminants and potential pathogenic bacteria. Disinfection, primarily aimed at eliminating pathogens, plays a crucial role in ensuring microbiologically safe drinking water. Commonly used disinfectants, such as chlorine and chlorine dioxide, are effective in pathogen inactivation. However, these chemicals can also react with natural organic matter (NOM) present in water, leading to the formation of disinfection by-products (DBPs), including THMs, chlorite, chlorate and haloacetic acids (HAAs) (Lin et al., 2020, Sorlini et al., 2014; Glica et al., 2020). NOM consists of a variety of dissolved and particulate organic compounds derived from decaying plant, animal, and microbial tissue. While chlorine generates THMs and HAAs, chlorine dioxide results in the formation of chlorite and chlorate. THMs are typically produced during the chlorination of NOM, while HAAs stem from reactions with the hydrophilic components of NOM and amino acids. Chlorites primarily form through the reaction of chlorine dioxide with NOM, while chlorates arise from disproportionation reactions of chlorine dioxide. The formation of these DBPs is influenced by factors such as the disinfectant type, dosage, and the composition of the organic matter, bromide levels, and the concentration of total organic carbon (TOC) in the water. DBPs degrade water quality and have been epidemiologically linked to adverse health outcomes, particularly the increased risk of cancer in major organs (Evans et al., 2020). Many DBPs are known to pose health risks, making the control of their formation a critical aspect of water treatment to maintain drinking water safety. Thus, the removal of NOM and its constituents from water is a global challenge, as its varying properties and concentrations can significantly affect the efficiency of treatment processes. Numerous technologies have been explored to address this issue, with adsorption standing out as one of the most effective strategies for NOM removal (Matilainen et al., 2006; Bhatnagar et al., 2017). Traditionally, activated carbon has been used in adsorption processes to remove NOM. Activated carbon is widely used as an adsorbent for water treatment due to its high surface area, porous structure, and ability to adsorb a wide range of contaminants. This porous structure is the main physical property that characterizes granular activated carbon (GAC) for the adsorption of contaminants dissolved in water. It is made up of pores of different sizes which, according to International Union of Pure and Applied Chemistry (IUPAC) recommendations, can be classified into 3 different groups: (i) micropores (less than 2 nm), (ii) mesopores (between 2 and 50 nm), and (iii) macropores greater than 50 nm.

Depending on the pore sizes the GAC will be more suitable for adsorbing different molecules sizes.

GAC is very suitable for water treatment with a predominance of contaminants of various molecular weights. It allows excellent results in the elimination of odour and taste, as well as in the retention of organic compounds, such as hydrocarbons, detergents, pesticides, dissolved oils, soluble dyes, chlorinated solvents, phenols and derivatives of hydroxyl groups and carcinogenic compounds.

Furthermore, the use of GAC for water treatment is easy to implement and maintain, making it the most practical and economical option for the consumer. The most common configuration is using the GAC as a filtration bed.

On the other side, adsorption of contaminants in GAC filters is a complex process due to the high number of variables involved in the process, including electrostatic, dispersion and electrochemical interactions, intrinsic properties of the solute and adsorbent and the temperature of the system.

Several factors influence the efficiency of the GAC filters:

- **Surface Area and Pore Structure:** More surface area and well-developed porosity improve adsorption capacity.

- **GAC origin and functional groups:** significantly influence its adsorption capabilities by affecting the material's surface area, pore structure, and chemical properties.
- **Type of Contaminant:** Activated carbon is more effective at removing organic compounds and chlorine than some inorganic ions.
- **pH of Water:** pH can affect the charge of both the adsorbent and contaminants, altering adsorption efficiency.
- **Contact Time:** Longer contact time between the water and activated carbon leads to more efficient adsorption.
- **Temperature:** Adsorption is generally more efficient at lower temperatures because higher temperatures can desorb adsorbed substances.

Research is ongoing to improve the efficiency of activated carbon for water treatment, enhancing adsorption capacities by developing more porous and selective activated carbons for specific contaminants. Recent studies have highlighted the potential of a wide variety of conventional and non-conventional adsorbents (Manamperuma et al., 2019). Although these advanced adsorbents are promising, their application is mostly limited to laboratory settings. Full-scale implementation and a deeper understanding of the interactions between modified adsorbents and NOM are needed. Additionally, combining adsorption with other treatment methods could further enhance NOM removal, opening new avenues for more selective and efficient water treatment solutions.

1.2 Objectives of the guideline

To effectively minimize DBPs formation, the most reliable strategy is to remove NOM prior to disinfection. Despite advancements in water treatment technologies, significant challenges remain in managing DBPs formation. One key limitation of current adsorbents is their lack of specificity, making it difficult to target the NOM fractions most responsible for DBPs production. A more proactive approach to water quality management is essential. This includes not only preventive measures to avoid contamination but also comprehensive monitoring of water quality throughout the entire supply chain.

The primary goal of this deliverable is to provide the procedures to be implemented in different scenarios to address these challenges by testing and ranking various adsorbent materials based on their ability to remove DBPs precursors, specifically NOM. One example of testing according to the guideline will be presented.

While advanced materials like modified adsorbents and nanomaterials show promise for improved NOM removal, concerns remain about their environmental impact. Risks include chemical leaching and the release of nanoparticles into ecosystems. Further research is needed to optimize the regeneration and reuse of these materials, enhancing cost-efficiency and ensuring sustainability in real-world applications. The evaluation focuses on both conventional and novel adsorbents, such as cellulose-based nanosponges. Batch and column experiments will assess their performance in reducing DBPs formation compared to commercial activated carbons.

By providing a comprehensive analysis of technical performance, this work will support the identification of the procedures to identify the most effective adsorbents and operational configurations. The findings will contribute to the development of safer, more efficient water treatment processes that meet regulatory standards while offering a clear ranking of materials to guide future technology selection. These results will also offer practical guidelines for scaling up improved water treatment technologies and inform further research on sustainable solutions.

2 Guidelines for adsorbent materials selection in several scenarios

The selection of the optimal type of GAC will depend mainly on the origin of the water and the organic compounds to be retained, which will define the degree and efficiency of the adsorption.

The methodological procedure to be followed to provide a ranking and selection of optimal adsorbents highly depends on the conditions and goal of such selection.

In this task an evaluation of different activated carbons and innovative materials for DBPs precursors reduction has been performed with the aim of developing guidelines for adsorbent materials selection and ranking in four different scenarios:

1) **Conversion from non-disinfected to disinfected drinking water supply (Chapter 2.1)**: this is the case of drinking water treatment plants that do not have a disinfection step but want to evaluate future combination of adsorption and disinfection for drinking water production;
2) **Upgrade of currently disinfected systems targeting precursors removal (Chapter 2.2)**: this is the case of drinking water treatment plants that already have a disinfection step but want to select the optimal adsorbent to target DBPs precursors removal;
3) **Development of innovative adsorbent materials (Chapter 2.3)**: this is the case of specific optimization of the adsorbent material and comparison with the benchmark activated carbon;
4) **Proposal of new treatment line scheme with pre-chlorination followed by adsorption (Chapter 2.4)**: this is the case in which a drinking water treatment plant needs to be built and high disinfectants doses are expected to be needed, therefore, new treatment line need to be re-think.

The following paragraphs report guidelines and procedure for each of these for scenarios. While Chapters 3 and 4 report materials and methods and preliminary results of one example of applications of the proposed guidelines for each of the four scenarios, as follows:

- The guideline for the conversion from non-disinfected to disinfected drinking water supply, that is the potential interest for both the cities (Berlin and Hamburg) in the German case studies (CS1) of this project, was tested by UBA in Berlin case study, later referred to as “CS1B”;
- The guideline for the upgrade of currently disinfected systems targeting precursors removal was tested by CAT in Tarragona case study, later referred to as “CS3T”;
- The guideline for the development of innovative adsorbent materials was tested by POLIMI in Milan case study, later referred to as “CS2M”;
- The guideline for the proposal of new treatment line scheme with pre-chlorination followed by adsorption was tested by EUT.

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2.1 Conversion from non-disinfected to disinfected drinking water supply

This paragraph focuses on the case of drinking water treatment plants that currently do not have a disinfection step, such as the case of CS1, but want to evaluate future combination of adsorption and disinfection for drinking water production.

The process outlined in this study is summarized in the flowchart presented in Figure 1, which illustrates the sequential steps from activated carbon selection to the evaluation of chlorine decay and disinfection by-product (DBP) formation. The experimental methodology will begin with the preparation of a list of commercially available activated carbons commonly utilized in water treatment plants. This will be followed by a thorough review of the characterizations of the selected activated carbons, which will lead to the selection of carbons with varying physicochemical characteristics. In the next phase, the selected activated carbons will be applied in the pretreatment of natural organic matter (NOM) at varying dosages, and the changes in the composition of NOM will be analyzed using liquid chromatography-organic carbon detection (LC-OCD). Subsequently, both untreated and pretreated samples will undergo chlorination and trihalomethane formation potential (THMFP) tests. The chlorine decay over time will be monitored in these samples, and the formation of DBPs will be quantified. This systematic approach will allow for the assessment of the impact of activated carbon pretreatment on chlorine stability and the formation of DBPs.

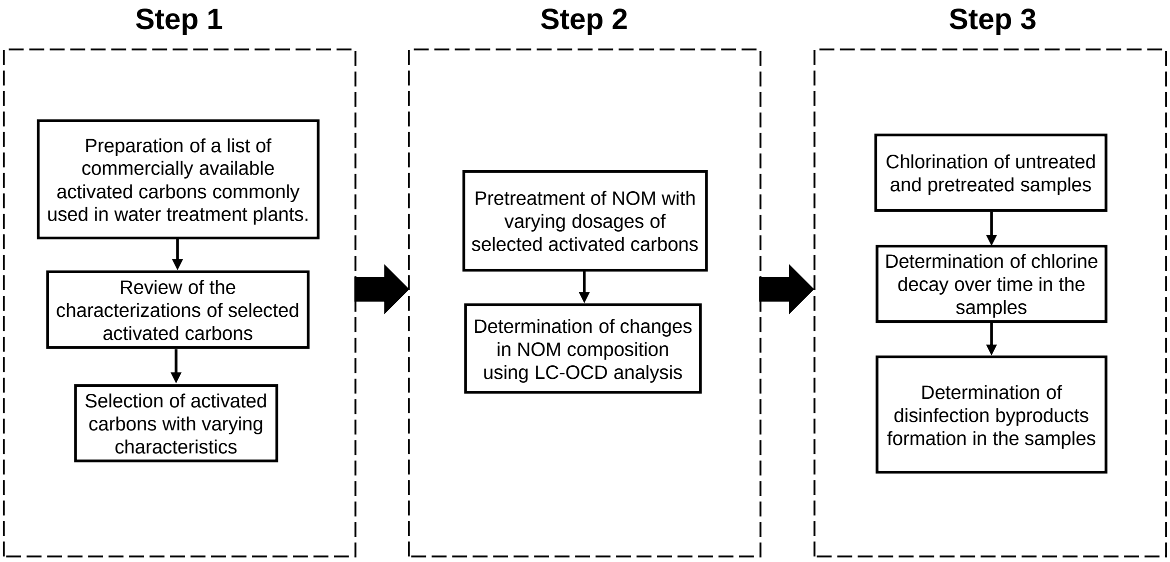

Figure 1: Experimental flow chart for evaluating activated carbon pretreatment effects on chlorine decay and disinfection byproducts.

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2.2 Upgrade of currently disinfected systems targeting precursors removal

This paragraph focuses on the case of drinking water treatment plants that already have a disinfection step but want to select the optimal adsorbent to target DBPs precursors removal.
For completing this objective, it is relevant to follow the procedure proposed in Figure 2 and 3: characterize the NOM of the feed waters matrixes in different times of the year where the surface raw water changes. THMFP must be done at the same conditions for the different yearly water matrixes with different NOM parameters concentration, to find which part of the NOM is more related to the THMs generation.

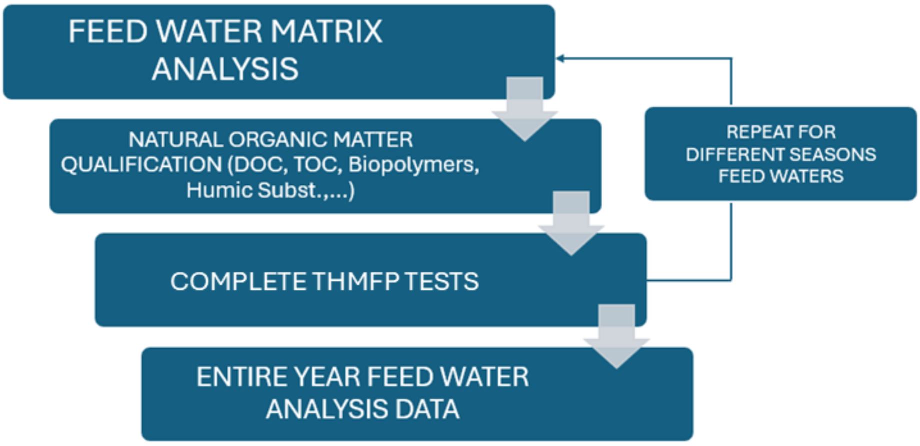

Figure 2: Workflow part 1 – Preliminary steps.

