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Process innovations and circular strategies for closing the water loop in a process industry

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ABSTRACT

By implementing advanced wastewater treatment technologies coupled with digital tools, high-quality water is produced to be reused within the industry, enhancing process efficiency and closing loops. This paper investigates the impact of three innovation tools (process, circular and digital) in a Solvay chemical plant. Four technologies of the wastewater treatment plant "WAPEREUSE" were deployed, predicting their performance by process modelling and simulation in the PSM Tool. The environmental impact was assessed using Life Cycle Assessment and compared to the impact of the current industrial effluent discharge. The circularity level was assessed through three alternative closed-loop scenarios: (1) conventional treatment and discharge to sea (baseline), (2) conventional and advanced treatment by WAPEREUSE and discharge to sea, (3) conventional and advanced treatment by WAPEREUSE and industrial water reuse through cross-sectorial symbiotic network, where effluents are exchanged among the process industry, municipality and a water utility. Scenario 1 has the lowest pollutants' removal efficiency with environmental footprint of 0.93 mPt/m^3. WAPEREUSE technologies decreased COD by 98.3%, TOC by 91.4% and nitrates by 94.5%. Scenario 2 had environmental footprint of 1.12 mPt/m^3. The cross-sectorial symbiotic network on the industrial value chain resulted in higher industrial circularity and sustainability level, avoiding effluents discharge. Scenario 3 is selected as the best option with 0.72 mPt per m^3, reducing the environmental footprint by 21% and 36% compared to Scenarios 1 and 2, respectively.

Nomenclature

ACLS	Alternative Closed-Loop Scenarios	MBR	Membrane Bioreactor
AI	Artificial Intelligence	MLVSS	Mixed Liquid Volatile Suspended Solids
AOP	Advanced Oxidation Process	MWTP	Municipal Wastewater Treatment Plant
API	Application Programming Interface	NOM	Natural Organic Matter
COD	Chemical Oxygen Demand	PFO	Pseudo-First Order
CSS	Circular Systemic Solution	PSM	Process Simulation Modelling
DOC	Dissolved Organic Carbon	PSO	Pseudo-Second Order
EBCT	Empty Bed Contact Time	RO	Reverse Osmosis
EF	Environmental Footprint	SDG	Sustainable Development Goal
EU	European Union	TOC	Total Organic Carbon
GAC	Granular Activated Carbon	TSS	Total Suspended Solids
GFH	Granular Ferric Hydroxide	UF	Ultrafiltration
LCA	Life Cycle Assessment	WDA	Windows Desktop Application
LCI	Life Cycle Inventory	WWRP	Wastewater Reclamation Plant
LCIA	Life Cycle Impact Assessment	ZLD	Zero Liquid Discharge

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1. Introduction

Industrialisation and urbanisation widen the gap between water availability and demand (Date et al., 2022). In addition, population growth is expected to increase, reaching up to 10.2 billion in 2060 (EuropeanCommission, 2020), leading to increased water demand and hence, water scarcity issues (Panagopoulos and Giannika, 2022). The total amount of abstracted water in the EU has been reduced by 15% in 2019 compared to 2000, with an increased abstraction rate of surface water (from 77% to 81%) and a decreased abstraction rate of groundwater (from 23% to 19%). SDG 6 "Clean water and sanitation" targets at sustainable management of water resources through water-use efficiency practices to deal with water scarcity that occurs when abstracted water exceeds long-term available water amount by 20% (UN DESA, 2023), (Gancheva et al., 2018). Overall, the industrial sector accounts for 40% of the total abstracted water in Europe (Education Indicators inFocus, 2013). Italy ranked 6th out of 36 European countries in terms of worst seasonal water scarcity issues in 2019 (DIRECTIVE, 2000).

Chemical industries have a significant impact on water resources. The necessity of minimising water consumption leads to the investigation of alternative water sources to be incorporated into the industrial production processes and the adoption of water reuse practices (Date et al., 2022), (Procházkov et al., 2023), (Guelli Ulson De Souza et al., 2011). A promising solution lies in the reuse of reclaimed water from industrial wastewater streams (European Environment Agency, 2021). A typical wastewater stream emanated from a chemical industry is characterised by high concentration levels of organic as well as inorganic contaminants and toxic substances (Nasr et al., 2007), (Bautista et al., 2008). It is common to treat such streams within a municipal wastewater treatment plant (MWTP) before leaching into the water bodies. Instead of discharging, further treatment usually aspires to reuse water within the plant (Verhuelsdonk et al., 2021), leading to closed-loop systems and sustainable industries (Rao and Rao, 2022). To this end, different treatment technologies have been studied, including coagulation, advanced oxidation process (AOP) (Metin and Çifçi, 2023), ultrafiltration (UF), reverse osmosis (RO) (Aktaş et al., 2017), membrane bioreactor (MBR) (Bielefeldt, 2009), adsorption and ion exchange (Tó et al., 2023).

Furthermore, it is worth mentioning the opportunity to exploit the redundant resources and waste generated during industrial wastewater treatment. In this regard, freshwater, alternative water resources, wastewater and material exchange among industries, companies, public and private authorities and any interested stakeholder seems promising (Ramin et al., 2024), (Henriques et al., 2022). The waste/by-products of an actor/supplier can be transformed into valuable input of another actor/recipient, who increases productivity and revenue with lower cost for purchasing raw materials and waste disposal, resulting in closed–water and –material loops (Wadströ et al., 2021). Thus, the definition of industrial symbiosis is introduced, where industries become closely interconnected via synergies, sharing resources, including water, wastewater, solid waste, by-products and energy (Neves et al., 2020; Angelis-Dimakis et al., 2022, 2023). Such symbiotic relationships lead to a decrease in wastewater discharge and contamination of the environment and freshwater consumption, while an increase in water circularity, water and materials reuse and recycling is achieved (Chin et al., 2021). Public and private companies, utility facilities, regional/national authorities and municipalities can participate in such symbiotic networks, sharing water, material and energy (Ramin et al., 2024), (Trö et al., 2023).

The goal of this paper is to model and simulate alternative wastewater treatment technologies constituting the industrial-scale wastewater treatment plant "WAPEREUSE", deployed in a Solvay chemical plant in Italy, and assess their performance and environmental impact. Closing the water-loop through industrial wastewater treatment and fit-for-purpose water reuse in a process industry is challenging, requiring the synergistic implementation of process, circular and digital innovations. In addition, the impact of the close collaboration among different sectors within the same area aspiring to create a materials-exchange symbiotic network is investigated. The novelty of this study lies in the investigation of the beneficial impact of such innovations in a chemical industry in conjunction with the evaluation of the cross-sectorial symbiotic network on the industrial value chain.

As a result, **Section 2** includes the description of the case study, the Solvay chemical plant, evaluates the current situation, indicates the potential innovation tools to be implemented and defines the alternative treatment scenarios. **Section 3** presents the models and assumptions made for the selected technologies and introduces the main definitions for the Life Cycle Assessment (LCA). **Section 4** provides the modelling and simulation results as well as the Life Cycle Impact Assessment of the alternative treatment scenarios (Scenario 1: on-site treatment and then discharge to the sea, Scenario 2: Further on-site treatment and then discharge to the sea, Scenario 3: On-site industrial treatment, cross-sectorial symbiotic network and safe reuse intra-factory). A scenario comparison is also included. Finally, **Section 5** highlights the main findings and limitations of this study.

2. Case study description

The Solvay chemical plant is located in Italy and produces several products, including peracetic acid, hydrogen peroxide, calcium chloride, plastic materials and hydrochloric acid. On the one hand, a large amount of water is required for the industrial purposes, but on the other hand, the industry participates in a consortium along with the municipality and a water utility company that has a wastewater reclamation plant (WWRP), by exchanging water and wastewater at a specific price to cover the total freshwater demand.

The main objectives of the industrial plant encompass a freshwater intake reduction by 25%, water reuse increase derived from the peroxide and peracetic acid production plant by 100% within the industrial boundaries, discharged wastewater from the peroxide and peracetic production plant decrease by 10% and carbon footprint savings increase. In addition, lower costs through industrial synergies and digital tools and services integration are key goals. The industry aspires to become environmentally friendlier, adopting sustainable strategies and adding value to water through fit-for-purpose practices, closed-water loops and digitalisation.

2.1. Evaluation of the current situation

A local water utility, which is a member of the consortium, and the local aquifer serve as freshwater suppliers for the Solvay plant. The production of peroxide and peracetic acid results in 10 m^3 of wastewater/h, which is currently treated on-site (Fig. 1). Overall, the treatment train is composed of skimming, lamella separator and granular activated carbon (GAC) filtration. After the last step, online sensors collect data related to flow rate, temperature and pH, which are stored in the Performance Improvement Measurement System and, if necessary, the Distributed Control System triggers warning signals.

Currently, approximately 87,600 m^3 of wastewater are being discharged into the sea annually, complying with the legal discharge limits, but causing environmental pollution. Wastewater qualitative characteristics are given in Table 6 (Scenario 1).

2.2. Innovation tools

Enhancing industrial water circularity and sustainability entails the deployment of a three-layered innovation strategy: (1) process-oriented practices through fit-for-purpose treatment technologies, (2) circular approaches at different levels and (3) digital tools, technologies and services.

