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**Agenda item 7: Technical Guidelines**

**Regional Guideline on Available Treatment Technologies for Urban Wastewater and Sewage Sludge and Decision Support Systems (DSS) for their Selection**

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#### **Note by the Secretariat**

The 22nd Ordinary Meeting of the Contracting Parties to the Convention for the Protection of the Marine Environment and the Coastal Region of the Mediterranean and its Protocols (COP 22, Antalya, Türkiye, 7-10 December 2021) adopted Decision IG.25/19 on the Programme of Work and Budget for the biennium 2022-2023. The Contracting Parties called for the preparation of technical guidelines to support implementation of measures of the adopted Regional Plan on Wastewater Treatment with a focus on available treatment technologies for energy efficiency and material recovery.

To this extent, the Secretariat prepared the current Guideline to address a number of technical aspects included in the adopted measures of the Regional Plan; more specifically, treatment of wastewater and sewage sludge; reclamation and reuse of treated wastewater; efficient operation and energy/nutrients recovery from treatment processes; and use of alternative energy sources based on advanced technologies which can be prioritized by applying Decision Support Systems (DSS).

The Regional Guideline on Available Treatment Technologies for Urban Wastewater and Sewage Sludge and Decision Support Systems (DSS) for their Selection was presented to the "Regional meeting to review guidelines on available treatment technologies for urban wastewater and sludge, industrial pre-treatment, and environmental standards and available desalination treatment technologies" (Ankara, 22-23 November 2022). The Meeting approved the document and requested the Secretariat to further elaborate on the following technical aspects:

- 1. *Best practices regarding materials and energy recovery technologies in the Mediterranean*. The Secretariat responded to this request and introduced six case studies as good practices. Two case studies are presented in Section 3.1; two in Section 3.2; and two in the Section 3.3. Moreover, the Secretariat provided three examples for the application of DSS in Section 6.2 at the request of the meeting.
- 2. *Newly emerging treatment technologies which are currently under development regarding water reclamation.* The Secretariat addressed this request by appending a new Annex III: "Newly Emerging Treatment Technologies and Potential Green Treatment Technologies based on Nature Based Solutions" containing two parts. Under Part I, the Secretariat elaborates further on "Newly emerging treatment technologies which are currently under development regarding water reclamation."
- 3. *Potential Green technologies eco-friendly procedures based on biotechnology as well as potential use of nature-based solutions that can be applied for material recovery and water reclamation*. The Secretariat addressed this request as part of the above-mentioned new Annex III. Under Part II, the Secretariat elaborates further on "Potential green technologies based on biotechnology as well as potential use of nature-based solutions that can be applied for material recovery and water reclamation."
- 4. *Updating information on the state of the art for the removal of contaminants of emerging concern as considered for proposal of revising the Urban Wastewater Treatment Directive*. The Secretariat addressed this request by adding an additional paragraph at the end of Section 4.2.

The Secretariat shared the final version of the Guide with Contracting Parties for "non-objection" as per the recommendation of the Meeting. No objections were received. Consequently, the proposed Guideline is presented herein to the MED POL Focal Points for their review and approval for the use by the Contracting Parties in support of implementation of relevant measures on treatment of urban wastewater effluents as stipulated in the Regional Plan on Urban Wastewater Treatment which was adopted by COP 22 (Antalya, Türkiye, 7-10 December 2021).

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## <span id="page-4-0"></span>**1. Introduction**

1. This "Regional Guideline on Available Treatment Technologies for Urban Wastewater and Sewage Sludge and Decision Support Systems (DSS) for their Selection" is developed under Article 7 of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources (LBS Protocol) of the Barcelona Convention, which stipulates that "the Parties shall progressively formulate and adopt, in cooperation with the competent international organizations, common guidelines."

2. This Guideline is also prepared in line with Decision IG.25/8 adopted by COP22 (Antalya, Türkiye, 7-10 December 2021) on the Regional Plans on Urban Wastewater Treatment and Sewage Sludge Management (herein referred to as the Regional Plans) which entered into force on 26 July 2022. Pursuant to Article VI of the Regional Plans addressing Technical Assistance, Transfer of Technology and Capacity Building, it is stipulated that "for the purpose of facilitating the effective implementation of Article V of the Regional Plans, the Contracting Parties collaborate to implement, exchange and share best practices directly or with the support of the Secretariat including resource efficiency, sustainable consumption and production, circular economy, resource efficiency, WEFE Nexus in the design, construction, operation and maintenance of the urban wastewater treatment plants."

3. To this aim, the present Guideline is elaborated to address specific technical aspects, including best practices in the Mediterranean, related to the adopted measures of the Regional Plans which pertain to the design and operation of wastewater treatment plants in order to assist the Contracting Parties in their implementation. These aspects include:

- a) Potential for recovery of materials and substances from wastewater treatment plants including supply of water, energy, and nutrients.
- b) Resource recovery technologies for municipal wastewater treatment plants including water reclamation and reuse technologies, energy recovery technologies, and fertilizers (nutrients) reclamation and recovery technologies.
- c) Treatment technologies for contaminants of emerging concern in wastewater including sources, occurrence and fate/transport of contaminants of emerging concern.
- d) Occurrence, detection and removal of microplastics in wastewater treatment plants.
- e) Decision Support Systems for selection of environmentally friendly technologies for wastewater treatment.