Once, it is determined which part of the NOM is more relevant to the THMs generation, different GAC will be tested to find which one reduces or absorbs better the desired NOM compounds.

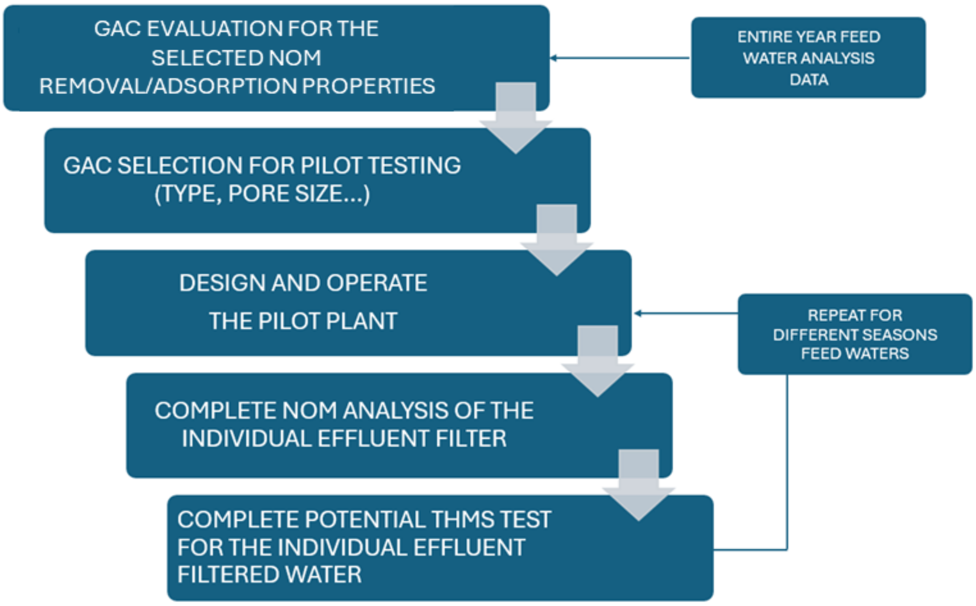

Figure 3: Workflow part 2 – Laboratory tests and data analysis.

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2.3 Development of innovative adsorbent materials

This paragraph provides guidelines in the case of specific development and optimization of the adsorbent material and comparison with the benchmark activated carbon.
The flowchart in Figure 10 outlines the steps for selecting the most effective adsorbent material to reduce NOM, which is a precursor to DBPs. The plan, which builds upon the activities conducted or scheduled for CS2M, includes the development of novel materials (e.g., cellulose-based nanosponges), their characterization, and laboratory tests (both batch and column experiments) to evaluate performance compared to benchmark materials (e.g., activated carbon). Additionally, it integrates the evaluation of THMFP and DBPFP to assess how DBPs are formed and what is the removal rate after using these materials.

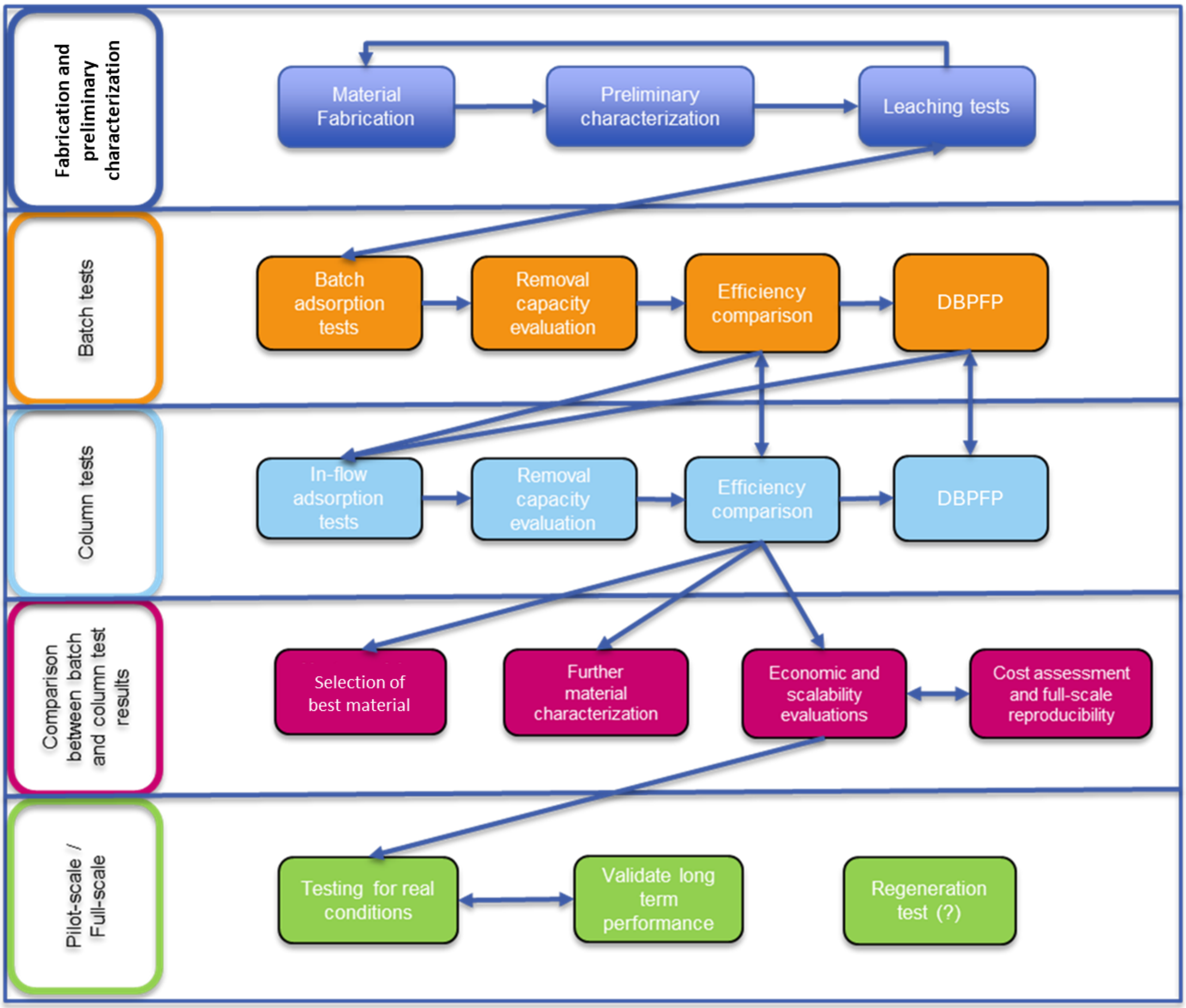

Figure 4: Flowchart of activities and tests for the preparation, characterization, and evaluation of the efficiency of a new adsorbent material.

In Figure 4 is a structured explanation of the key points and actions to follow, along with their respective objectives. The first stage focuses on the **fabrication** of the adsorbent material, which in this case could be a cellulose-based nanosponge. During the synthesis, different types of cellulose can be evaluated, such as virgin versus recycled cellulose, to determine which yields better performance or is more cost-effective. Following fabrication, the **preliminary characterization** stage begins. This involves measuring essential properties like porosity, surface charge, molecular structure, and surface area. These characteristics are crucial because they influence how effectively the material will adsorb NOM. Another important step is conducting **leaching tests** to ensure that the material itself does not release organic compounds into the water. If significant leaching is detected, it would be necessary to analyze the individual components of the material to refine its formulation, ensuring that the material remains effective and safe for use in water treatment.

Once the material has been developed and preliminarily characterized, it undergoes **batch adsorption tests** to evaluate its performance. In this phase, the adsorption efficiency of the new material is compared with benchmark adsorbents, such as activated carbon. These tests determine the material's adsorption capacity through isotherm analysis, providing an initial indication of its effectiveness in removing NOM from water. Following these tests, the next step is to assess the **formation potential of DBPs (DBPFP)** in a batch setup. After the adsorption process, a controlled amount of disinfectants, such as sodium hypochlorite or chlorine dioxide, is added to the samples. The formation of DBPs, like trihalomethanes (THMs), chlorite, and chlorate, is then measured to assess how effectively the new material reduces the precursors of DBPs. This stage is crucial for comparing the new material's ability to minimize DBPs relative to other adsorbents and identifying whether the material targets specific fractions of NOM, such as humic substances, which are known to contribute more significantly to DBPs formation.

Based on the results of the batch tests, the most promising materials are selected for **column tests**, which better simulate real filtration conditions. These experiments evaluate how the material performs under dynamic conditions, such as its capacity to remove NOM over time.

Similar to the batch tests, THMFP and DBPFP are conducted after the column experiments. Disinfectants are added to the samples collected at different bed volumes (BV) of treatment, and the formation of DBPs is measured. Additionally, the tests analyze the relationship between NOM removal and DBPs formation, providing insights into how well the material performs compared to benchmark adsorbents in dynamic systems.

Following the column tests, the next step is to **select the best material** based on a combination of factors, including NOM removal efficiency and DBPs reduction. The analysis focuses on identifying the specific NOM fractions, such as humic substances, that are most effectively removed, particularly those that contribute significantly to DBPs formation when reacting with disinfectants like sodium hypochlorite or chlorine dioxide.

Once a new material has been selected, **economic assessments** are conducted to evaluate its production costs. For example, in the case of nanosponges, this might involve comparing the costs of using virgin versus recycled cellulose or analyzing how large-scale production impacts overall costs and expected outcomes. At this stage, a comprehensive cost-benefit analysis is crucial, balancing the material's efficiency in removing NOM and reducing DBPs against its cost per unit, ensuring that the material remains both effective and economically viable for widespread application.

In parallel, the **economic and scalability evaluations** are performed. This step determines whether the material can be produced on a large scale while maintaining consistent quality. It also evaluates the feasibility and economic sustainability of applying the material in real-world water treatment plants.

To evaluate the material's performance in a real-world environment, a **pilot plant** will be constructed. This facility will simulate real-world operating conditions, allowing for the assessment of the material's long-term effectiveness and scalability By testing the material in this setting, we can identify areas for improvement and ensure its suitability for widespread deployment.

Through this comprehensive process, the material's performance in both NOM removal and DBPs formation reduction is thoroughly evaluated, offering a holistic approach to selecting the most suitable adsorbent for real-world applications. This method ensures that the best-performing materials are not only effective but also economically and practically feasible for use in water treatment.

2.4 Proposal of new treatment line scheme with pre-chlorination followed by adsorption

This paragraph proposes a guideline in the case in which a drinking water treatment plant needs to be built and high disinfectants doses are expected to be needed. Therefore, a new treatment line needs to be considered, and here it is proposed with a pre-chlorination step followed by adsorption. Thus this guideline reports how to investigate the effect of water chlorination previous to activated carbon adsorption. The flowchart of this investigation is reported in Figure 5.

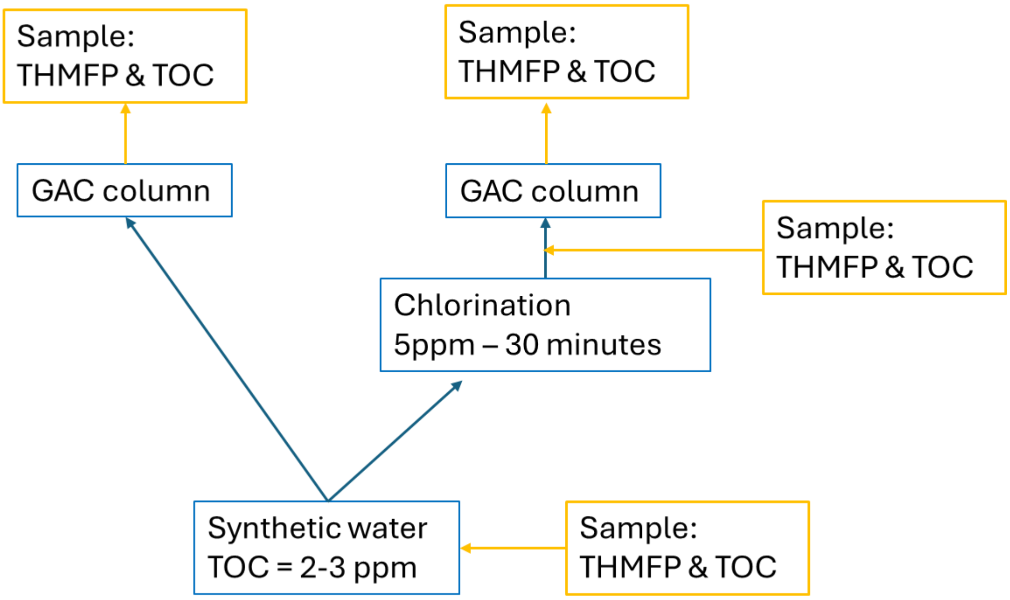

Figure 5: Workflow for assessing the effect of pre-chlorination on adsorption performance.