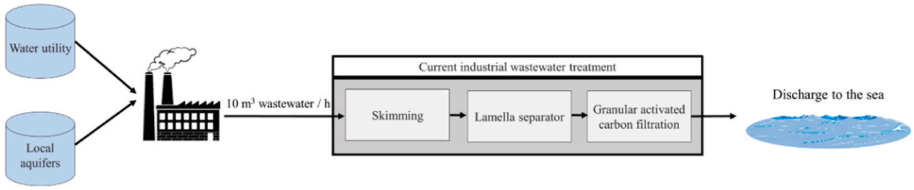

Fig. 1. Current wastewater treatment in the Solvay chemical plant.

2.2.1. *Process innovation*

Advanced wastewater treatment technologies are implemented to treat the industrial wastewater and produce water of such quality to comply with the reuse requirements within the industry. Wastewater treatment can lead to in-process and/or intra-factory water reuse, since reclaimed water is utilised to fulfil the water demand for cooling and other purposes. In-process refers to water reuse within the same process that produced the wastewater, while intra-factory to water reuse within a different process of the factory.

Both process-oriented practices include the deployment of fit-for-purpose wastewater treatment technologies, comprising the WAPEREUSE system, based on target contaminants that are modelled and simulated. In this regard, the performance of alternative technologies is assessed by using in-process modelling that requires a deep understanding of the technologies to foretell the final product's quality, water recovery, energy requirements, chemicals consumption, sludge production (if applicable) and process-specific parameters. The industrial value chain of the case study is simulated using the Process Simulation Modelling (PSM) tool, which will be presented in detail along with the simulated treatment scenarios in section 2.2.3.

2.2.2. *Circular innovation*

By reusing the reclaimed water, environmental pollution is prevented and freshwater demand and wastewater release to the water bodies decrease. The creation of a cross-sectorial symbiotic network among an industrial partner, a municipality and a water utility is able to promote sustainability and circularity, industrial and urban, and reduce the environmental impact (Trö et al., 2023).

Material Flow Analysis and Material Flow Networks and LCA are essential tools to verify the beneficial impact of such interactions. LCA has been used to quantify the environmental impact of different industrial wastewater treatment technologies (Do Thi et al., 2023). Hereafter, the cross-sectorial symbiotic network among the Solvay chemical plant, the municipality and the water utility is called as "circular systemic solution". Its simulation encompasses water and wastewater exchange among the three actors, identifying all input and output flows and water losses. Intra-factory water reuse for cooling and other purposes is attempted by creating this synergy.

Further treatment of the currently on-site treated wastewater stream is considered within the WAPEREUSE pilot-scale system, consisting of four advanced technologies: neutralisation, AOP and/or adsorption, MBR and GAC. Following treatment, three alternative closed-loop scenarios (ACLS) for achieving water efficiency and circularity are examined (Fig. 2) (Karkou et al., 2022):

- **ACLS 1:** The WAPEREUSE effluent is sent to the Municipal Wastewater Treatment Plant (MWTP) for further treatment and the secondary effluent is sent to WWRP Aretusa of the water utility to be processed. The tertiary effluent is mixed with freshwater supplied by the WWRP Aretusa and it is sent back to the process industry to be reused for cooling purposes, covering the total water demand.
- **ACLS 2:** The WAPEREUSE effluent is sent to WWRP Aretusa for tertiary treatment and then is mixed with freshwater supplied by the WWRP Aretusa. Finally, it is sent to the process industry for reuse purposes.
- **ACLS 3:** The WAPREUSE effluent is reused directly to the process industry for cooling and other purposes.

Hence, three actors (Solvay plant, municipality and water utility) from different sectors comprise the Consortium Aretusa that exchange water and wastewater, leading to economic and environmental benefits. It is a multi-stakeholder consortium in which the actions of each partner are strongly interrelated, having an impact on the others. However, in this consortium there are financial and technological constraints. The water utility must send a maximum of 3.8 million m^3/y to the Solvay plant. Solvay is obliged by the Consortium Aretusa to pay 1.40 €/m^3 and 10.00 €/m^3 to send the wastewater for secondary and tertiary treatment, respectively. It is assumed that the municipality pays 0.78 €/m^3 to send the secondary effluent to the WWRP Aretusa. On the other hand, Solvay is obliged to pay 0.175 €/m^3 for the freshwater supply by the WWRP Aretusa. The cost for discharge is zero, on the basis of having treated the industrial wastewater to reach the legislative regulations. In addition, there are specific water reuse requirements to be fulfilled from each actor in order to receive the effluent stream, as presented in Table 1.

Overall, the criteria are (waste)water quality and demand, water reuse requirements and water tariffs. Modelling the actors'

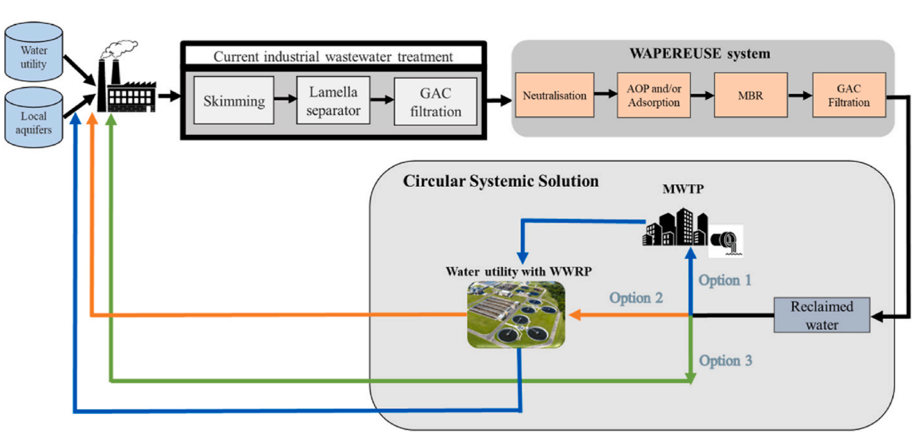

Fig. 2. Interdependencies among the process industry, municipality and water utility (blue: ACLS 1, orange: ACLS 2, green: ACLS 3).

Table 1
Constraints for the quality parameters of industrial wastewater of the Solvay chemical plant.

Quality parameter	Unit	Send to MWTP	Send to WWRP Aretusa	Send for industrial reuse
pH	–	5.5–9.5	5.5–9.5	7.0–8.0
Chemical oxygen demand (COD)	g/m^3	500.0	125.0	100.0
Nitrates	g/m^3	133.0	89.0	89.0
Sulphates	g/m^3	1000.0	1000.0	1000.0
Aluminium	g/m^3	2.0	1.0	1.0
Iron	g/m^3	4.0	2.0	2.0

interrelations will reveal the most beneficial option for sharing, indicating the flow rate and composition of exchanged water.

2.2.3. Digital innovation

Digital tools and technologies as circularity facilitators deal with implementation hurdles due to a lack of knowledge sharing related to the benefits of CE practices and symbiotic networks, accurate and efficient data analysis tools and models and unawareness of physical infrastructure sharing opportunities (Trevisan et al., 2023). The modelling approach adopted in this study was realised in the PSM tool, whose principles are based on the Material Flow Analysis and Material Flow Networks, by modelling material and energy flows across the industrial production chain. The PSM Tool has been initially developed as a prototype in the context of the European funded project EcoWater (Arampatzis et al., 2016; Angelis-Dimakis et al., 2016; Georgopoulou et al., 2016, 2017) and has been extensively upgraded within the AquaSPICE project (Karkou et al., 2023), but the tool has been also utilised for industrial-scale slaughterhouse wastewater treatment (Teo et al., 2023), oil refinery (Sarantinoudis et al., 2023) and steel industry (Tsinarakis et al., 2022). PSM is a standalone tool developed in the. NET Framework using Visual Basic and C#, which is used to model and simulate complex water systems. It consists of a Windows Desktop Application (WDA) as well as a Web Application Programming Interface (API). The WDA enables the model graphical design and construction, material and energy flows specification indicating the input–output interrelations, process-related parameters determination and results reporting. It communicates bidirectionally with the API to upload to upload the external to the PSM tool process models. This way, the Web API enables the simulation of the system, making feasible the interaction between the digital and the physical system (Sarantinoudis et al., 2023). Each technology is modelled as a process, interconnected with all resources that are modelled as flows. The user can modify the input data and the model parameters, perform simulations and then "what-if" scenario analysis to compare and assess the respective results. Therefore, the PSM tool acts as a visualisation tool for representing the physical system as a digital one. In this regard, process modelling and simulation entails the calculation of all unknown flows and results in the prediction of effluent's composition, water recovery, processes and system's efficiency, required energy, and consumed amount of chemicals. However, this tool has not been designed for feasibility studies or commercial purposes.

Real-time and software-based sensors are key digital aspects that measure several parameters, helping to monitor and control the performance of the different technologies and thus the treatment train. Simulating the processes can predict their performance and response to any operational change. Deploying artificial intelligence (AI) methods, descriptive statistics and predictive analytics, including data-driven models and hybrid models, is becoming more popular in the wastewater treatment sector (Marin-Ramirez et al., 2024), (Bahramian et al., 2023). Indicatively, predictive analysis can estimate when membrane fouling will occur, or resin beds will be exhausted. Alerts, warning signals, statistics regarding past and future performance of the processes based on historical data, trends for deviations over time, suggestions to change operational parameters and trigger mechanisms for the smooth system operation comprise noteworthy results. To this end, operational parameters (temperature, sludge retention time, aeration, etc.) are adjusted properly and mechanisms are triggered, such as bypass valves, air compressors and chemical dosing pumps, to ensure the safe operation and system's optimisation.