4. This Guideline is intended to assist wastewater engineers and treatment plants operators to select and implement the appropriate resource recovery technologies for water, energy and nutrients as well as assess available technologies for removal of contaminants of emerging concern and microplastics based on Decision Support Systems for selection of environmentally friendly, economically viable and socially acceptable wastewater treatment technologies.

## <span id="page-4-1"></span>**2. Potential for Recovery of Materials and Substances from Wastewater Treatment**

5. In the past 10 years, the circular economy has grown rapidly supporting the widely accepted sustainable development concepts; and even goes beyond them. The water sector is well positioned to improve by this transition given its inherent circularity and the valuable and essential resources it manages which are primarily found in wastewater (Panchal et al., 2021). Although the principal objective of WWTP design is the effective treatment of wastewater for safe and environmentally friendly discharges, WWTP's performance can be sustainably improved by integrating innovative resource recovery technologies into the design of treatment processes.

6. There are various types of materials and substances that can be extracted in the form of resources from wastewater, including water, energy, biofuels, nutrients, and biopolymers. Some of these resources are becoming increasingly limited as the world's population and urbanization increase (Dagilienė et al., 2021; Kehrein et al., 2020). Resource recovery contributes to reducing the carbon

footprint of wastewater treatment plants (Kehrein et al., 2020). In recent years, the water-energy-food nexus has been viewed as a more effective way to comprehend the intricate interactions across resource systems (Fetanat et al., 2021). Ensuring the security of these three interconnected sources is crucial for the Mediterranean region.

## <span id="page-5-0"></span>2.1 Water Supply

7. Wastewater from household, industrial, and agricultural sources is produced daily in vast quantities. The global wastewater discharge is projected to be 400 billion cubic meters per year, contaminating about 5,500 billion cubic meters of water per year (Zhang & Shen, 2019). There is potential for reuse of wastewater mainly in agriculture. Currently, approximately 20% of all agricultural land is irrigated; supplying 40% of total agricultural production (FAO, 2020). While solving water scarcity, wastewater reuse, untreated or poorly treated wastewater for crop irrigation, can generate public health risks if treatment, storage, and piping are not adequate (Fuhrimann et al., 2016). The link between water security and climate security is becoming increasingly evident. Recovering lost wastewater and making water reuse safer are therefore priorities. The region needs to accelerate the expansion of financially sustainable treatment facilities. But these measures should be accompanied by the adoption of on-farm and post-harvest practices that ensure safe water reuse in food supply chains.

8. In the Middle East region, wastewater reuse potential remains largely untapped. Of the total 21.5 billion cubic meters of municipal wastewater generated each year, only around 10% is treated and reused directly for irrigation, landscaping, industrial processes and so on. A further 36% is reused indirectly, for example by farmers drawing water from streams or rivers containing wastewater. Indirect use is often informal and unsafe because of the lack of treatment. The majority of municipal wastewater – 54% – is lost when it is discharged to the sea or evaporates (IWMI, 2022).<sup>[1](#page-5-2)</sup> A notable exception is found in Israel where nearly 80% of wastewater was reclaimed for reuse as early as 2013 (Futran, 2013), and is currently estimated at 90% which is mainly used in Agriculture (Fluence,  $2020$  $2020$ ).<sup>2</sup>

## <span id="page-5-1"></span>2.2 Energy Supply

9. The growing use of renewable energy sources to generate electricity, such as water for hydropower and biomass for bioenergy, has beneficial economic and mitigating effects, but can have a negative impact on water supplies that are already strained (Zarei, 2020). A typical wastewater treatment plant requires between  $0.3$  and  $0.6$  kWh/m<sup>3</sup> of energy to operate (He et al., 2019). Recovery of the chemical energy available in sewage is economically attractive since the thermal energy potential of digestion of the organic matter in wastewater is more than the energy requirement of a typical wastewater treatment plant (Fernández-Arévalo et al., 2017).

10. Energy recovery in the form of biogas, biodiesel, hydrogen, electrical power, and heat energy from wastewater treatment plants can be achieved using heat pumps, mechanical and thermal pretreatment processes, and high-temperature streams by heat exchangers (Bertanza et al., 2018). The most feasible and widely practiced method to generate power and heat is by use of biogas produced by anaerobic digestion. For example, a recent study (Kehrein, et al. 2020) suggests that for a heat exchange or heat-pump system installed to recover heat energy of 5°C, 24 hours per day, for 365 days a year, the total recoverable heat from municipal WWTP effluents in the Netherlands would be 40% of all heat energy derived from gas, coal or biomass combustion processes.