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3 Materials and methods for applications of the proposed guidelines in several scenarios

This chapter outlines the materials and methods used in the experimental procedures performed to test the application of the guidelines proposed in Chapter 2 for each of the presented scenarios. Specifically, it details the chemical reagents, adsorbent materials, water matrices, and the methodologies employed for adsorption and disinfection tests and the measurement of DBPs.

3.1 Chemicals

For chlorination and trihalomethane formation potential (THMFP) tests a stock solution of sodium hypochlorite at 14-15% vol (140 g Cl_{2eq}/L), CAS 7681-52-9, was provided by B&C S.r.l. For disinfection by-products formation potential (DBPFP, following the same procedure as for THMFP) a 2 $gClO_2$/L stock solution was prepared weekly using an Oxiperm® Pro OCD-162 generator (5 $gClO_2$/h, Grundfos, Italy), based on the reaction between sodium chlorite and hydrochloric acid, both of technical grade (Chimitex, Italy). The solutions were stored in headspace-free amber glass vials at 4 °C. Sodium thiosulfate (Carlo Erba, Italy) was used to quench residual chlorine. For the titration of disinfectant stock solutions and the measurement of free chlorine, the 4500-Cl G method was followed. All chemicals used were analytical grade and purchased from Sigma Aldrich (USA), except for DPD salt, which was obtained from Hach Lange (EU) and applied using a DPD Free Chlorine Reagent Swiftest™ Dispenser.

Samples with synthetic water matrices and groundwater (case study #2 Milan (CS2M)) were tested, a phosphate buffer solution was added. The buffer was prepared following the APHA 5710B method by dissolving 68.1 g of anhydrous potassium dihydrogen phosphate (KH_2PO_4) and 11.7 g of sodium hydroxide (NaOH) in 1 L of Milli-Q (MQ) water. The solution was refrigerated when not in use and filtered through a glass fiber filter if a precipitate formed. The buffer maintains the pH at 7.0, which was verified before use with a discardable sample portion.

In all tests temperature (T) and pH were measured using handheld meters. pH probes were calibrated at least weekly using two- or three-point calibration with pH standards of 4.0, 7.0, and 10.0.

For pH adjustments and titrations, reagent-grade sodium hydroxide (NaOH) and hydrochloric acid (HCl), all with ≥ 99% purity (p.a., ISO), were used. These chemicals, provided by Sigma Aldrich, were diluted in ultrapure water for experimental use. Solutions of HCl and NaOH at 1.0 N and 0.1 N concentrations were prepared as needed.

In case study #3 Tarragona (CS3T) chlorination tests performed in pilot scale to evaluate the effect of water chlorination prior to GAC, solutions of Milli-Q water were prepared containing 2,4,6-Trichlorophenol (Scharlab) and 2,4,6-Tribromophenol (Scharlab).

3.2 Water samples

In CS2M batch tests, conducted to investigate natural organic matter (NOM) from different sources, various water matrices were utilized. Suwannee River NOM (SRNOM, purchased from IHSS) was selected to represent river-derived NOM, while humic acid (HA, purchased from Sigma Aldrich) was chosen to specifically evaluate the behavior of the humic component. For a comparative analysis focused on the role of organic matter, two synthetic matrices were prepared by dissolving SRNOM and HA in MQ water. SRNOM and HA were dosed to achieve a final dissolved organic carbon (DOC) concentration of 3 mg/L.

The characteristics of the NOM utilized in the experiments are summarized in Table 1. HA and SRNOM solutions were prepared by gently stirring the powder in ultrapure water for several hours to achieve complete dissolution. The resulting solution was then filtered through a 0.45 µm cellulose filter to remove any undissolved particles, resulting in a clear NOM solution suitable for further experiments.

Table 1: Summary of natural organic matter sources used in this study.

NOM category	Selected substance	Acronym	Origin	Supplier	Product no.
Humic acids	Humic acid	HA	Soil extracted	Sigma-Aldrich	53680
Aquatic NOM	Suwannee River NOM	SRNOM	RO isolated	IHSS	2R101N

To further assess the behavior of NOM in relation to the characteristics of real water (NOM, salinity and other inorganic compounds), groundwater from a drinking water treatment plant in Milan was selected. This groundwater was used both in its natural form and spiked with SRNOM or HA (DOC = 3mg/L) for testing. CS2M real water is a deep groundwater treated by GAC filters with an Empty Bed Contact Time (EBCT) of 11 minutes. Real water samples were collected from the inlet to the granular activated carbon (GAC) filters, upstream of the disinfection process at the full-scale treatment facility. The pH was adjusted to 7 using 0.1 M NaOH and 0.1 M HCl. Additionally, 20 mL of phosphate buffer (prepared according to APHA 5710 method guidelines) per liter of matrix was added to the water matrices. Before testing, all water samples were pre-filtered using a 0.45 µm membrane (polyamide, Durapore®).

For the CS3T adsorption tests conducted at the pilot scale, synthetic water was prepared by dissolving two DBPs precursors, 2,4,6-trichlorophenol and 2,4,6-tribromophenol, in ultrapure (MQ) water. The solution was adjusted to achieve a total organic carbon (TOC) concentration of 2-3 mg/L, with each compound contributing 50%.

In case study #1 Berlin (CS1B), tap water, which is unchlorinated and contains high DOC levels (5 mg/L), was used in the THMFP tests conducted.

3.3 NOM measurement: TOC, absorbance, fluorescence

NOM has been characterized by means of three different methods: TOC, absorbance spectrum and fluorescence.

In CS2M, the Total Organic Carbon (TOC) concentration (ranging from 0.1 to 5.0 mg/L) was measured using infrared spectroscopy in accordance with ISO 8245:1999. For EUT, Total Organic Carbon was measured as Non-Purgeable Organic Carbon (NPOC) following the methodology outlined in "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998, pp. 5-20. The measurement was performed using the Analytikjena multi N/C 3100 analyzer.

The absorbance spectrum (190-900 nm) was measured using the Hach Lange UV-VIS DR6000 spectrophotometer.

For fluorescence measurements, the Agilent Cary Eclipse fluorescence spectrophotometer was used. For both absorbance and fluorescence spectrum measurements, a quartz cuvette with a 1-cm optical path having all four transparent faces was used. For each analysis, the cuvette was rinsed with deionized water and subsequently with the sample before making the measurement. Ultrapure water was used as a reference for both the Excitation-Emission Matrix (EEM) Raman measurement and the spectrophotometer absorbance measurement. The parameters for the evaluation of EEM and Raman value are given in Table 2. The final fluorescence assessment was carried out both in terms of total fluorescence (integral of the EEM, corrected for scatters) and in terms of peaks. In fact, using fluorescence values in certain regions of the spectrum, called peaks, indices can be calculated, which are traditionally linked to organic compounds, such as humic and fulvic acids (A, C, M, D) and proteins (B, T, N) (Wünsch et al., 2019). The MATLAB program (version R2022b) was used to process the fluorescence data, specifically the drEEM-0.6.3 package was used, and a code was developed by which Raman and Rayleigh scatters were corrected through the absorbance spectrum performed on the respective sample.

Table 2: Parameters for the evaluation of EEM and Raman value.

Parameter	Unit of Measure	Raman	EEM
Voltage	V	680	680
Corrected Spectra	-	Yes	yes
Excitation λ	nm	350	365-450
Emission λ	nm	365-450	270-600
Emission and Excitation Slit	nm	10	10
Scan speed	nm/min	Slowest	1,200 (Fast)

3.4 DBPs analysis (THMs, chlorite, chlorate)

In CS2M tests, total trihalomethanes (TTHMs) samples were analyzed using GS-MS: an EST Analytical Econ Evolution purge and trap concentrator and Centurion WS autosampler were interfaced to the Shimadzu GCMS-QP2020 NX. A VOCARB 3000 (k) analytical trap was configured with the P&T unit. A narrow bore inlet liner was used in the GC-MS to improve peak shape and allowed high split injections when transferring sample from the P&T concentrator. The methods followed for the analyses are EPA 5030C 2003 and EPA 8260D 2018. Data was acquired in full scan mode from *m/z* 35 to 330. Prior to the MDL experiment, both the GC-MS and P&T instruments were conditioned. The P&T was conditioned by baking the VOCARB 3000 trap at 260 °C for 8 minutes. The GC-MS column was conditioned by removing the column from the MS, but it remained connected to the GC inlet; the GC oven temp was ramped from 35 °C to 280 °C and held for 20 mins before returning to the starting method conditions. The Limit of Detection (LOD) is 20 ug/L. The experimental parameters for both GC-MS and P&T systems are listed in Table 3.

Table 3: GC-MS and P&T operating conditions.

Gas Chromatography	**Nexis GC-2030**
Injection port mode	Split mode; 40:1 split ratio
Carrier gas	Helium
Injection port temperature (°C)	200
Column	SH-I 624 Sil MS, 30 m x 0.25 mm ID x 1.4 um
Flow control mode	Linear velocity, 32 cm/sec
Oven Temperature	35°C (4.0 minutes), 14°C/min to 220°C (7 minutes)
Mass Spectrometer	**QP2020 NX**
Interface Temperature (°C)	180
Ion Source Temperature (°C)	200
Detector Voltage	Relative to Tune -0.2 kV
Threshold	100
Scan Range	m/z 35 to 330 Event time 0.18 seconds
Purge and Trap Concentrator	**EST Encon Evolution and Centurion Autosampler**
Trap	VOCARB 3000

Gas Chromatography	**Nexis GC-2030**
Trap Ready Temp (°C)	35
Mort ready Temp (°C)	39
Desorb Preheat Temperature (°C)	245
Desorb Temperature (°C)	250
Trap Bake Temperature (°C)	260
Mort Bake Temperature (°C)	210
Purge Flow Rate (ml/min)	Helium, 40
Dry Purge Flow Rate (ml/min)	Helium, 40
Desorb time (min)	1
Bake time (min)	8
Dry purge time (min)	2
Purge and Trap Autosampler	**EST Centurion WS**
Sample loop size (ml)	5
Sample fill mode	Loop
Internal standard volume (ul)	5
Surrogate standard volume (ul)	5
Analysis Time	
GC Run Time	34 min

In the tests conducted by EUT for the CS3T pilot plant tests, trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were analyzed with HS-GC-µECD (7694E Headspace Sampler, 6890 Plus GC system). The method reference is described in "R.-s. Zhao, 2004. Headspace líquid-phase microextraction of trihalomethanes in drinking water and their gas chromatographic determination. Talanta 62, 751-756."

For the Total Trihalomethanes determination in CS3T, the water quality laboratory at the drinking water treatment plant of the CAT has been using a method of extraction by head space with subsequent chromatographic separation and detection with GC-ECD. Initially, 2g of salt is added to the HS vial and then 10mL of sample with its respective internal standard. Then the analytes are extracted by Head-Space and the target analytes are identified and quantified by capillary column gas chromatography using an electron capture detector (GC/ECD). Analytes are quantified using procedural standard calibration.

For the CS2M, chlorite and chlorate samples were analyzed by MM using an IC 944 Professional UV/VIS Detector Vario (Metrohm, Switzerland), using a Metrosep A Supp 7 - 250/4,0 column and a Metrosep A Supp 10 Guard HC/4,0 precolumn. The method followed for the analyses is the APAT CNR IRSA 4020 Man 29 2003. Calibration curves for chlorite and chlorate were prepared by analysis of standard concentrated solutions @1000 ug/L. The LOD is 7.5 µg/L. The method was validated according to the International Conference on Harmonisation guidelines.

For the analysis of haloacetic acids (HAAs) in CS3T drinking water, the water quality laboratory at the drinking water treatment plant of the CAT has been using the *standard EPA method 552.3 "Determination of haloacetic acids and dalapon in drinking water by liquid-liquid microextraction, derivatization, and gas chromatography with electron capture detection"*. A 40-mL volume of sample is adjusted to a pH of 0.5 or less and extracted with 4 mL of either methyl tert-butyl ether (MTBE) containing the internal standard. The haloacetic acids that have been partitioned into the organic phase are then converted to their methyl esters by the addition of acidic methanol followed by heating for 2 hours. The solvent phase containing the methylated haloacetic acids is separated from the acidic methanol by adding 7 mL of a concentrated aqueous solution of sodium sulphate. The aqueous phase is discarded. The extract is then neutralized with a saturated solution of sodium bicarbonate and the solvent layer is removed for analysis. The target analytes are identified and quantified by capillary column gas chromatography using an electron capture detector (GC/ECD). Analytes are quantified using procedural standard calibration.

3.5 Lab-scale chlorination and ClO_2 disinfection with DBPs formation potential tests

In all disinfection tests, the aforementioned water matrices were used. Labware was pre-treated to remove any chlorine demand by soaking it in a 1 mL/L commercial bleach solution for at least 1 hour. The labware was then rinsed with ultrapure water. Each bottle was rinsed with the corresponding sample. Disinfectant dosages were carefully administered using a pipettor, ensuring the pipette tip remained submerged to prevent localized areas of high disinfectant concentration. In the CS3T chlorination tests (performed by EUT) the testing solution was chlorinated with NaClO 15% to reach a final concentration of mg/L of free chlorine for 30min. After the 30-minute chlorination, free chlorine was quenched with sodium thiosulfate 0,1M.