A near-real time dynamic LCA can calculate relevant indicators, including water footprint, carbon footprint, eutrophication, eco-toxicity and human toxicity based on sensors data and process modelling outputs. Hence, environmental impact and eco-efficiency of the production plant are assessed in real-time and can support decision-making.

2.3. Alternative treatment scenarios

Scenario 1 is the baseline scenario, which represents the on-site treatment within the Solvay plant, with the effluent stream with flow rate 0.0416 m^3/h being discharged to the sea (Fig. 3A).

Scenario 2 enhances the wastewater treatment by deploying the WAPEREUSE industrial-scale system on-site before its discharge to the sea (Fig. 3B). The acidic industrial wastewater with flow rate 0.0416 m^3/h is firstly neutralised by adjusting the pH using sodium hydroxide or calcium hydroxide. The hydrogen peroxide is then oxidized. The combination of the oxidation process with adsorption increases the COD biodegradability. The third stage, i.e. MBR, removes organic matter and nitrates, while GAC filtration, which receives wastewater with flow rate of 0.037 m^3/h, decreases COD further. The effluent stream is expected to be less contaminated before being discharged to the sea compared to Scenario 1.

Scenario 3 represents a cross-sectorial symbiotic network, aspiring to allow industrial safe water reuse (Fig. 3C). The on-site industrial wastewater treatment is followed by the treatment within WAPEREUSE (as in Scenario 2) and then the circular systemic solution is deployed, involving secondary and tertiary treatment before its intra-factory reuse. Essentially, Scenario 3 integrates Scenario 1 (on-site treatment) and Scenario 2 (treatment within WAPEREUSE), but expands the network by deploying the cross-sectorial symbiotic network comprised of the process industry, municipality and water utility. The goal of freshwater intake reduction is inextricably linked to this consortium since wastewater treatment and water exchange reduce the freshwater supply from external parties.

3. Models and methods

An overview of the methodological steps followed in this study, consisted of four phases, is depicted in Fig. 4. Section 3.1 presents the process models for the wastewater treatment technologies to be simulated and section 3.2 explains the LCA approach followed in this study to assess the environmental impact of the interventions.

3.1. Technology modelling

As for pre-treatment stages, a skimmer, lamella separator and GAC filter are included in Scenario 1. Effluent characteristics are given in Table 6 (Scenario 1). The following technologies are modelled by mechanistic models (section 3.1.1-3.1.4) since they comprise the WAPEREUSE, whose performance is predicted.

- Neutralisation
- Advanced Oxidation Process and/or Adsorption
- Membrane Bioreactor
- Granular Activated Carbon filtration

The characteristics, equations used and assumptions made to model

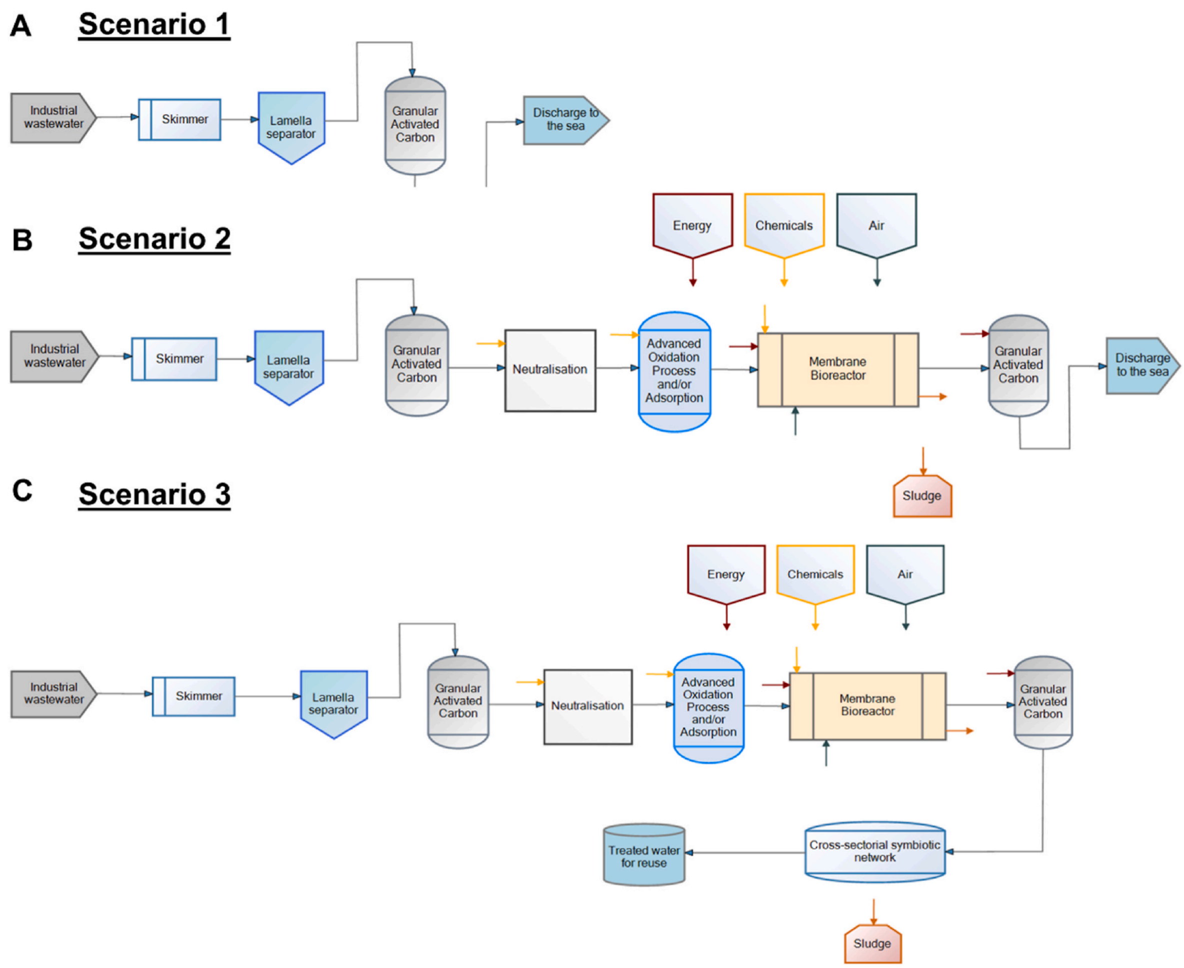

Fig. 3. Process flow diagram of alternative treatment scenarios (1, 2, 3) in the PSM tool.

and simulate the technologies are referred to in the following sections, aspiring to predict the effluent composition, water recovery, chemicals consumption and energy requirements. Secondary and tertiary treatment takes place within the MWTPs of Cecina and Rosignano Marittimo, and WWRP Aretusa, respectively (see composition in Table 3).

3.1.1. *Neutralisation*

Neutralisation results in pH control of the treated wastewater since it reaches the neutral value by adding chemicals (Metcalf and Eddy, 2014). When wastewater is highly acidic or alkaline, neutralisation is required as a pre-treatment stage, either before other technologies or discharge into the environment (Goel et al., 2005), since such streams should not be discharged into a water body without any prior treatment (Nemerow, 2007). Acidic streams are usually neutralised by sodium hydroxide or sodium carbonate due to ease of use and effectiveness (Metcalf and Eddy, 2014). The pivotal step of the process modelling is the dose determination of the neutralising agent (Goel et al., 2005).

Lab-scale experiments resulted in the consumption of 1.75 L of 30% w/w sodium hydroxide solution per 1 m^3 of treated wastewater. The neutralisation takes place in a continuous-stirred tank reactor, which is perfectly mixed ensuring homogeneity, isothermal at room temperature (15–20 °C) and constant volume V (m^3). With the aim to predict the pH at the outlet of the tank, mass balances of the anions (eq. (1)) and cations (eq. (2)) are formulated. The concentration of the ions, $[H^+]$ (mol/L), is used to calculate the pH of the solution (eq. (3)).

$$Q_w \bullet C_w - (Q_w + Q_{NaOH}) \bullet a = V\frac{da}{dt} \tag{1}$$

$$Q_{NaOH} \bullet C_{NaOH} - (Q_w + Q_{NaOH}) \bullet b = V\frac{db}{dt} \tag{2}$$

$$pH = -\log_{10} C_{H+} \tag{3}$$

Where Q is the flow rate (m^3/h), C is the concentration of a specific compound (g/m^3), V is the tank volume (m^3), t is the time (h), a is the sum of the anions concentration (mol/L), and b is the sum of the cations concentration (mol/L). The subscripts w, NaOH and H^+ stand for treated wastewater, sodium hydroxide solution and protons, respectively.

3.1.2. *Advanced oxidation process and/or adsorption*

The heterogeneous Fenton process degrades the organic contaminants through reactions that take place on the catalyst's surface (Zhang, 2020). In the case of a solid-form catalyst with specific sites, the reactions are heterogeneous, consisting of several consecutive steps. Firstly, the mass transport of reactants from the bulk solution to the solid surface, i.e., the external surface of the catalyst, takes place. If the catalyst is porous, the intraparticle transport of the reactants occurs and then adsorption at the interior sites of the catalyst particle. Then the adsorbed reactants react with the adsorbed products. Afterwards, the adsorbed products can be desorbed and products from the interior sites are transported to the outer surface of the catalyst particle (Metcalf and Eddy, 2014). The influencing process parameters include the initial concentration of the target compound, hydrogen peroxide dosage, pH, temperature, as well as surface area and ionic strength of the catalyst (Zhang, 2020). The long-term stable and reusable solid catalysts consist of catalytic active components to the surface, on which Fenton reactions

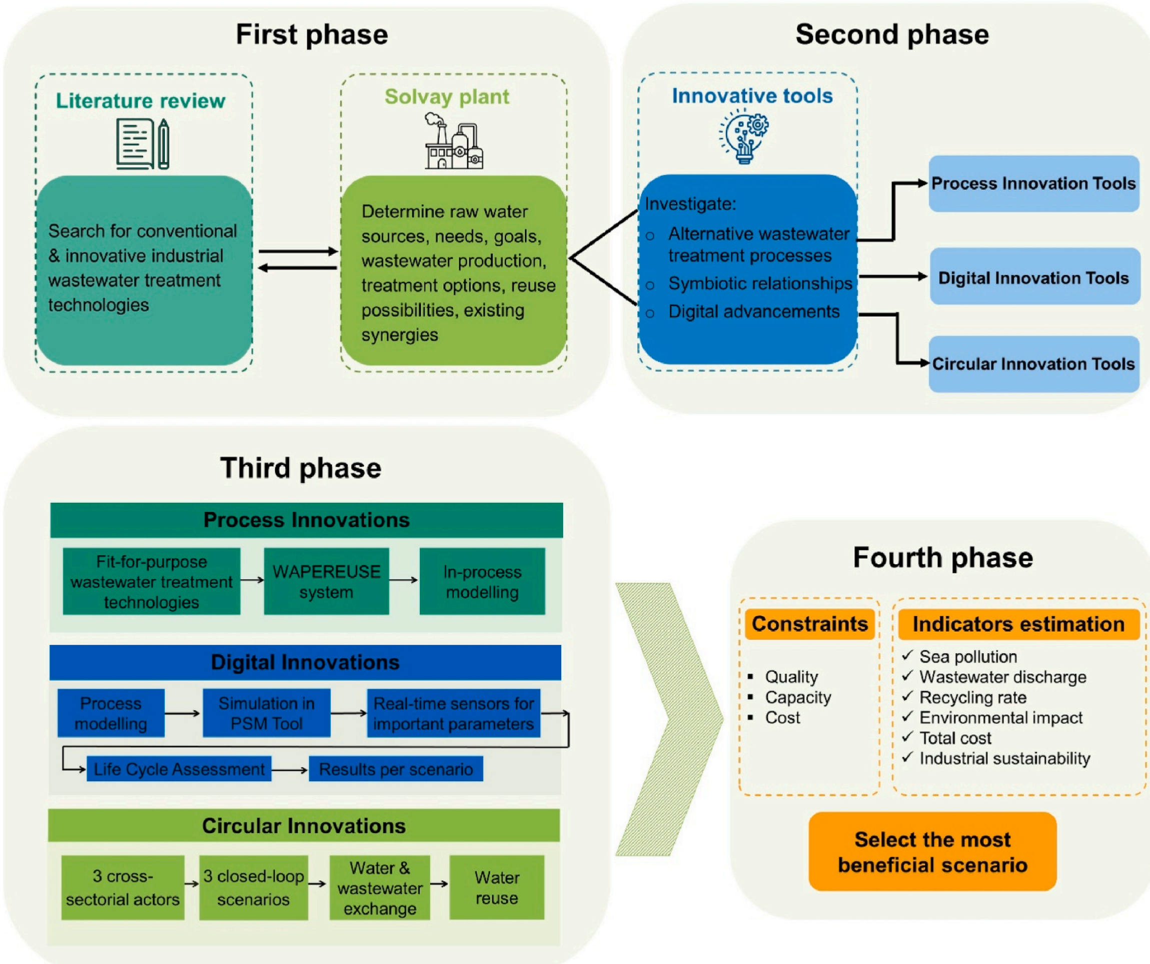

Fig. 4. Methodological steps followed in this study.

Table 2
Technical specifications for the column and GFH characteristics.

Column technical specification	Unit	Value
Flow direction	–	Upflow
Number of columns	number	2
Radius	cm	25
Empty bed contact time	min	35
Bed height of GFH	cm	60
Mass of GFH within a column	kg	25
Bulk density	kg/m^3	1150
Specific surface area	m^2/g	300
Particle size range	mm	0.2–2.0

take place, resulting in an efficient cycling of Fe^{3+} and Fe^{2+} (hui Zhang et al., 2019). This process has been extensively studied for organic matter (Genz et al., 2008), phosphate (Zhao et al., 2015), dye (Ali et al., 2013), (Farshchi et al., 2018) and phenol removal (Zárate-Guzmá et al., 2019).

In this study, granular ferric hydroxide (GFH) solid particles are used to remove the hydrogen peroxide from the wastewater and possibly increase the biodegradability of COD in a fixed bed column. Table 2 summarises the technical specifications of the column and the catalyst's characteristics.

The process efficiency lies in the activity of reactive oxygen species, i.e. $^{\bullet}OH$, $^{\bullet}HO_2$, $^{\bullet}O_2^-$, which are generated from the reactions between the catalysts and the hydrogen peroxide and oxidize the target compounds (He et al., 2016). The reactions regarding the heterogeneous Fenton catalysis are described by (4)-(10) (Zhang, 2020).

$$\equiv Fe(III) + H_2O_2 \rightarrow \equiv Fe(HO_2)^{2+} + H^+ \quad (4)$$

$$\equiv Fe(HO_2)^{2+} \rightarrow \equiv Fe(II) + {}^{\bullet}HO_2 \quad (5)$$

$$\equiv Fe(II) + H_2O_2 \rightarrow \equiv Fe(III) + OH^- + {}^{\bullet}OH \quad (6)$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + {}^{\bullet}HO_2 \quad (7)$$

$$\equiv Fe(II) + {}^{\bullet}O_2^- \rightarrow \equiv Fe(III) + O_2 \quad (8)$$

$$\equiv Fe(III) + {}^{\bullet}HO_2 \rightarrow \equiv Fe(II) + HO_2^- \quad (9)$$

$$\equiv Fe(II) + HO_2^- \rightarrow \equiv Fe(III) + {}^{\bullet}HO_2 \quad (10)$$

Empty bed contact time (EBCT) is defined as the ratio of bed volume over the influent flow rate (Zhang et al., 2016). The adsorbed amount of each pollutant, q_e (mg/g), is calculated as:

$$q_e = \frac{(C_o - C) \bullet V}{m} \quad (11)$$

Where C_o and C (mg/L) are the pollutant concentration at the inlet and outlet, respectively, V (L) is the solution volume and m (g) is the mass of the GFH (Zhao et al., 2015). Therefore, eq. (12) is used to calculate the removal efficiency for each pollutant, R_i (%) (Kavitha and Palanivelu, 2016).

$$R_i = \left(1 - \frac{C}{C_o}\right) \bullet 100\% \quad (12)$$

Table 3
Influent and effluent composition in MWTPs Cecina, Rosignano Marittimo and WWRP Aretusa.

Resource	Unit	Influent of MWTP Cecina	Effluent of MWTP Cecina	Influent of MWTP Rosignano	Effluent of MWTP Rosignano	Influent of WWRP Aretusa	Effluent of WWRP Aretusa
pH	–	7.43	7.53	7.67	7.53	7.50	7.58
COD	g/m^3	218.33	35.03	206.33	63.40	35.00	23.00
TSS	g/m^3	268.40	10.00	217.33	17.67	14.00	10.00
Nitrates	g/m^3	–	14.03	–	6.53	12.00	13.05
Phosphorus	g/m^3	7.30	2.43	6.57	2.33	3.00	2.70
Conductivity	μS/cm	–	1,893,670	–	2,848,330	2406	2320
Chlorides	g/m^3	–	354.33	–	598.67	487.00	493.00
Sulphates	g/m^3	–	–	–	–	144.00	160.00
Aluminium	g/m^3	–	–	–	–	–	0.10
Iron	g/m^3	–	–	–	–	–	0.10
Hydrogen peroxide	g/m^3	–	–	–	–	–	0.00
Water	m^3/h	–	144.16	–	375.34	410.00	410.00

3.1.3. Membrane bioreactor

The goal of this process is to remove the COD and nitrates. The side-stream MBR consists of two compartments, an anoxic and an aerobic tank, a sedimentation tank and 4 UF membranes in series. Within the biological component, the contaminants are degraded by utilising the microorganisms and within the UF membranes the solids are separated from the wastewater and recirculated in the reactor (Lindamulla et al., 2021). MBRs have been widely studied for industrial wastewater treatment, focusing on COD, phosphorus, ammonium and nitrates removal (Deowan et al., 2019; Petta et al., 2017; Bazrafshan et al., 2021; Ahmadi et al., 2019; Nadeem et al., 2022). MBR's process model encompasses both biological and physical treatment, described by an activated sludge model and a membrane filtration model (Mannina et al., 2021a). Many researchers have engaged with MBR modelling (Deowan et al., 2019), (Mannina et al., 2021b; Nelson et al., 2019; Phan et al., 2014; Roy et al., 2020; Lahdhiri et al., 2020). The MBR process model used in this study, characteristics and assumptions made are referred to in a previous study (Teo et al., 2023). Based on the lab-scale experimental phase, the addition of glycerol as an external carbon source and air supply of 1–2 m^3/h/diffuser are required. Among the process parameters, mixed liquid volatile suspended solids (MLVSS) are 2700 mg VSS/L, temperature was in the range of 15–25 °C and the food-to-microorganisms ratio equals 0.50 g O_2/g VSS. Hence, the respective model modifications were made.