THMFP tests were performed in each case study following the APHA 5710 B method, a standard procedure widely used to estimate the maximum possible concentration of THMs that could be generated. Despite its widespread use, the method has some limitations. Low chlorine residual concentrations can lead to an underestimation of THMFP. An excess of chlorine is added initially, ensuring that sufficient residual chlorine remains after incubation for accurate THMs formation and DBPs estimation. Samples is doped with the required hypochlorite concentration (5-7 mgCl_2-eq/L). After a 7-day incubation period, the free chlorine residual is measured to ensure it remains between 3 and 5 mg/L, critical for ensuring the completion of the THMs formation reaction. If the chlorine residual falls below 3 mg/L, incomplete formation of THMs may occur, requiring the sample to be discarded. All samples were prepared in triplicate. The sample's pH is initially adjusted to 7.0 ± 0.2 using a phosphate buffer (prepared following the method by dissolving potassium dihydrogen phosphate and sodium hydroxide in water), and the reaction is carried out at a controlled temperature of 25 ± 2°C. Finally, the sample is analyzed for THMs (POLIMI, CAT, EUT, UBA) and HAAs (CAT). The same methodology was applied using ClO_2 (5-7 mgCl_2-eq/L) to measure the formation of chlorites and chlorates (POLIMI and MM).

For residual chlorine concentration measurement, an 8-point calibration curve (9 replicates for each point) for NaClO was determined according to the 4500-Cl G method (APHA, 2017), using potassium permanganate solution as standard, where 0.891 mg/L potassium permanganate solution corresponds to 1 mgCl_2-eq/L as NaClO in the DPD reaction. The calibration curve for ClO_2 was obtained by the previous one by dividing the slope by 1.9, which is the ratio between the equivalent weights (mg/eq) of ClO_2 and Cl_2 (APHA, 2017). Absorbance at 515 nm of each solution for the calibration curve determination was measured immediately. The free chlorine in the samples, after a 7-day contact time, was measured following the DPD colorimetric method (4500-Cl G). N,N-diethyl-p-phenylenediamine (DPD) and 5 mL of the previously mentioned buffer were added to each 100 mL sample. The absorbance was then read at 515 nm to determine the free chlorine concentration.

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3.6 Sorbent materials: activated carbon and cellulose-based nanosponges

In CS2M adsorption tests, three commercial activated carbons (AC) and three innovative cellulose-based nanosponges (CNS) were tested (CNS1, CNS2, CNS3). The AC were supplied by Jacobi Carbons Italia. They vary in terms of origin, porosity (ranging from micro to macro-porosity) and surface charge due to their differing Point of Zero Charge (pH_{PZC}) values, meaning that they exhibit a negative charge when the pH of the matrix is higher than the pH_{PZC}, and vice versa. The characteristics of the activated carbons applied in CS2M samples are detailed in the Table 4.

Table 4: Main characteristics of the commercial AC materials provided by Jacobi used in the experimental tests at CS2M.

Adsorbent	**Origin**	**Activation**	**Iodine Index (mg/g)**	**Main Porosity**	**pH_{PZC}**
CP1	Vegetal (coconut)	Physical	1000	Micro	8,0
BP2	Mineral	Physical	850	Meso	9,2
MP25	Mineral	Physical	1000	Meso Macro / Macro	9,1

Cellulose-based nanosponges were synthesized using cotton linters as the cellulose source. The fibers underwent a TEMPO-mediated oxidation reaction, where TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl radical acted as a catalyst in the presence of sodium hypochlorite (12-14 % w/v solution) and potassium bromide (95% purity), producing TEMPO-oxidized cellulose nanofibers (TOCNF). Two cross-linkers were used for nanosponge preparation: branched polyethyleneimine (bPEI) with molecular weights of 25 kDa and 1.8 kDa. Anhydrous citric acid served as a co-cross-linker with bPEI 25 kDa, while varying water content was applied in formulations with bPEI 1.8 kDa. The resulting nanosponges were characterized by surface morphology *via* Scanning Electron Microscopy (SEM) and chemical structure analysis using Fourier Transform Infrared Spectroscopy (FTIR).

The GAC used in CS3T adsorption tests in pilot plant with synthetic water matrices was supplied from KEMIRA brand (Kemisorb 530 GR, granulometry 12x40 US Std, hardness > 90 %p/%p). GAC already installed at the Ampolla DWTP (CS3T) was compared with the six GACs reported in Table 5.

For the CS1B experiments, Norit SAE Super powdered activated carbon (PAC) supplied by Cabot was used in the pretreatment studies.

Table 5: Main characteristics of the commercial AC materials used in the experimental tests in CS3T.

Acronym	**Commercial Name**	**Type**	**Iodine Index**	**% Ashes**	**% Hardness**
F1	Kemisorb 530Gr	100% agglomerate	950	12	95
F2	Kemisorb 530Gr	100% bituminous	1.000	8	90
F3	Kemisorb 510 Gr	100% vegetal	1.150	2	98
F4	Kemisorb 510 Gr + Kemisorb 530Gr	50% vegetal + 50% bituminous	1.075	5	94
F5	Kemisorb 530 Gr + Kemisorb 510	70% vegetal + 30% bituminous	1.045	6,2	92
F6	Kemisorb 530 Gr	100% bituminous	900	5	90

4 Preliminary results for applications of the proposed guidelines in several scenarios

In this task an evaluation of different activated carbons and innovative materials for DBPs precursors reduction has been performed with the aim of developing guidelines for adsorbent materials selection and ranking in four different scenarios:

1) **Conversion from non-disinfected to disinfected drinking water supply (Paragraph 4.1)**;
2) **Upgrade of currently disinfected systems targeting precursors removal (Paragraph 4.2)**;
3) **Development of innovative adsorbent materials (Paragraph 4.3)**;
4) **Proposal of new treatment line scheme with pre-chlorination followed by adsorption (Paragraph 4.4)**.

The following paragraphs report the obtained results in the application of the guidelines and procedure for each of these for scenarios.

4.1 Guideline application for scenario 1: Conversion from non-disinfected to disinfected drinking water supply

This paragraph focuses on the case of drinking water treatment plants that currently do not have a disinfection step, such as CS1, but want to evaluate future combination of adsorption and disinfection for drinking water production.

Some preliminary experiments were conducted using the process guideline outlined in Figure 1, with a single commercial activated carbon and CS1B tap water (see chapter 3). A mesoporous activated carbon was selected but further experiments will be performed with other commercial activated carbons with different porosity. Figure 6 shows the effect of PAC pretreatment on chlorine consumption in tap water over a 2-hour period. The graph plots normalized chlorine concentration (C/C_0) over time for untreated water and water treated with different PAC dosages (5, 10, and 20 mg/L). Untreated water shows the fastest chlorine decay, while increasing PAC dosages slow the rate of chlorine consumption. The 20 mg/L PAC treatment results in the slowest decline, indicating that higher PAC dosages more effectively preserve chlorine levels. These findings highlight PAC's role in stabilizing chlorine during water treatment, with implications for optimizing disinfection. Comparing the composition of NOM before and after treatment with different PAC doses reveals slight removal of humic substances, building blocks and low molecular weight acids (Figure 7).

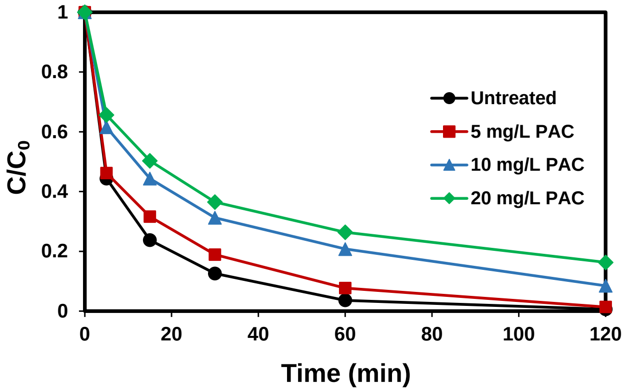

Figure 6: Chlorine consumption in tap water over time with varying PAC dosages.

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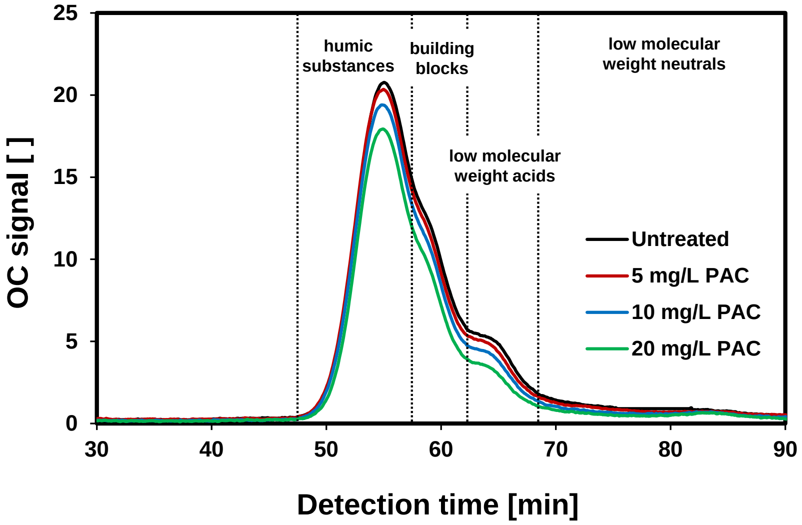

Figure 7: LC-OCD chromatograms of tap water before and after treatment with varying PAC dosages.

Figure 8 illustrates the impact of pretreatment on trihalomethanes (THMs) formation in tap water after chlorination, comparing THM levels across different PAC dosages. The results show that THM levels in all samples were relatively similar, with no significant influence of pretreatment with varying PAC dosages on THM formation. Therefore, future experiments within Task 2.3 will explore other activated carbons with different characteristics to identify those more effective in reducing THMs formation potential.

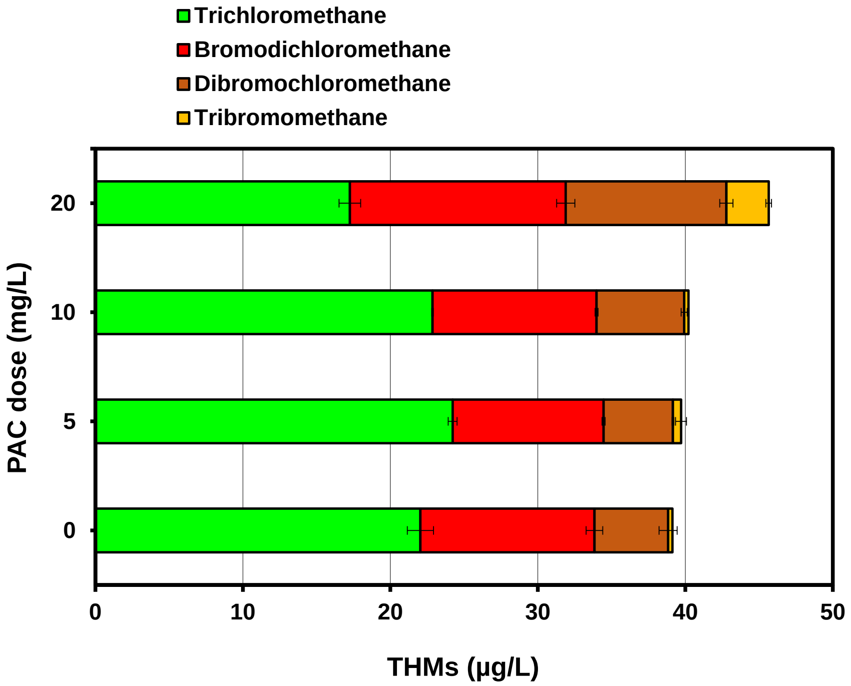

Figure 8: Formation of THMs due to chlorination of tap water before and after treatment (120 minutes) with varying PAC dosages.

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4.2 Guideline application for scenario 2: Upgrade of currently disinfected systems targeting precursors removal

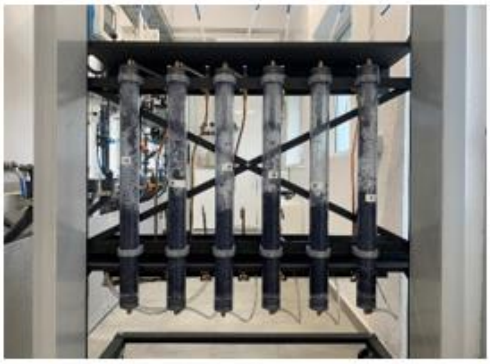
This paragraph focuses on the case of drinking water treatment plants that already have a disinfection step but want to select the optimal adsorbent to target DBPs precursors removal, as in the case of CS3T L'Ampolla drinking water treatment plant (DWTP).