3.1.4. Granular activated carbon filtration

GAC has been widely implemented for wastewater treatment in process industries owing to its large surface area that allows the adsorption of dissolved organic substances (Benstoem et al., 2017), its capability to operate continuously without requiring a carbon-liquid separation (Jjagwe et al., 2021) and small particle sizes (Adeleke et al., 2019). GAC has been used for the removal of various pollutants from wastewater, including COD (Zahmatkesh et al., 2023), (Almadani, 2023), natural organic matter (NOM) (Zhang et al., 2022), arsenic (Kalaruban et al., 2019), color and odor (Ziemba et al., 2020), dissolved organic carbon (DOC) and turbidity (Liang et al., 2022), (Kennedy et al., 2015), TOC (Hatt et al., 2013), nitrates (Demiral and Gündüzog, 2010) and phosphates (Zach-Maor et al., 2011). The influencing parameters are the pH of the solution, the concentration of the target pollutant in the inlet, EBCT, dosage and surface groups of activated carbon and temperature as well (Benstoem et al., 2017), (Jjagwe et al., 2021).

Solutes are transported through the liquid film (film diffusion), into the adsorbent's surface (surface diffusion) and the pores (pore diffusion) (Yuan et al., 2022). The adsorption rate is calculated by kinetic models with pseudo-first order (PFO) or pseudo-second order (PSO) as the most effective ones. On the one hand, the PFO model considers the available binding sites for adsorption for equilibrium until contact time reaches 30 min and the adsorbed amount of pollutant at any time t (min), q_t (mg/g), i.e., adsorption capacity, is calculated as:

$$q_t = q_e \bullet \left(1 - e^{-k_1 \bullet t}\right) \tag{13}$$

Where q_e (mg/g) is the adsorbed amount of pollutant on GAC at equilibrium, or equilibrium adsorption uptake, and k_1 (min^{-1}) is the PFO rate constant.

On the contrary, the PSO model assumes that not only internal but also external mass transfer mechanisms contribute to pollutants' adsorption. The corresponding equation that represents the adsorbed amount of pollutant on GAC at any specific time t is:

$$q_t = \frac{q_e^2 \bullet k_2 \bullet t}{1 + q_e \bullet k_2 \bullet t} \tag{14}$$

Where k_2 (g/mg/min) is the pseudo-second order rate constant (Jjagwe et al., 2021). Both adsorption-related parameters, q_t and q_e, can be calculated by using the following equations, respectively:

$$q_t = \frac{C_o - C_t}{m} \bullet V \tag{15}$$

$$q_e = \frac{C_o - C}{m} \bullet V \tag{16}$$

Where C_o (g/m^3) is the concentration in the influent, C (g/m^3) is the concentration in the effluent, C_t (g/m^3) is the concentration at any time t, m (g) is the mass of adsorbent, and V (m^3) is the volume of the treated wastewater. The removal percentage of a specific contaminant, R (%), is calculated as (Mozaffari Majd et al., 2022):

$$R = \frac{C_o - C}{C_o} \bullet 100\% \tag{17}$$

When the equilibrium state is reached, adsorption isotherms can indicate the concentration profile of the pollutants in both phases, liquid and solid, throughout the GAC column. For water treatment systems, Langmuir and Freundlich isotherms are the most common ones. On the one hand, monolayer sorption onto homogeneous surface is considered by Langmuir isotherm (eq. (18)). On the other hand, multilayer sorption onto heterogeneous surface is assumed for Freundlich isotherm (eq. (19)).

$$\frac{C_e}{q_e} = \frac{1}{Q_m \bullet K_L} + \frac{C_e}{Q_m} \tag{18}$$

$$q_e = K_F \bullet C_e^{1/n} \tag{19}$$

Where Q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir adsorption constant representing the apparent adsorption energy, and K_F and n are the Freundlich adsorption constants (Jjagwe et al., 2021). The goal is to remove the organic matter, phenolic compounds, ammonium and heavy metals. Table 9 (Appendix) reports the coefficients of iron, ammonium and COD for the aforementioned adsorption models, as reported in previous studies.

3.1.5. Secondary treatment

The MWTPs of Cecina and Rosignano Marittimo treat the municipal wastewater streams by deploying secondary treatment processes. Influent and effluent composition is shown in Table 3 (data from 2020) (Santiloni, 2020). The secondary effluent enters the WWRP Aretusa (data from 11/2019-09/2020) for tertiary treatment (Kleyböcker et al., 2021).

Based on previous studies, a typical MWTP consumes 0.6 kWh/m^3 (Simon-Vá et al., 2020). The average consumption from 17 activated sludge MWTPs is found to be 0.903 kWh/m^3 (Siatou et al., 2020), Santos et al. (2022) reported the range of 0.38–1.26 kWh/m^3 (Santos et al., 2022), Plappally and Lienhard (2012) reported 0.10–1.89 kWh/m^3 (Plappally and Lienhard V, 2012), while Gude (2015) mentioned 0.33–0.60 kWh/m^3 for wastewater treatment by activated sludge. In this study, it is assumed a conventional MWTP with activated sludge that consumed 0.60 kWh/m^3 of treated wastewater.

3.1.6. Tertiary treatment

The WWRP Aretusa consists of seven consecutive treatment technologies: equalisation, coagulation/flocculation, lamellar sedimentation, sand filtration, biological filtration, GAC filtration and UV disinfection. Influent and effluent characteristics have been published (Kleyböcker et al., 2021) (shown in Table 3). The excess wastewater stream from MWTPs is discharged to the river. To this end, the flow rate of influent and effluent stream is the same.

The total energy consumption of the WWRP Aretusa is estimated equal to 0.50 kWh/m^3. As far as chemicals consumption, coagulation/flocculation require 140 tons/y aluminium polychloride (30 g/m^3) as coagulant and 12 tons/y polyelectrolyte (3 g/m^3) as flocculant (Kleyböcker et al., 2021).

3.2. Life Cycle Assessment approach

A Life Cycle Assessment has been performed to assess the environmental impact of these three scenarios, following the four steps described in the ISO14040/44:2006:

- Goal and Scope Definition, i.e. determining the objective of the analysis, the system boundaries, and the functional unit;
- Life Cycle Inventory (LCI), i.e. listing all the inflows and outflow from and to the environment.
- Life Cycle Impact Assessment (LCIA), i.e. selecting the impact assessment method, and estimating the corresponding indicators;
- Interpretation of results.

The Life Cycle assessment was performed using SimaPro 9.2 Academic License and the most recent version (3.9) of the ecoinvent database.

3.2.1. Goal and Scope Definition

The goal of the LCA analysis is to assess the environmental impact of the three ACLS for the treatment of the aqueous effluent of the Solvay plant. The functional unit needs to be selected in such a way to allow an objective comparison across the three different scenarios and should express the same final function. As stated by Corominas et al., the most used functional units in the case of wastewater treatment assessment are (i) the volume of the wastewater treated, (ii) the removal ratio of a specific pollutant or (iii) in very rare cases, the lifetime of the treatment plant (Corominas et al., 2013). Volume-based units are the most common options used by 60% of the studies reviewed and thus 1 m^3 of wastewater was also selected as the functional unit for this study.

3.2.2. Life Cycle Inventory

The foreground LCI for Scenario 1 was based on data obtained through lab-scale experiments of the industrial wastewater stream (wastewater composition, first column of Table 6). However, the comparison of its composition to other wastewater streams derived from other chemical process industries will point out their correlation. For this reason, the typical characteristics of other streams, as reported in previous studies, are summarised in Table 4.

The foreground LCI for Scenarios 2 and 3 is based primarily on modelling data and is presented on Table 6. Within the scope of this study, the inventory data include power consumption, chemicals consumption, solid waste disposal and emission of effluents, as illustrated in the next section. The characterisation factors selected were based on values for Italy, and where these were not available, for Europe or the rest of the world.

3.2.3. Life Cycle Impact Assessment

The Environmental Footprint (EF) was selected as the impact assessment method since it is adopted by the European Commission in the Environmental Footprint transition phase of the commission and is the impact assessment method that is currently being preferred by LCA practitioners for industrial system assessment. This method involves the calculation of 17 midpoint impact indicators, as presented in Table 5, which are similar and analogous to all other available methods in SimaPro software, but also has the advantage that combines all the midpoint indicators into one single-score endpoint indicator, the Environmental Footprint, expressed in ecopoints (Pt). One milli ecopoint (mPt) represents the annual environmental impact of an average European inhabitant. The potential drawback of a single score indicator is the introduction of subjectivity in its calculation, in the conversion of the physical units to ecopoints. However, since it is widely adopted method, it can be used confidently to assess the environmental performance of the novel technologies and compare them with other studies.

It has to be also noted that, contrary to other methods (e.g. CML), the Environmental Footprint includes Water Use/Water Depletion as one of the 17 indicators, and thus there is no need for a separate calculation. However, the EF methodology (and none of the other available ones) does not currently account for an environmental impact related to the change in pH. Thus, a correction factor was created, using the moles of H^+_{eq} as a proxy value for the pH.

4. Results

The predicted values, as resulted from the process modelling and simulation of the three alternative treatment scenarios using the PSM tool, are exploited to populate the LCI and the LCIA results.

4.1. Process modelling

Table 6 illustrates the results from the process modelling and simulation for the three alternative scenarios, divided into six categories: chemical, electricity, wastewater supply, wastewater discharge, wastewater composition and sludge production. Process modelling and simulation of the circular systemic solution has been incorporated only in Scenario 3.

The current situation is represented by Scenario 1 and the presented values correspond to the composition of the industrial effluent stream that is discharged to the sea (Fig. 3A). Scenario 2 introduces the technologies of the WAPEREUSE pilot-scale system, resulting in the production of water of lower contamination levels (Fig. 3B) before being discharged to sea. Sodium hydroxide was used for neutralisation, leading to the reduction of the concentration of nitrates by 45.0% and sulphates by 60.6%. Hydrogen peroxide was used for AOP to enhance the process efficiency. As far as MBR process, glycerol was added as external

Table 4
Typical characteristics of wastewater from chemical industries reported in literature.

Resource	Unit	Aktaş et al. (2017)	Dinç et al. (2021)	Wei et al. (2013)	Nasr et al. (2007)	Cao et al. (2016)	Masid et al. (2010)
pH	–	9.7	2.2	6.56	6.1–9.5	7.6–9.2	8.1
COD	g/m^3	1571	10,055	1091	1870–3924	240–728	19,600
TOC	g/m^3	–	2597	410	–	–	–
Total Nitrogen	g/m^3	232	–	160	–	10–247	–
Nitrates	g/m^3	–	–	–	–	0.3–93	–
Sulphates	g/m^3	2008	9325	–	–	–	602
Chlorides	g/m^3	1500	–	–	–	3729–6593	14,653
Phosphorus	g/m^3	1.41	–	–	0.8–30	–	–
Hydrogen peroxide	%	–	0.1374	–	–	–	–
Conductivity	μS/cm	9243 ± 1053	18,500 ± 0.270	–	–	–	–

Table 5
Set of Midpoint Impact Categories analysed in this study in alphabetical order and their abbreviations.

Impact category		Unit
Acidification	AP	mol H^+ eq
Climate change	GWP	kg CO_2 eq
Ecotoxicity, freshwater	ETP	CTUe
Eutrophication, freshwater	FEP	kg P eq
Eutrophication, marine	MEP	kg N eq
Eutrophication, terrestrial	TEP	mol N eq
Human toxicity, cancer	HTPC	CTUh
Human toxicity, non-cancer	HTPNC	CTUh
Ionising radiation	IRP	kBq U-235 eq
Land use	LU	Pt
Ozone depletion	ODP	kg CFC11 eq
Particulate matter	PM	disease inc.
Photochemical ozone formation	PCOP	kg NMVOC eq
Resource use, fossils	ADPF	MJ
Resource use, minerals and metals	ADPM	kg Sb eq
Water use	WDP	m^3 depriv.

carbon source while sodium hypochlorite and citric acid were assumed to be used for cleaning. MBR process led to COD removal by 97.28%, which is in agreement with (Di Trapani et al., 2019) (98.97%) (Ahmadi et al., 2019), (up to 97%) and (Belibagli et al., 2023) 99.8% when combined with precipitation using calcium hydroxide as a pre-treatment method, and nitrates removal by 38.68%, which has a good agreement with (Basu et al., 2014) (32 ± 18% for 0–30 days). The addition of GAC increased the removal efficiency to 87.86%. The enhancement of nitrates removal was confirmed by experiments on a NdAMO-MBR (nitrate-dependent anaerobic methane oxidation - membrane bioreactor) system (up to 100%) (Lu et al., 2020). Overall, the WAPEREUSE technologies achieved a decrease in COD by 98.3%, TOC by 91.4%, sulphates by 60.6%, nitrates by 94.5%, aluminium by 50.0% and iron by 96.6%, while bacteria were almost removed. During the heterogeneous Fenton process, the hydrogen peroxide was completely removed. These results demonstrate the effectiveness of the four technologies at reducing the pollutants concentration.

Scenario 3, shown in Fig. 3C, introduces the cross-sectorial symbiotic network, into which secondary and tertiary treatment are involved through water sharing with the municipality and water utility, respectively. Aluminium polychloride and polyelectrolyte were used as chemicals for tertiary treatment. The wastewater composition at the inlet and outlet of MWTPs and WWRP Aretusa is shown in Table 3, based on which the removal efficiencies of pollutants of the treatment systems were calculated and incorporated in the process modelling of Scenario 3. This scenario led to conductivity decrease (59.5%) and further removal of sulphates and nitrates by 19.9% and 70.4%, respectively. In addition, aluminium was reduced by 60%. Conductivity, pH and COD levels increased slightly because of the freshwater composition supplied by the WWRP Aretusa. However, this scenario allows the intra-factory reuse of the treated wastewater, reducing the freshwater consumption by the Solvay plant. The detailed results of this cross-sectorial symbiotic

Table 6
Predicted chemicals and electricity consumption, sludge production, wastewater supply, discharge and composition for each scenario.

Resource	Category	Scenario 1	Scenario 2	Scenario 3
Sodium hydroxide	Chemical	–	21.25 g/h	21.25 g/h
Hydrogen peroxide		–	0.0225 g/h	0.0225 g/h
Sodium hypochlorite		–	41.60 g/h	41.60 g/h
Citric acid		–	0.029 g/h	0.029 g/h
Glycerol		–	22.24 g/h	22.24 g/h
Aluminium polychloride		–	–	15.98 g/h
Polyelectrolyte		–	–	1.37 g/h
Electricity (for MBR)	Electricity	–	2.97 kWh/m^3	2.97 kWh/m^3
Electricity (for GAC)		0.33 kWh/m^3	0.66 kWh/m^3	0.66 kWh/m^3
Electricity (for secondary treatment)		–	–	0.60 kWh/m^3
Electricity (for tertiary treatment)		–	–	0.50 kWh/m^3
Wastewater to WAPEREUSE	Wastewater supply	–	0.0416 m^3/h	10.00 m^3/h
Wastewater from WAPEREUSE to MWTP		–	–	10.00 m^3/h
Wastewater from MWTP to WWRP Aretusa		–	–	10.00 m^3/h
Freshwater from WWRP Aretusa		–	–	430.00 m^3/h
Water from WWRP Aretusa to Solvay		–	–	440.00 m^3/h
Wastewater discharge to the sea	Wastewater discharge	0.041 m^3/h	0.0376 m^3/h	0.00 m^3/h
pH	Wastewater composition	2.00	7.00	7.57 g/m^3
Conductivity		6000 μS/cm	5919.13 μS/cm	2401.80 g/m^3
COD		1000 g/m^3	16.34 g/m^3	22.85 g/m^3
TOC		350 g/m^3	29.93 g/m^3	–
Hydrogen peroxide		300 g/m^3	0.00 g/m^3	0.00 g/m^3
Sulphates		511 g/m^3	200.98 g/m^3	160.93 g/m^3
Nitrates		850 g/m^3	46.68 g/m^3	13.81 g/m^3
Aluminium		0.50 g/m^3	0.25 g/m^3	0.10 g/m^3
Iron		0.60 g/m^3	0.02 g/m^3	0.10 g/m^3
Escherichia coli		100,000 UFC/100 mL	147.45 UFC/100 mL	–
Sludge	Sludge production	–	0.0039 m^3/h	0.0039 m^3/h

*Indicates experimental data, provided by the Solvay chemical plant.

network integrated into Scenario 3, which comprised of three alternative options, as described in section 2.2.2, are reported in the next section.

4.2. Circular systemic solution

The circular systemic solution (CSS) describes the cross-sectorial symbiotic network within the three actors' consortium (Solvay chemical plant, municipality with the MWTP and the water utility with the WWRP Aretusa). The deployment of this CSS seems promising when Solvay plant decides to cover the freshwater demand for cooling and other purposes by using alternative water sources through the symbiotic network. The simulation of the CSS is part of Scenario 3 and determined that the most beneficial and acceptable solution is ACLS 1. The decision is made at the outlet of the WAPEREUSE, considering two criteria: the WAPEREUSE effluent's composition and the water reuse requirements as constraints for sharing among the three actors. If the quality complied with the water quality reuse requirements of the process industry, the water would be sent directly to Solvay for cooling and other purposes. However, this is not the case, as indicated by the process modelling results and ACLS 3 is rejected.

Then, ACLS 2 is prioritised to be investigated. Considering that the quality characteristics of the WAPEREUSE effluent comply with the permissible limits for industrial reuse, as defined in Table 1, ACLS 2 is feasible and hence the effluent is sent to the water utility for tertiary treatment. Therefore, freshwater supplied by the water utility and the reclaimed water are mixed and sent to the Solvay plant for industrial reuse, covering the water demand. The expenses are calculated based on the water tariffs among the actors, as reported in section 2.2.2. To this end, 10 m^3/h of the industrial effluent from Solvay is suitable to be sent to the water utility with the WWRP Aretusa for tertiary treatment with the total cost of 100 €/h. Since water demand for cooling and other purposes has been determined as 15 m^3/h and 425 m^3/h, respectively, 430 m^3/h of freshwater (from WWRP Aretusa) is also supplied to the Solvay plant at the cost of 75.25 €/m^3, after having been mixed with the tertiary effluent, reaching total charge of 175.25 €/h. Mass balances are formulated to calculate the final composition and supply after the mixing process. The symbiotic relationship is beneficial for the process industry since less freshwater is supplied by external partners and hence cost savings increase. Resource sharing leads to less wastewater discharge into the environment through reuse and recycling practices, denoting a lower environmental impact. In addition, the water utility benefits from the symbiotic network that acts as a profitability tool since the water sharing between them is accompanied by a water tariff.