In CS3T drinking water is produced from a surface water source using GAC filters as part of the process of the L'Ampolla drinking water treatment plant (DWTP), with bituminous GAC due to its high efficiency removal for heavy metals, organic matter and organic chemicals such as pesticides and herbicides found in discrete concentrations in the raw water. Afterwards, the finish water is chlorinated before traveling through the distribution network. CAT has more than 400 kilometres of a branched network with almost 200.000 m^3 of potable water storage capacity. Within the network, CS3 has up to seven re-chlorination systems in strategic network points, order to always ensure a minimal of 0,2 mg/L of free chlorine in all the delivery points. Therefore, it is key to remove the precursors of disinfection-by-products in the treatment plant before the water gets chlorinated several times to ensure that it is safe for drinking. In CS3 the main concern is to select the right absorbent material to remove not just the heavy metals, pesticides and herbicides, but to target also the right part of the organic matter that is directly related to the generation of DBPs.

For this research project, some preliminary experiments were conducted using the process guideline outlined in Figure 2 and 3. Firstly, CAT already has monitoring data from the raw water and after each treatment step of the DWTP (first step described in Figure 2). Thus, CAT directly started from the second part of the guideline workflow (Figure 3) to select suitable GACs according to removals of relevant NOM constituents to quantify the resulting THMs formation after the standard chlorination, and to determine the breakthrough curves to provide information about the media lifetime. These selected GACs (Table 5, see section 3.6) were tested in a total of six (6) columns as a pilot study (Figure 9).

In addition, the GAC already installed at the Ampolla DWTP (CS3) was compared with the six GACs selected to add the aging factor of the GAC on the NOM removal.

Diameter	5,4	cm
Height	54	cm
Filter Bed Height	30	cm
Maximum flow	11	L/h
Minim flow	4	L/h



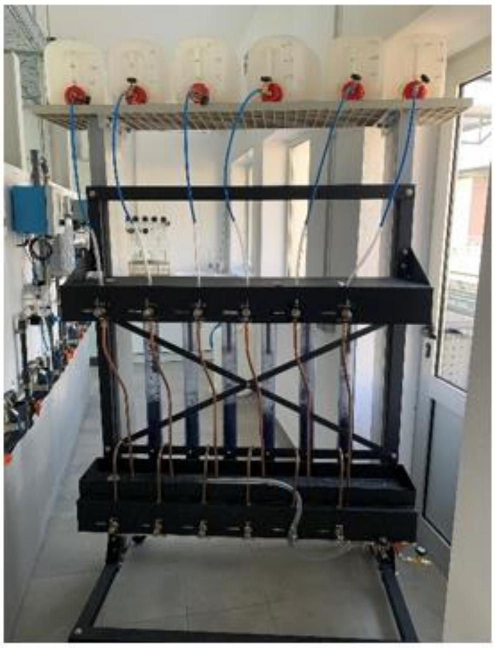


Figure 9: Pilot plant activated carbon columns and description of main operating parameters.

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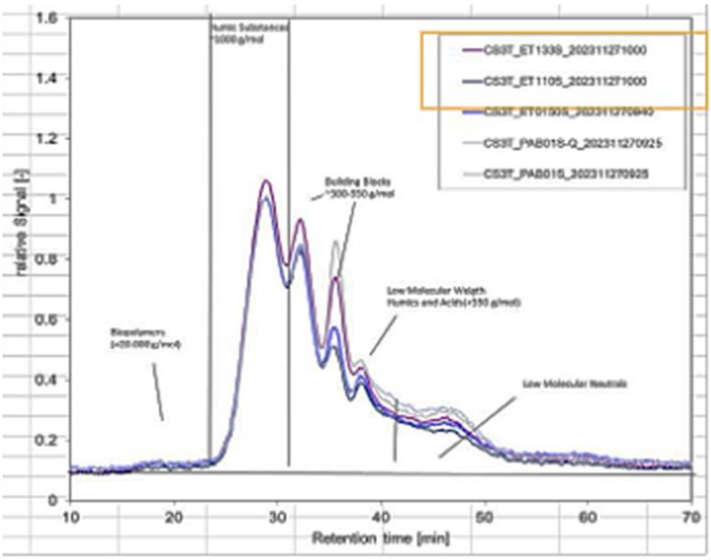
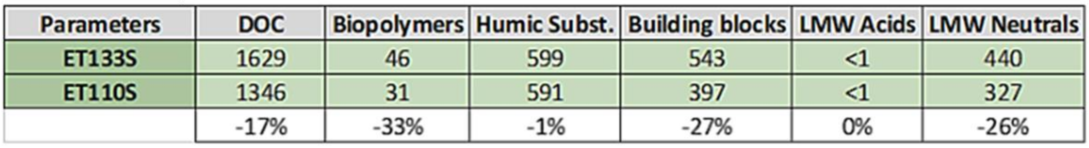
Samples from the L'Ampolla DWTP treatment processes effluents waters were sent to the DVGW Research Center TUHH for the analysis of fluorescence, absorbance, TOC/DOC and LC-OCD-UVD-OND. For this project, the results from the samples *CS3T_ET133S* – output of PostOzonation (before GAC filters) and the *CS3T_ET110S* - output of the GAC filters were used to understand the reduction of the different NOM materials at the actual GAC installed at the Ampolla DWTP (Figure 10).

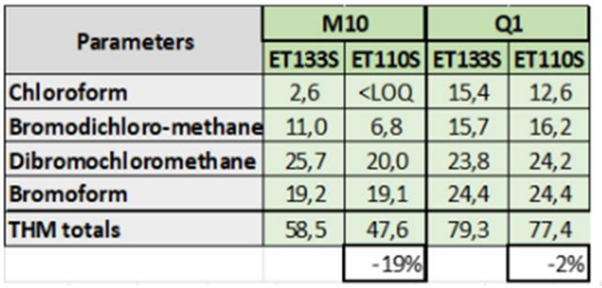




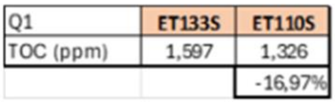
Parameters	DOC	Biopolymers	Humic Subst.	Building blocks	LMW Acids	LMW Neutrals
ET133S	1629	46	599	543	<1	440
ET110S	1346	31	591	397	<1	327
	-17%	-33%	-1%	-27%	0%	-26%

Figure 10: Evolution of the NOM in the input and output of the granulated active carbon filters of the plant. ET133S (input of carbon filters). ET110S (output of carbon filters). Sampling campaign February 2024. LC-OCD data analyses performed by DVGW-TUHH.

Table 6: DBPs potential reduction in the input and output of the granulated active carbon filters of the plant. ET133S (input of carbon filters). ET110S (output of carbon filters). Sampling campaign February 2024. DBPFP tests performed by CAT.



Parameters	M10		Q1	
	ET133S	ET110S	ET133S	ET110S
Chloroform	2,6	<LOQ	15,4	12,6
Bromodichloro-methane	11,0	6,8	15,7	16,2
Dibromochloromethane	25,7	20,0	23,8	24,2
Bromoform	19,2	19,1	24,4	24,4
THM totals	58,5	47,6	79,3	77,4
		-19%		-2%



Q1	ET133S	ET110S
TOC (ppm)	1,597	1,326
		-16,97%

Regarding the data interpretation, especially of the size exclusion chromatography LC-OCD and fluorescence coupled with the PARAFAC algorithms (data not shown), it will be necessary to wait for the second measurement campaign to take better conclusions on the interaction of the NOM parameters on the DBPs formations.

At the same time, CAT technicians performed the first pilot testing on the six selected commercial GACs, with the aim of doing a THMFP test, with THMs concentration after 7 days, on the six different

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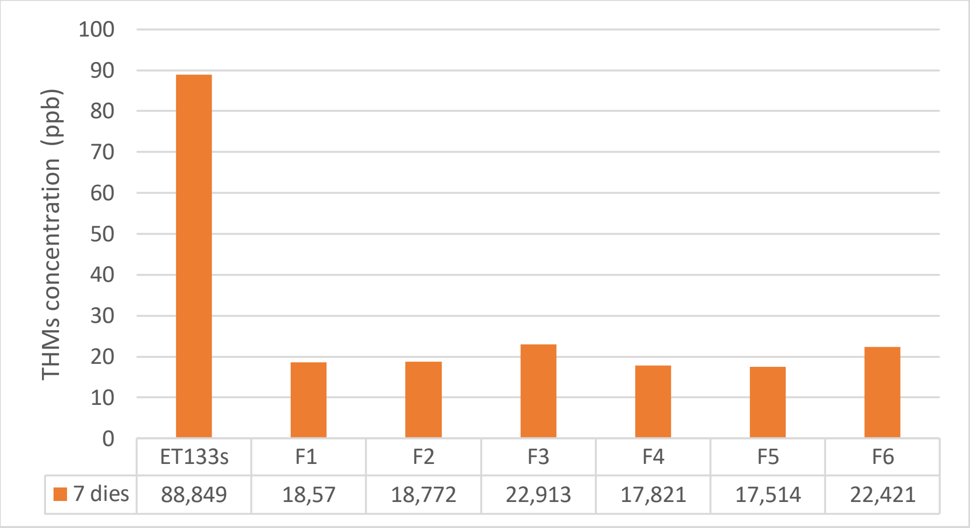
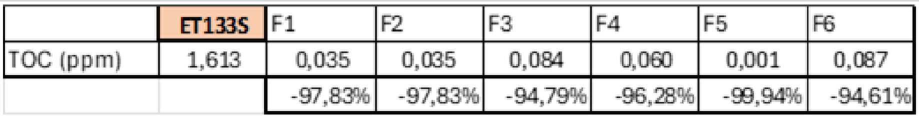
effluent waters, to determine if there is a GAC that shows bad performance from the beginning (Figure 11). TOC concentrations, reported in Figure 11, were determined in house too.





	ET133S	F1	F2	F3	F4	F5	F6
TOC (ppm)	1,613	0,035	0,035	0,084	0,060	0,001	0,087
		-97,83%	-97,83%	-94,79%	-96,28%	-99,94%	-94,61%

Figure 11: THMs formation potential after 7-day filtration with columns of six different activated carbons (F1-F6 correlative according to table 5) and the unfiltered water matrix (ET133S, input activated carbon stage filters). Tests were performed so far in single repetition.

From this first trial, similar DBPs potential reduction numbers were found as well as the similar numbers of TOC reduction (reported in the table under Figure 11).

Longer filter runtimes and more effluent water analysis will help determine the best GAC selection for NOM removal and DBPs reduction.

4.3 Guideline application for scenario 3: Development of innovative adsorbent materials

This paragraph outlines preliminary results obtained by POLIMI in the application of the guidelines in the case of specific development and optimization of the adsorbent material and comparison with the benchmark activated carbon.

Some preliminary experiments were conducted using the process guideline according to all the steps outlined in Figure 4, with multiple adsorbent materials and water matrices. Results of these experiments are reported in the following paragraphs.

4.3.1 Experimental plan

An experimental plan has been built according to the guideline reported in Figure 4, following all the proposed steps.

Synthesis of new materials depend on the case study. Specific information on the synthesis of CNS are reported in section 4.3.2.

Leaching studies were conducted to investigate the potential leaching of substances from the newly developed nanosponges after a 72-hour contact period with deionized water. This involved comprehensive spectroscopic analyses, including absorbance and fluorescence spectrum measurements, to detect any released components. Different dosages (15, 50 mg/L) of the nanosponges were tested, along with their individual components, to determine if leaching occurred.

Following the leaching studies, preliminary adsorption batch tests were performed to assess how well the best nanosponge interacted with various aqueous matrices. These tests also spanned a contact period of 72 hours to allow for adsorption equilibrium. The selected water matrices included combinations of deionized water and real water spiked with HA and SRNOM (see paragraph 3.2). Both the new nanosponge and benchmark activated carbon were evaluated at varying dosages of 5, 10, 15, 20, and 50 mg/L after the 72-hour contact period. The effectiveness of the adsorption was determined by absorbance and fluorescence after filtering the samples through a 0.45 µm membrane to separate the adsorbent from the water.

Finally, samples were subjected to formation potential tests using sodium hypochlorite and chlorine dioxide as disinfectants (5-7 mg Cl_2 eq/L). The focus was on identifying key target DBPs: trihalomethanes, chlorites, and chlorates, under conditions established in earlier methodologies.

The experimental plan is primarily designed to evaluate the performance of nanosponges in removing different NOM and simulate their behavior in various water matrices. This approach helps to assess not only the efficiency of nanosponges in controlled environments but also their performance in more complex settings, such as real water samples drawn from water treatment plants. Furthermore, the introduction of NOM into these more complex matrices facilitates the exploration of phenomena such as micelle formation and other chemical interactions that may occur in the presence of other inorganic compounds. So, a detailed understanding of the materials' performance across various conditions is provided, offering valuable insights for real-world applications (Figure 12). In conclusion, this experimental plan aims to offer deep insights into the factors influencing the adsorption and removal of NOM by nanosponges. It is expected that the performance of the nanosponges will vary depending on the type of NOM used and the complexity of the water matrix. Through this comparative study of different scenarios, the research aims to enhance the design of more efficient treatment systems in DWTP.

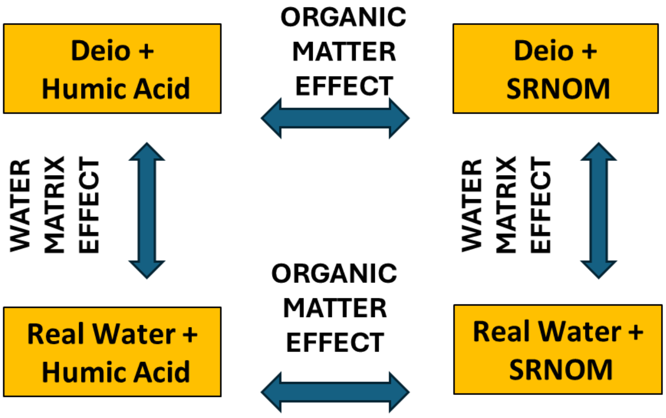


Figure 12: Comparison of different matrix and NOM configurations planned for the execution of the batch isotherm tests.

To simulate real-world water treatment conditions, the most promising material from the batch experiments is further tested in a continuous flow system using Rapid Small-Scale Column Tests (RSSCTs), which are a sub-category of Column Tests. The matrices used are the same as for batch studies. The breakthrough curves are used to evaluate NOM removal efficiency under continuous flow. Samples are taken at different points along the breakthrough curve and subjected to DBPFP tests using NaClO and ClO_2.

The complete experimental plan, reported in Table 7, aims to comprehensively evaluate the efficacy and safety of the new adsorbent materials in NOM removal and DBP mitigation, both in batch and continuous flow conditions.

Table 7: Experimental plan for batch and column tests.

Test	Conditions	Matrices	Dosages	Analysis
Leaching tests	Contact time: 72h; DI water	Deionized water (DIW)	Adsorbent: 15, 50 mg/L + CNS individual components	Absorbance spectrum, fluorescence (EEM integral, peaks)
Batch adsorption	Contact time: 72h; 0.45 µm filtration	DIW + NOM, Real water + NOM	Adsorbent: 5, 10, 15, 20, 50 mg/L	Absorbance spectrum, fluorescence (EEM integral, peaks), TOC
THMFP/DBPFP (for both batch and column tests)	NaClO & ClO_2	DIW + NOM Real water + NOM	5-7 mg Cl_2eq/L	THMs, chlorites, chlorates
Column tests (RSSCTs)	Continuous flow; Feed flowrate = 1-4 mL/min	DIW + NOM Real water + NOM	Adsorbent mass: 200 – 300 mg	Breakthrough curve for NOM, absorbance spectrum, fluorescence (EEM integral, peaks), TOC

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4.3.2 Fabrication and preliminary characterization of the nanosponges

CNS were synthesized through a multi-step protocol (Fiorati et al., 2020). First, high-quality cotton linter fibers were used as the cellulose source. A TEMPO-mediated oxidation reaction was performed under mild, aqueous conditions, selectively oxidizing the primary hydroxyl groups at the C6 position of the cellulose, resulting in the formation of TOCNF. Following the oxidation step, two different cross-linkers were used: bPEI 25 kDa and bPEI 1.8 kDa, with citric acid used as a co-cross-linker in the formulation containing bPEI 25 kDa to enhance mechanical stability and eco-safety. TOCNFs were mixed with the respective bPEI in an aqueous solution, with controlled ratios to achieve the desired degrees of cross-linking and porosity. For the bPEI 25 kDa formulation, a mixture of bPEI, TOCNF, and citric acid was used in a ratio of 1:1:18%, with the citric acid percentage calculated based on the moles of primary amines in bPEI (7.39 $mmol_{NH2}/g_{bPEI}$). On the other hand, for the bPEI 1.8 kDa formulation, the ratio of bPEI to TOCNF was set at 1:2, without the addition of citric acid. The decision to avoid the co-cross-linker was made since bPEI 1.8 kDa is less cytotoxic than bPEI 25 kDa (Thomas et al.,2005), suggesting a potentially lower ecological toxicity.

The resulting mixture was cast into moulds, followed by freeze-drying (24 hours of freezing, freeze-drying conducted at 50 μbars and – 50 °C) to remove water without collapsing the porous structure, favouring the formation of micro- and nano-pores. The freeze-dried samples underwent thermal treatment with a thermal ramp from 60 °C to 100 °C, maintaining this final temperature for 16 hours and inducing cross-linking between the carboxyl groups of the TOCNF and the amine groups of the bPEI, thereby forming a stable three-dimensional network. CNS were finally washed with deionized water to remove unreacted bPEI and dried at open air overnight. A schematic representation of CNS synthesis is reported in Figure 13.

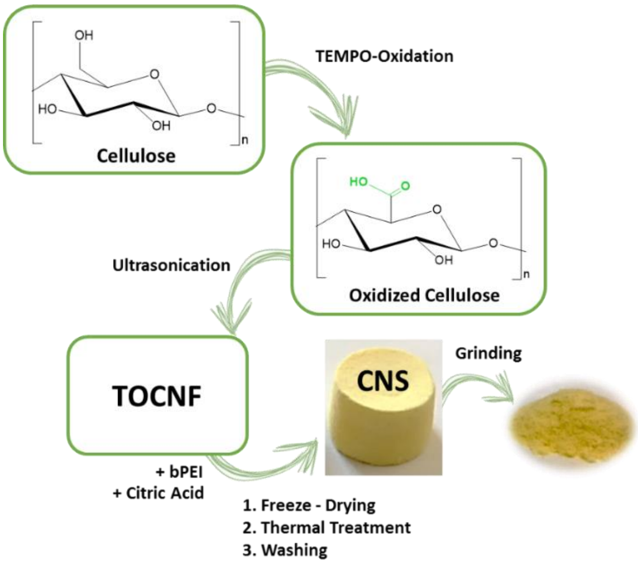

Figure 13: Experimental steps for the synthesis of CNS.

Different amounts of water were incorporated in the formulation with bPEI 1.8 kDa to modulate the porosity of the nanosponges, resulting in structures with tunable characteristics.

Morphological characterization of the CNS was conducted using Scanning Electron Microscopy (SEM), as shown in Figure 14. The analysis of different formulations revealed qualitative differences in pore structure. Specifically, the bPEI 1.8 kDa formulation exhibited larger pores, while the bPEI 25 kDa formulation displayed a higher density of smaller pores. The lamellar structure observed in the bPEI 1.8 kDa formulation can be attributed to the increased concentration of TOCNF in the formulation, if compared to the CNS bPEI 25 kDa.

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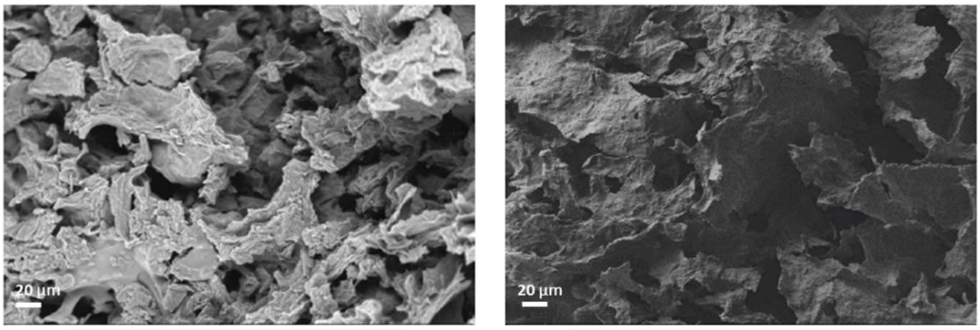
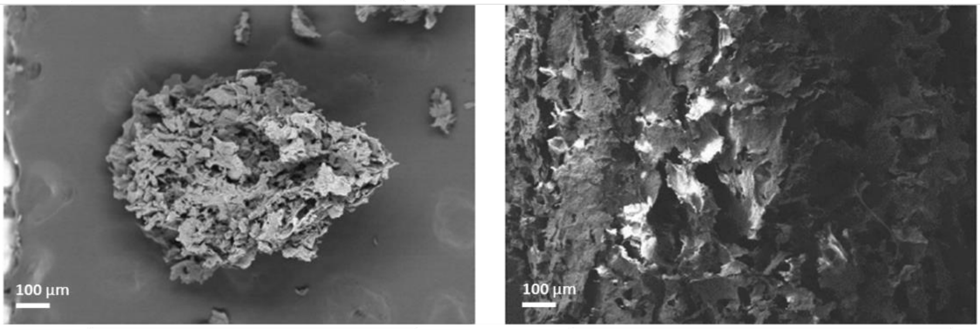


a) CNS bPEI 25 kDa formulation **b)** CNS bPEI 1.8 kDa formulation



c) CNS bPEI 25 kDa formulation **d)** CNS bPEI 1.8 kDa formulation

Figure 14: SEM analyses of CNS with bPEI 25 kDa (**a**, **c**) and 1.8 kDa (**b**, **d**) at different magnifications (**a**, **b**: 1000x; **c**, **d**: 150x).

FTIR analysis was conducted to identify the chemical bonds present in CNS. The FTIR spectra revealed characteristic peaks, as illustrated in Figure 15. A prominent peak at 1725 cm^{-1} is associated with the C=O group, while the peak at 1636 cm^{-1} corresponds to the C-N bond of the amide linkage. Additionally, a peak around 3300 cm^{-1} indicates the presence of an N-H bond, suggesting a single hydrogen atom attached to the nitrogen in the amine group. Furthermore, a peak at 1450 cm^{-1} can be observed, which is attributed to the bending of the C-H bond.

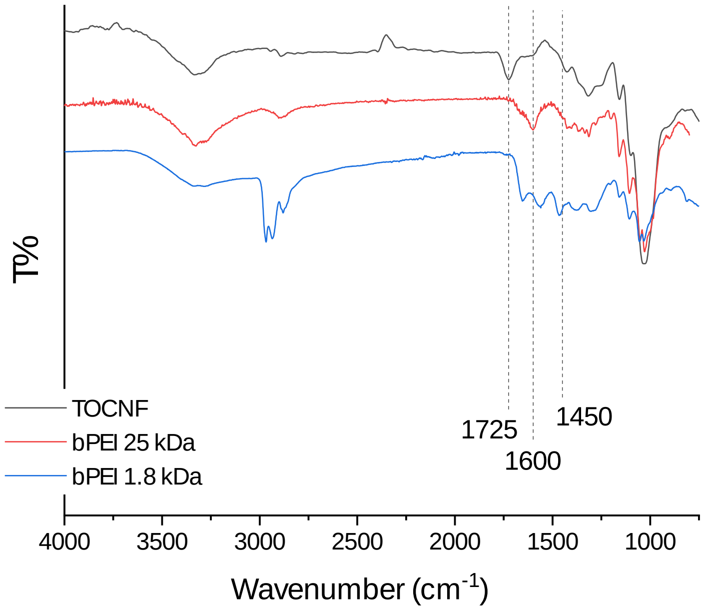


Figure 15: FTIR spectra of TOCNF (black), bPEI 25 kDa CNS (red) and bPEI 1.8 kDa CNS (blue).

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4.3.3 Leaching tests for cellulose-based nanosponges

Preliminary leaching tests conducted on three different CNS (CNS1, CNS2, CNS3) formulations revealed partial release of substances which was detected through both absorbance at 254 nm (UVA$_{254}$) and fluorescence measurements (Figure 16a and 16b). The degree of leaching is highest at higher dosages (>20 mg/L), where the release of organic matter into the water significantly overwhelms any potential adsorption effects. The UVA$_{254}$ is typically associated with aromatic organic compounds, suggesting that components within the nanosponges are dissolving into the solution. Specifically, TOCNF and bPEI show the highest fluorescence integrals, particularly the first one, which demonstrates the largest contribution to the overall leaching (Figure 17a). The CNS formulations, while showing lower fluorescence compared to their individual components sum, still exhibit significant leaching, confirming that both TOCNF and bPEI are likely responsible for this behavior. By analyzing the fluorescence response, it can be seen an increase especially for the A and C peaks (Figure 16b), which are characteristic of humic and fulvic substances, the data confirm that TOCNF and bPEI are the main contributors to leaching. Their significant impact on these peaks indicates that the nanosponges are releasing organic compounds similar to NOM typically found in water, potentially interfering with disinfection processes.