4.3. Life Cycle Impact Assessment

The LCIA results show that whilst the four-wastewater treatment operations were effective at reducing the impacts of some of the indicators, they also contributed impacts across other indicators. Based on the overall environmental footprint, Scenario 3 can be selected as the best option, although the impact for specific categories has increased (due to chemicals and energy consumption).

The normalised and weighted impact assessment and the breakdown of the environment impact per flow for the three scenarios is presented in Table 7 and Fig. 5. For scenario 1, the impacts are mostly due to the wastewater discharge without any advanced treatment (together with electricity consumption for GAC) and thus only six indicators have a non-zero value. The acidification of the wastewater stream, due to the low pH, is the most significant issue and accounts for 49% of the total impact. Marine eutrophication, due to the total nitrates, accounting for over 31% of the total impact, freshwater eutrophication (due to COD) and freshwater ecotoxicity (due to Al, Fe and COD), making up a further 13% and 7%, respectively, are the other major issues identified. The small values for climate change and resource depletion are due to the electricity used for the GAC.

Table 7
Normalised environmental impact assessment of the three scenarios (expressed in milliecopoints – mPt per m^3 of wastewater treated).

Impact category	Scenario 1 – Conventional treatment and Discharge	Scenario 2 – Conventional and Advanced treatment and Discharge	Scenario 3 – Conventional and Advanced treatment and Reuse
Total	**0.93**	**1.12**	**0.72**
Climate change	0.01	0.14	0.15
Ozone depletion	0.00	0.00	0.00
Ionising radiation	0.00	0.01	0.01
Photochemical ozone formation	0.00	0.02	0.02
Particulate matter	0.00	0.04	0.04
Human toxicity, non-cancer	0.00	0.01	0.01
Human toxicity, cancer	0.00	0.01	0.01
Acidification	0.45	0.05	0.05
Eutrophication, freshwater	0.12	0.05	0.04
Eutrophication, marine	0.29	0.15	0.03
Eutrophication, terrestrial	0.00	0.02	0.02
Ecotoxicity, freshwater	0.05	0.16	0.14
Land use	0.00	0.18	0.18
Water use	0.00	0.04	−0.23
Resource use, fossils	0.01	0.10	0.10
Resource use, minerals and metals	0.00	0.14	0.14

For Scenario 2, the total impact is due to both the wastewater discharge and the resources consumed for the treatment process before being discharged to sea. Three of the four major environmental hotspots (i.e. acidification, marine and freshwater eutrophication) have been improved via the treatment process, (with acidification being reduced by almost 90% and marine eutrophication almost halved). This is due to the increase in the pH of the discharged water and the significant reduction of the nitrates and the COD of the effluent. However, overall, the contaminant reduction thanks to treatment is not high enough to overweigh the added environmental impact (due to the use of five different chemicals and almost ten times more electricity) and has resulted in Scenario 2 being more environmentally impactful than Scenario 1. Some new environmental hotspots can now be identified since the system now contributes towards climate change, resource use and land use, while freshwater ecotoxicity has also increased.

Scenario 3 represents an industrial wastewater treatment system, leading to industrial safe water reuse as shown in Fig. 3C. In this scenario, the wastewater derived from the chemical plant is treated on-site and the effluent is sent for secondary and tertiary treatment, before its intra-factory reuse. Although the difference between Scenario 2 and 3 in most of the indicators is minimal, the main positive factor is the reduction of the freshwater use (which is expressed by a negative value to the corresponding water use indicator and is clearly illustrated in Fig. 5). However, apart from the reduction in the freshwater abstracted, this also means that a slightly lower amount of chemicals will be used, leading to an overall reduction of the environmental footprint by 21% and 36% compared to Scenarios 1 and 2, respectively.

4.4. Scenario comparison

Scenario 1 represents the current situation in the chemical plant and is used as a baseline. Scenario 2 introduces the WAPEREUSE technologies compared to scenario 1. These four wastewater treatment

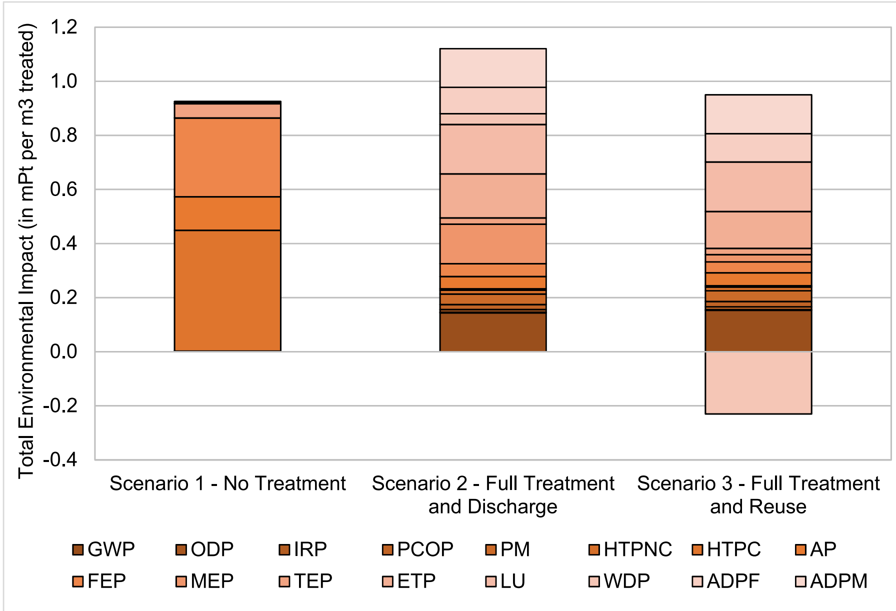

Fig. 5. Environmental impact assessment of the three scenarios (expressed in milliecopoints – mPt per m^3 of wastewater treated).

technologies (neutralisation, AOP/adsorption, MBR and GAC) resulted in higher removal efficiency of all pollutants, except for conductivity, while the acidic nature of the final stream was also dealt with. Water recovery was 91.7%, while sludge production reached 9.5% of the total treated wastewater. Overall, the pollutants concentration in the stream discharged into the sea were much lower than the respective values for scenario 1.

On the other hand, scenario 3 provides the opportunity to recover water with even lower pollutants concentration that can be reused within the Solvay plant to partially substitute the freshwater resources. This is attributed to the high removal efficiency of the involved treatment technologies for all pollutants, including conductivity. However, this scenario entails the sharing of resources within the Consortium Aretusa, which means that is more costly than the other two scenarios, but it is the only one that makes feasible the water reuse instead of discharging the final stream into the sea. Hence, there is no water discharge into the sea, preventing environmental pollution and making the process industry more sustainable through the established cross-sectorial symbiotic network.

Energy consumption has been estimated for all scenarios. In scenario 1, energy is required only for GAC, while in scenario 2 both GAC and MBR consume energy to operate. Finally, in scenario 3 energy is required for GAC, MBR, secondary and tertiary treatment technologies. Regarding the total cost for each scenario, both energy consumption and water tariffs among the three actors of the Consortium Aretusa have been taken into account. Based on Eurostat, the electricity price in Italy reached 0.2354 €/kWh for 2022 (Eurostat). This value was used to calculate the total cost for energy requirements.

Wastewater quality characterisation is derived from the process modelling results, as shown in Table 6. In Scenarios 1 and 2, the final wastewater stream is being discharged to the sea, after its treatment. To this end, sea pollution due to the pollutants' concentration of the wastewater, i.e., wastewater quality, is high and medium, respectively. On the contrary, there is no discharge to the sea in scenario 3.

In terms of environmental impact, as explained in Section 4.3 and illustrated in Table 8, Scenario 3 has the lowest environmental, since it combines contaminant reduction and water reuse (leading to a decrease of freshwater use), without the use of energy and chemicals outweighing the positive contributions to the total environmental footprint.

From the chemical plant's perspective, the total cost for each scenario refers to the cost for water sharing, wastewater discharge to the sea and electricity cost for the energy requirements (operational cost). In addition, the cost for freshwater supply from external partner is estimated for each scenario. The equations used are the following:

Table 8
Scenario comparison in terms of wastewater quality, environmental impact and cost related to the Solvay chemical plant.

Parameter	Unit	Scenario 1	Scenario 2	Scenario 3
Sea pollution	–	High	Medium	Zero
Wastewater discharge	m^3/h	0.041	0.0376	0.00
Recycling rate	%	0.00	0.00	100.00
Environmental impact	mPt	0.93	1.12	0.72
Operational cost	€/h	0.003	0.035	8.54
Freshwater supply cost	€/h	77.00	77.00	75.25
Total cost	€/h	77.003	77.035	83.79
Industrial sustainability	–	No	No	Yes

Operational cost = ∑(Energy consumption • Energy tariff • Treated water)

Freshwater supply cost = Water tariff • Treated water

Total cost = Operational cost + Freshwater supply cost

Where energy consumption (kWh/m^3) is the energy consumed by the technologies implemented, energy tariff (€/kWh) is the normalised energy cost in Italy, water tariff (€/m^3) is the normalised cost for water as determined within the Consortium Aretusa and treated water (m^3/h) is the flow rate of the water in the inlet of the system.