(a) (b)

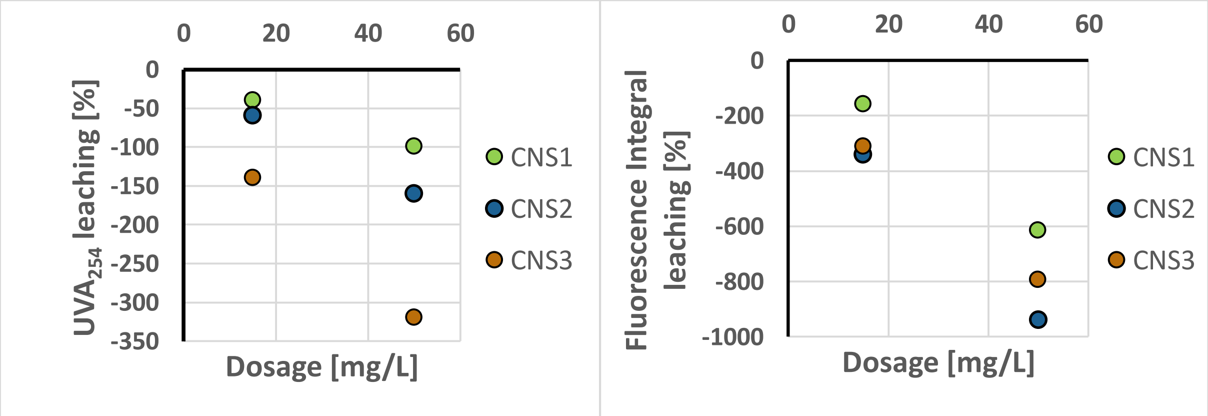

Figure 16: Leaching tests of 3 different CNS formulation in DIW, evaluated in terms of (a) UVA$_{254}$ and (b) fluorescence integral.

(a) (b)

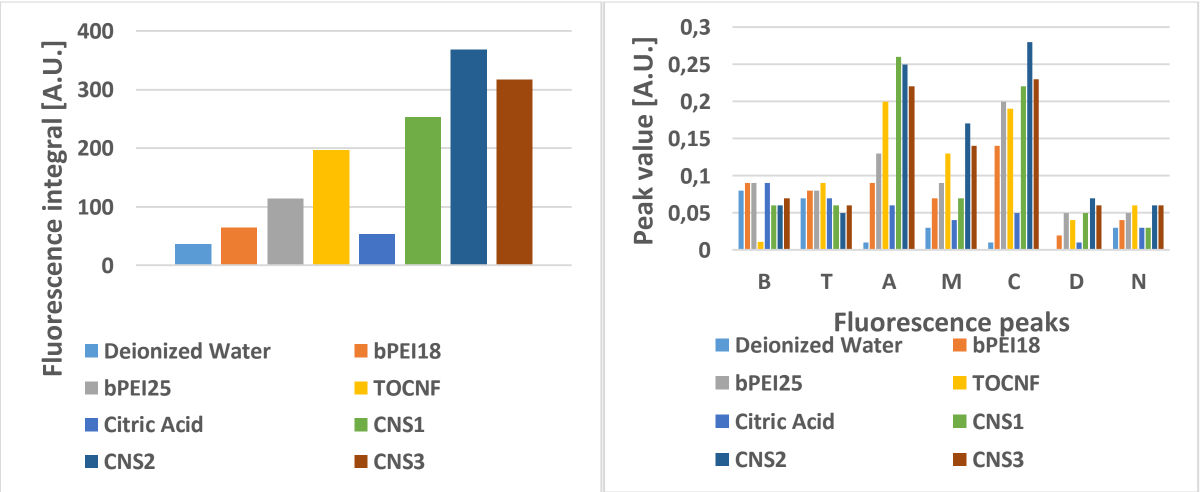

Figure 17: Leaching tests of each component of nanosponges, evaluated in terms of (a) fluorescence integral and (b) fluorescence peaks.

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This leaching behavior is particularly concerning when trying to remove organic matter, as it suggests the material itself is adding to the organic load. Pre-washing the nanosponges could potentially mitigate this issue by removing loosely bound or unreacted components before use in water treatment applications. Further studies are necessary to assess the long-term stability of these materials and whether modifications or pre-washing steps can reduce leaching. This will be further evaluated within T2.3.

4.3.4 Batch tests: benchmark activated carbons NOM removal and comparison with cellulose-based nanosponges

In the tests conducted with activated carbon, the organic matter removal efficiency increased as the porosity of the carbon improved (Figures 18 and 19). When focusing on the effect of NOM, particularly in tests with synthetic matrices, it became clear that high molecular weight compounds, such as humic acids, were more easily removed through the macropores of the activated carbon due to their larger size and complex structure. This is evident in Figure 18, where the reduction of fluorescence peaks A and C becomes more pronounced as the adsorbent dosage is increased, indicating greater removal of these humic substances.

A comparative analysis between the nanosponge and mesoporous activated carbon revealed that the nanosponge achieved removal efficiencies that were quite similar, particularly in the reduction of fluorescence peaks related to NOM. However, an important observation was made regarding the behavior of the nanosponge at higher dosages. While the removal of humic fractions remained effective, the increased release of compounds from the nanosponges at elevated dosages began to counteract the overall removal trend. Despite this, the material continued to perform well in reducing the humic content of NOM, although the leaching phenomenon suggested that higher doses could potentially limit the efficiency in practical applications.

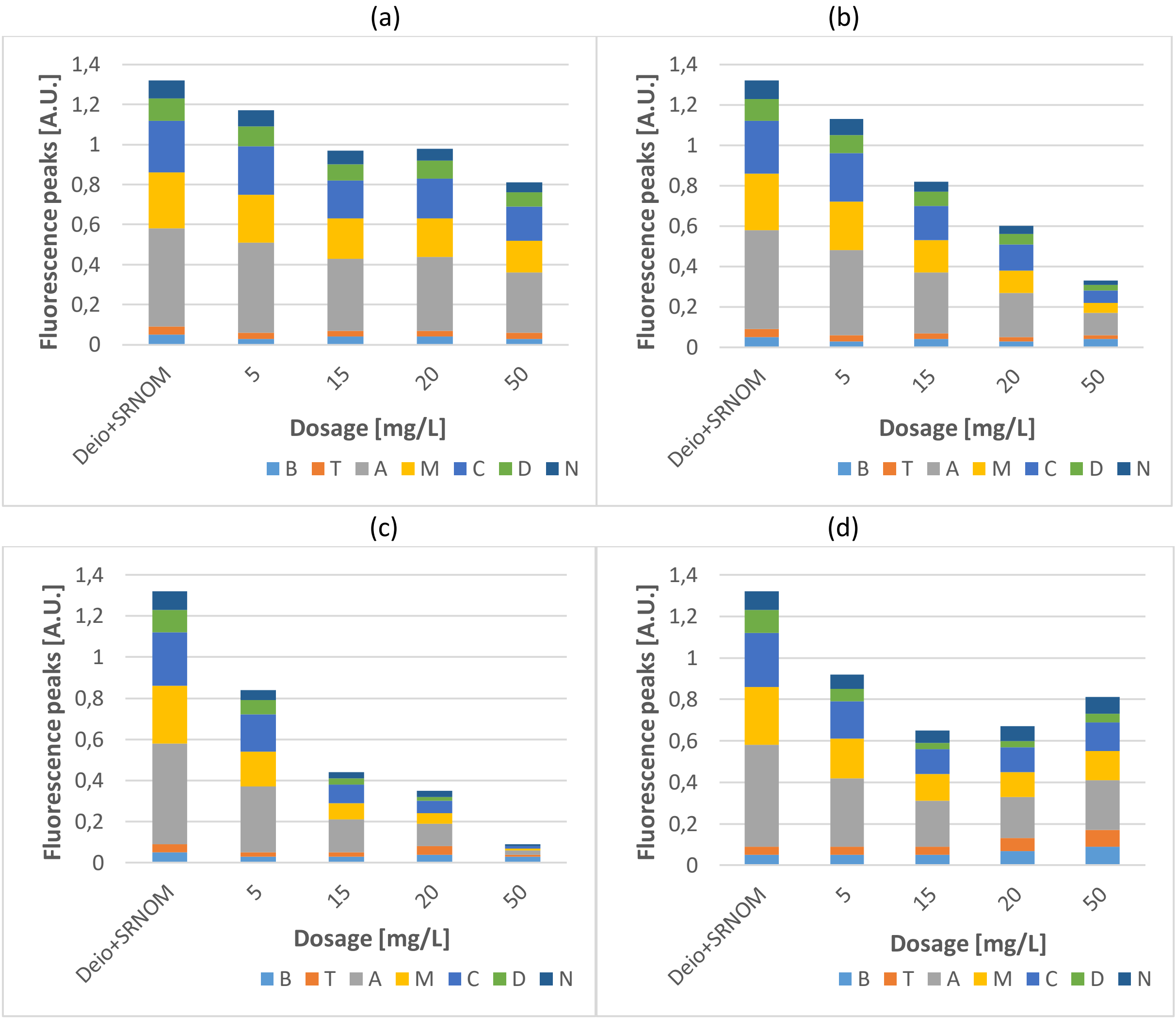
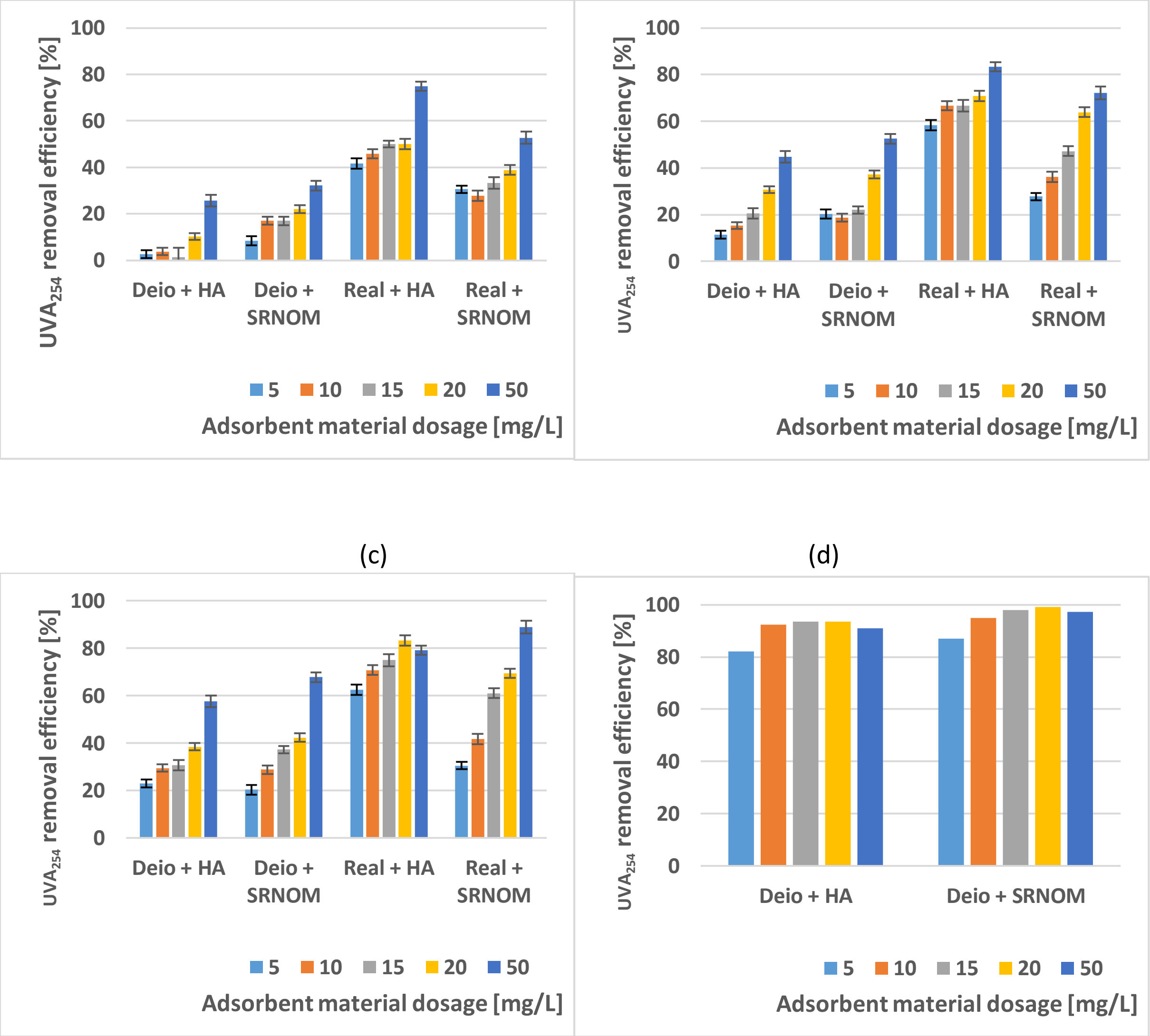


Figure 18: Fluorescence peak removal in the test with deionized water + SRNOM at 3 mg/L and a 72-hour contact time for (a) CP1 (microporous activated carbon), (b) BP2 (mesoporous activated carbon), (c) MP25 (macroporous activated carbon), and (d) the CNS1.

When comparing the removal of UVA_{254} (Figure 18), the removal trends for activated carbons closely mirror those observed for fluorescence. Notably, the CNS1 demonstrated over 80% absorbance removal efficiency even at low dosages (these tests were conducted in deionized water with varying types of NOM). The difference between absorbance and fluorescence removal observed for the nanosponges can be attributed to the intrinsic nature of the target substances. In some cases, absorbance and fluorescence may yield different results due to variations in the chemical bonds of the target molecules, specifically the differences in phototropic or fluorophoric properties. This means that while some compounds absorb UV light effectively, they may not exhibit strong fluorescence, or vice versa, depending on their molecular structure and bond types.