In scenario 1, the total cost is estimated to be 0.003 €/h for GAC process and wastewater discharge to the sea and 77.00 €/h for supplying freshwater from Aretusa (440 m^3/h for 0.175 €/m^3). In scenario 2, 0.035 €/h is required for the processes of GAC and MBR and for discharging wastewater to the sea and 77.00 €/h for supplying freshwater from Aretusa (440 m^3/h for 0.175 €/m^3). In scenario 3, the total cost refers to the processes of two GAC units, MBR, wastewater sharing between the Solvay plant and the water utility. Specifically, the operational cost reaches 8.54 €/h for two GAC units and MBR, while the cost for freshwater supply from the water utility is 75.25 €/h since only 430 m^3/h are required from Aretusa to cover the water demand within the industry.

The operational cost in scenario 3 is higher compared to the other scenarios, but the cost for freshwater supply is slightly lower. However, there is no environmental pollution and wastewater discharge to the sea since the total industrial wastewater from the peroxide and peracetic acid plant is reused within the industry. To assess the most beneficial scenario, it is important to consider all aspects (sea pollution, environmental impact, total cost and industrial sustainability). Hence, scenario 3 is the only that paves the way towards circularity and industrial sustainability.

5. Discussion and conclusions

Freshwater reserves are continuously decreasing due to over-abstraction and -exploitation. The adoption of the Zero Liquid Discharge (ZLD) concept is now urgent more than ever in the process industries. The circular economy is considered a valuable solution for a more sustainable industrial sector. Exchange of resources, extension of the products life cycle by maintaining them in the production and supply chain as long as possible, reduction of waste and optimisation of processes entail core measures for a circular economy. However, the deployed solutions should enhance circularity but be also economically feasible for a chemical process industry. Palea et al. proved the beneficial impact of CE practices at a business level from an environmental and economic point of view, encouraging the decision-makers to invest and implement such solutions (Palea et al., 2023). Crutchik et al. reported the environmental and financial benefits of the proper co-treatment of municipal wastewater and waste derived from the food industry (Crutchik et al., 2023). This study is a result of three innovation tools: (i) process, (ii), circular and (iii) digital ones that takes into account environmental and economic criteria to assess the alternative treatment scenarios of the industrial wastewater.

Resource-efficient and waste reuse practices for closing the loop gain attention (Keijer et al., 2019). Conventional and advanced wastewater treatment technologies were deployed in the Solvay chemical plant, modelled and simulated using the PSM Tool. Process modelling and simulation are the core tools of the process and digital innovations. First principle models resulted in the prediction of the effluent composition and supply, removal efficiencies of the pollutants, chemicals and energy consumption. This way, the recovery of resources by the wastewater treatment technologies is predicted, facilitating the water management system. The coupling of model-based tools and monitoring services can be used to assess process efficiency, circularity and environmental performance (Wiprä et al., 2024). Online and offline sensor data have been considered across the production chain, measuring the quality parameters and operating conditions of the WAPEREUSE technologies. All processes and material flows are monitored and analysed across the production chain. Serious environmental concerns arise, with climate change and eutrophication being the most important impact categories (Keijer et al., 2019). This is reflected in the LCA results of scenarios 1 and 2, which indicate that eutrophication and climate change are the most impactful categories, respectively. The digital innovation is reinforced by the dynamic LCA that assesses the environmental impact of the investigated treatment scenarios and identifies production processes that should be improved (Keijer et al., 2019), (Ranade and Bhandari, 2014). Overall, the digital and cyber-physical transformation of the industrial sector is known as Industry 4.0, describing the integration of digital tools and services into the value chain aspiring to enhance monitoring, data collection and exchange, traceability, interconnectivity, dynamic assessment and optimisation and interoperability. Ranieri et al. recommended the integration of AI tools to control and improve the WWTP's performance, resulting in lower greenhouse gases emissions (Ranieri et al., 2023). The three-layered approach adopted in this study related to process-circular-digital innovations is favored by the sufficiency of available data, allowing to be utilised as a decision-support tool for industrial strategic planning.

The creation of symbiotic networks and industrial synergies is a powerful tool to reinforce circularity and bring business opportunities in large-scale process industries, building trustful and transparent cooperative relationships among different actors. Optimised resource management and exchange can result in economic benefits and lower environmental pollution since the generated waste is re-incorporated into the process industry and not discharged into the sea. Cross-sectorial networks, such as Consortium Aretusa, are potent enablers for the ZLD concept. In this study, the cross-sectorial symbiotic network (scenario 3) gives the opportunity to Solvay chemical plant to minimize waste generation, increase water reuse within the industry and reduce significantly the environmental impact at a cost of around 12.2 €/h.

Currently, the regulatory and policy landscape focuses mainly on wastewater treatment, discharge limits, reclaimed water quality requirements and monitoring needs for specific contaminants. In the future, however, by-products and water exchange standards and procedures will have to be defined in order to be followed by cross-sectorial stakeholders. To this end, a collaborative policy framework will be formulated to promote resource efficiency and waste reduction, encompassing sector-specific performance indicators and establishing official materials-exchange online platforms providing financial, and not only, incentives to the stakeholders.

This study presented a case study where three alternative scenarios were assessed, implementing process, digital and circular innovation tools. Further research is recommended to investigate even more profitable circular economy-driven solutions for closing the water loop in the process industries. Also, further studies should be oriented to energy cogeneration processes to reduce electricity consumption and emissions within the WWTP (Ramí et al., 2024), innovative wastewater treatment technologies, such as membrane photobioreactor process (Shafiquzzaman et al., 2023) and granular sludge disintegration (Lv et al., 2024), as well as combined treatment methods coupled with digital tools, such as microalgae-bacteria utilisation in cooperation with AI and machine learning techniques (Sahu et al., 2023). The integration of real-time monitoring services, i.e., sensors and AI tools, across the industrial production chain (Yalin et al., 2023) and market-placed online platforms for by-products exchange (Mah et al., 2024) should be investigated in the long-term. Finally, replication and scalability strategies have to be studied (Schlü et al., 2023), expanding the key motivations, critical constraints and potential profits of the different cross-sectorial stakeholders. Hence, the results of this study highlight the importance of cross-sectorial symbiotic networks among industrial and non-industrial actors focusing on enhanced water circularity, lower waste generation and environmental impact but with higher economic value from the point of process industry's view.

CRediT authorship contribution statement

Efthalia Karkou: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Data curation, Conceptualization. **Athanasios Angelis-Dimakis:** Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **Marco Parlapiano:** Writing – review & editing, Validation, Data curation. **Nikolaos Savvakis:** Conceptualization. **Owais Siddique:** Visualization, Investigation, Data curation. **Antonia Vyrkou:** Visualization, Investigation, Data curation. **Massimiliano Sgroi:** Writing – review & editing, Validation. **Francesco Fatone:** Writing – review & editing, Funding acquisition. **George Arampatzis:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix

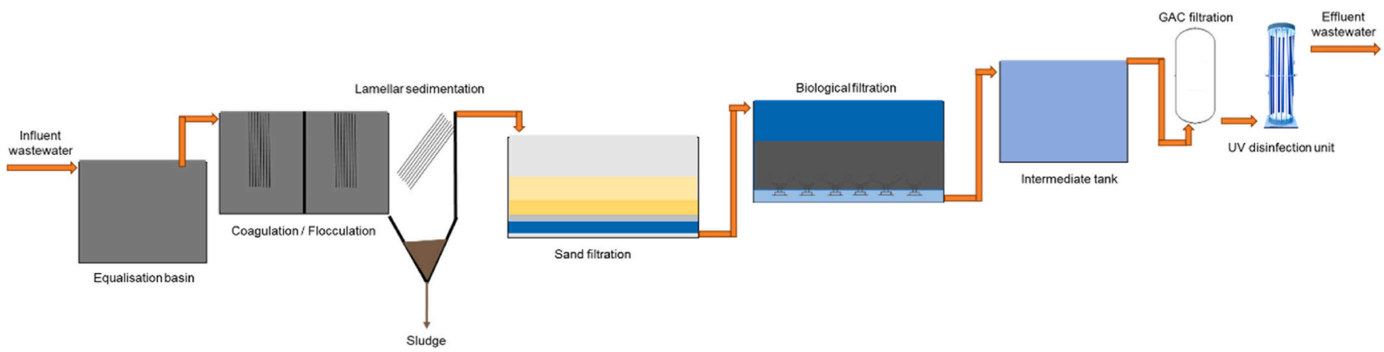

Fig. 6. Configuration of the treatment train of WWRP Aretusa

Table 9
Coefficients reported in literature for pseudo-first order, pseudo-second order, Langmuir adsorption, and Freundlich adsorption models for different contaminants removal from wastewater by activated carbon

Conta-minant	Pseudo-first order model				Pseudo-second order model				Langmuir adsorption model			Freundlich adsorption model			Operating conditions	Refe-rence
	$q_{e(exp)}$	$q_{e(cal)}$	k_1	R^2	$q_{e(exp)}$	$q_{e(cal)}$	k_2	R^2	K_L	Q_m	R^2	K_F	1/n	R^2		
Fe^{3+}/Fe^{2+}	2.367	0.302	0.0129	0.389	2.367	2.367	0	1	0.61	50.38	0.9695	53.4	0.625	0.9182	30 °C, 5 mg/L	Das and Mishra (2020)
NH_4^+	0.070	0.047	0.0004	0.939	0.070	0.071	0.036	0.992	0.411	0.124	0.9023	0.046	0.3571	0.9362	12.5–27.5 °C, 10 mg/L, 20 g/	Salim et al. (2021)
COD	–	63.92	0.0117	0.920	–	2.42	13.12	0.994	0.074	500	0.986	21.35	0.5051	0.996	360 mg/L, 0.265 g	Aber and Sheydaei (2012)

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