When comparing the matrix effect, it was observed that activated carbons showed higher removal efficiency in real water under similar NOM dosage conditions. This could be due to the complex interactions occurring between NOM and the compounds present in real water matrices, such as salts and inorganic components, which can form micelles or influence adsorption behavior, further enhancing the efficiency of activated carbon in these more challenging environments.

(a) (b)



(c)

(d)

Figure 19: UVA$_{254}$ removal in adsorption batch tests conducted in different water matrices with NOM initial concentration always at 3 mg/L, with a 72-hour contact time for (a) CP1 (microporous activated carbon), (b) BP2 (mesoporous activated carbon), (c) MP25 (macroporous activated carbon), and (d) the CNS1.

4.3.5 Batch tests: DBPs formation potential related to precursor removal

Initial tests on DBPs formation potential, conducted using NaClO (THMFP) and ClO_2 (DBPFP) in deionized water with humic acid, demonstrated a significant reduction in TTHMs formation when employing the nanosponge. Compared to activated carbon, the nanosponge achieved a reduction in TTHMs formation by 20 to 40%. This suggests a notable effectiveness of the nanosponges in mitigating the precursors responsible for the formation of these disinfection by-products. However, the formation of chlorites and chlorates appeared to be less influenced by the removal of NOM (specifically humic acid). This might be due to the disproportionation reactions of chlorine dioxide (ClO_2), which are not as directly impacted by NOM removal as TTHMs formation. Disproportionation occurs when ClO_2 reacts with water, generating chlorite (ClO_2^-) and chlorate (ClO_3^-) as by-products, and these reactions can occur independently of organic content, which might explain the weaker correlation between NOM removal and the formation of these compounds.

Furthermore, the higher oxidative potential of chlorine dioxide compared to sodium hypochlorite could lead to more significant breakdown of NOM, but this process does not necessarily reduce the formation of chlorite and chlorate. These compounds are formed as a result of the inherent instability

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of ClO_2 in water, which leads to its breakdown even in low-NOM environments. These initial findings are promising, and additional tests currently ongoing to further evaluate the nanosponges' potential in real-world scenarios. The results of these initial DBPs formation tests are illustrated in Figure 20.

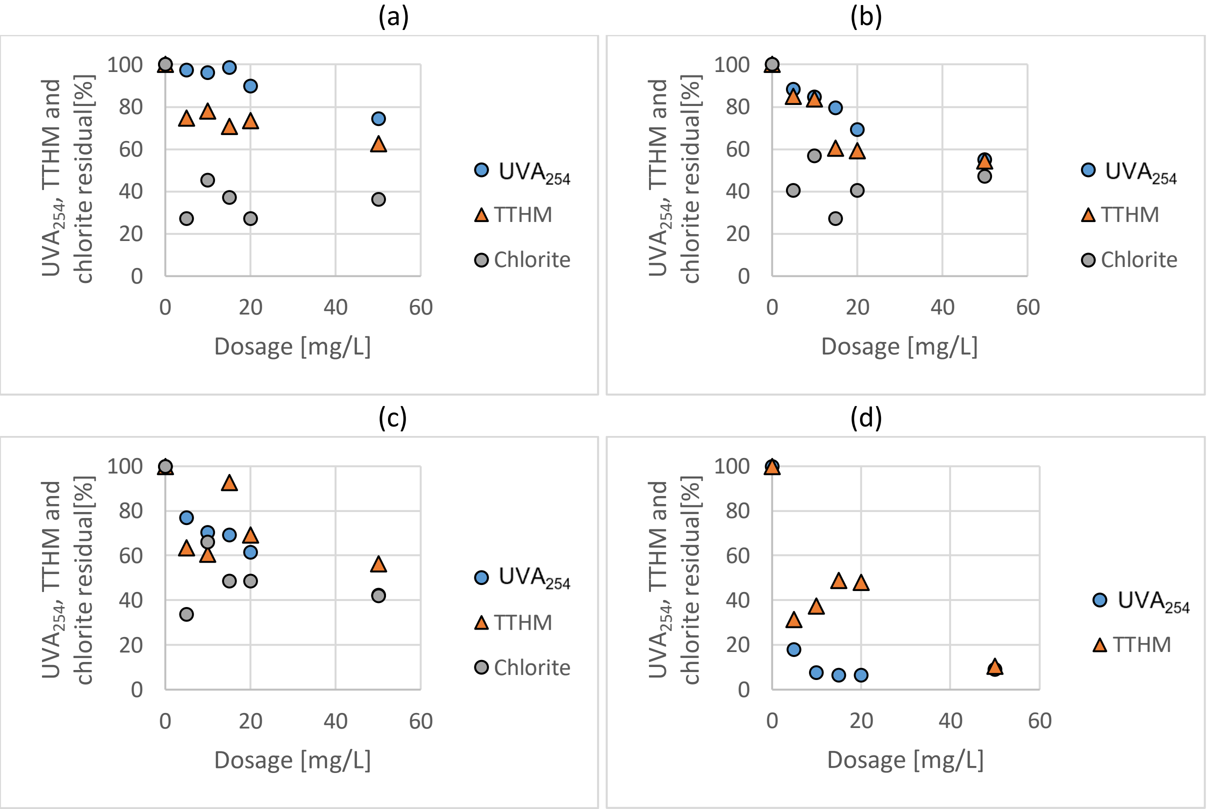

Figure 20: THMFP and DBPFP tests results performed on deio water + HA sample after isotherm tests: UVA_{254} (a,b,c,d), TTHMs (a,b,c,d) and chlorite residual (a,b,c) for (a) microporous AC, (b) mesoporous AC, (c) microporous AC and (d) CNS1 at different dosages (5, 10, 15, 20, 50 mg/L).

The upcoming activities include the finalization of batch disinfection test replicates and the execution of column tests using the RSSCT system. During these tests, it is planned to select 5 points on the breakthrough curve of the AC and perform THMFP and DBPFP. This will be performed also on optimized CNS after revising the fabrication and/or pre-treatment washing to minimize the leaching effects. CNS and AC results will be compared according to guideline in Figure 4.

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4.4 Guideline application for scenario 4: Proposal of new treatment line scheme with pre-chlorination followed by adsorption

This paragraph outlines preliminary results obtained by EUT in the application of the guideline in the case in which a new drinking water treatment plant needs to be built and high disinfectants doses are expected to be needed. Therefore, a new treatment line needs to be considered, and here it is proposed with a pre-chlorination step followed by adsorption.
Some preliminary experiments were conducted using the process guideline outlined in Figure 5. Results of these experiments are reported in the following paragraphs.

4.4.1 GAC isotherm characterization

8 falcons were prepared with different GAC amounts: 1g, 2g, 4g, and 8g (in duplicates). One set of falcons was filled up with 40ml of the control solution (synthetic water, not chlorinated). The other set of falcons was filled up with the same synthetic water but chlorinated (new treatment: 5ppm / 30 min). After 1 day, TOC was measured at each sample.

4.4.2 Effect of chlorination before GAC adsorption

5 liters of synthetic water were prepared and divided into 2.5L (one bottle for the control; and the other for the new treatment). The 'new treatment' bottle was chlorinated (30minutes, 5ppm). Then, both samples were pumped to a GAC column (two different GAC columns). Samples were grabbed to measure TOC and THMFP at each step: water inlet (synthetic water), post-chlorination, and columns outlet (Figure 21).

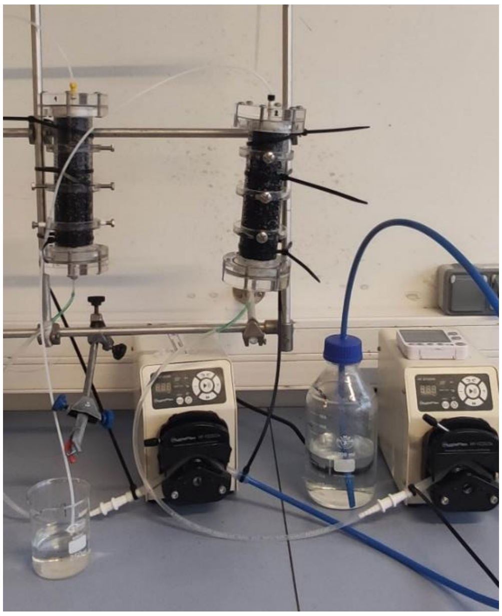

Figure 11: Column test experiment setup.

Evaluation of the experimental data will be performed to build a proposal for the scale-up of this idea in real drinking water facility, that now is schematized in Figure 22.

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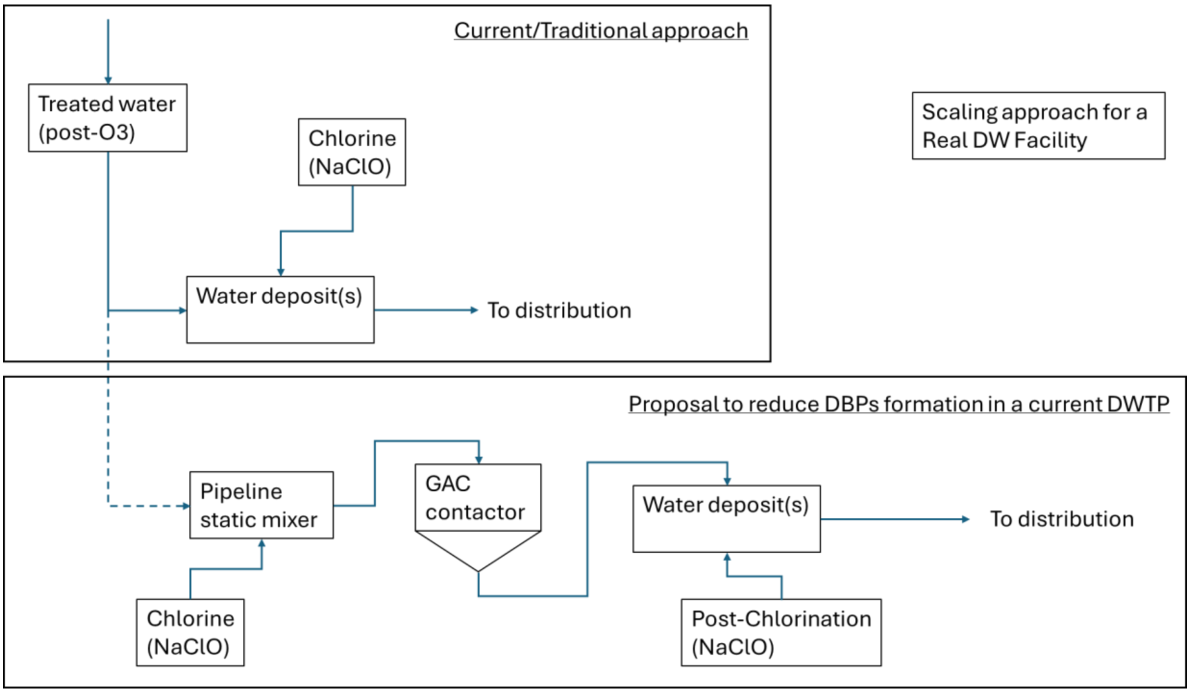

Figure 22: Proposal for a scaling-up approach including the post-adsorption strategy in a real drinking water facility.

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5 Conclusions

This deliverable provides four key guidelines, accompanied by corresponding flowcharts, designed to help in the selection and investigation of adsorbent materials in relation to disinfection practices. These guidelines are tailored to address four distinct scenarios where GAC are evaluated for their role in DBPs formation:

I. Conversion from non-disinfected to disinfected drinking water supply;
II. Upgrade of currently disinfected systems targeting precursors removal;
III. Development of innovative adsorbent materials;
IV. Proposal of new treatment line scheme with pre-chlorination followed by adsorption.

In each scenario, the framework guides water utilities on how to select the most appropriate adsorbent materials and operational configurations to balance the removal of NOM while minimizing the formation of harmful DBPs.

The experimental results obtained throughout this research reveal several insights into optimizing water treatment strategies. The results provided valuable insights into optimizing adsorbent materials to minimize DBPs formation risks while maintaining effective water treatment processes. The findings could inform water utilities, adsorbent materials producers and decision makers and pave the way for the adoption of advanced water treatment solutions, contributing to global efforts to ensure safe drinking water in a climate change scenario. Future research in the next year before the end of this task (October 2025) will focus on enhancing material stability and expanding testing to a wider range of water sources. Moreover, new efforts will be made to combine not only technical performance evaluations of these adsorbents but also considers their sustainability, scalability and cost-effectiveness.

Lastly, the adoption of these advanced materials and treatment technologies may require updates to regulatory frameworks to ensure compliance with drinking water standards and sustainability objectives. Overall, advanced treatment technologies have the potential to play a significant role in addressing global water challenges, ensuring safer access to drinking water.

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