11. When compared with aerobic treatment, anaerobic-based treatment processes offer the potential to considerably minimize energy consumption of wastewater treatment by avoiding aeration and achieving energy-neutral wastewater treatment through biogas production (Dai et al., 2015; McCarty et al., 2011; Seib et al., 2016; Sills et al., 2016). However, in order to be effective and energy

<span id="page-5-2"></span><sup>1</sup> https://www.iwmi.cgiar.org/

<span id="page-5-3"></span><sup>2</sup> https://www.fluencecorp.com/israel-leads-world-in-water-recycling/

positive, municipal wastewater requires pre-concentration of wastewater due to its medium to low organic matter content (Ozcan et al., 2022).

#### <span id="page-6-0"></span>2.3 Nutrient Recovery

12. Nutrient (fertilizers) recovery from wastewater has the potential to increase the sustainability of wastewater treatment, minimize the costs associated with nutrient removal, and supply additional nutrients for food production. However, the removal of nutrients from reclaimed water used in agriculture will ultimately result in increased inputs of nutrients for cultivation (Sun et al., 2016).

13. Many studies published in the recent decade contained thorough information on nutrient recovery from wastewater in terms of mechanisms, the effects of various significant elements, future directions, and so on (Ma et al., 2018; Yan et al., 2018); however, just a few applications concentrate on the financial issues. Economic feasibility is a more essential factor than technical feasibility in deciding whether the nutrient recovery system can be utilized at the plant scale.

#### <span id="page-6-1"></span>**3. Resource Recovery Technologies for Municipal Wastewater Treatment Plants**

## <span id="page-6-2"></span>3.1 Water reclamation and reuse technologies

14. Considering that around 99% by weight of the matter contained in wastewater is water, reclaiming and reusing this source is a more sustainable option than, for example, desalination or long distance fresh-water transfers, particularly for addressing water scarcity problems and the global climate change-related water stress in the framework of circular economy.

15. In this context, the term "Resource Recovery Rout" (RRR) is defined as the route taken by a resource entering to a wastewater treatment plant; extracted and refined with the help of certain technology before finally being used (Kehrein et al. 2020). While resource extraction happens on site at the WWTP, refining and usage can be undertaken elsewhere. Selecting the appropriate technology for extraction/reclamation of water is critical depending on various factors.

16. Reclamation/recovery technologies can be classified as a function of their applicability and suitability for resource removal. They can be further categorized under the appropriate treatment phases as indicated in Table 1:

- a. Primary reclamation/recovery technologies which fall under primary treatment processes for domestic wastewater. These are generally insufficient to be used alone.
- b. Secondary reclamation/recovery technologies which constitute part of the secondary treatment processes. These are capable of obtaining water suitable for reuse; and
- c. Tertiary reclamation/recovery technologies which are part of the tertiary treatment processes (excluding disinfection) with an end-product allowing reuse and full tertiary treatment, including pre-treatment for disinfection.

17. Primary treatment technologies such as screening, centrifugation, coagulation, and flotation are all included in this category, as they are all used in the basic stage of wastewater treatment. These technologies are typically employed in case of a significant water pollution. The main purpose of primary treatment is removal of solid and/or suspended particles using these technologies for ensuring the efficient functioning of the treatment plant.

18. Secondary treatment technologies comprise biological methods for bacteria to remove soluble and insoluble contaminants. There are many aerobic and anaerobic bacteria that can be utilized in different biological wastewater treatment processes to remove various water contaminants. These technologies vary based on their configuration and operation design, i.e., suspended growth, attached growth, etc.

19. Tertiary water treatment technologies are very important in wastewater treatment strategies. The techniques used for this purpose can be grouped in three main clusters such as: filtration, disinfection and advanced oxidations.

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20. Main examples of advanced treatment technologies to reclaim water from municipal WWTPs are presented in Figure 1, classified under filtration, disinfection and advanced oxidation technologies.



#### *Table 1: Wastewater treatment technologies for resource recovery from municipal wastewater*

<span id="page-7-0"></span><sup>&</sup>lt;sup>3</sup> The level of treatment currently under revision by the EU Commission for the Urban Wastewater Treatment Directive will be considered when revisions are finalized.



*Figure 1: Main examples of technologies to reclaim water from municipal wastewater treatment plants*

21. The following notes provide further insights into the applicability of the aforementioned technologies for water reclamation and reuse:

- a. Filtration by adsorption using activated carbon (AC) in conjunction with sand and gravel can improve effluent quality, making it suitable for water reuse. These carbonaceous compounds have the ability to reduce COD, total organic carbon (TOC), chlorine, and many other hydrophobic organic contaminants like pharmaceuticals after being activated by physical and/or chemical agents at high temperatures.
- b. Several non-biodegradable organic pollutants, such as pharmaceuticals, dyes and pesticides, can be degraded by subjecting them to advanced oxidation processes (AOPs), which generate hydroxyl radicals (OH) as highly reactive oxidant agents. It is common practice to apply AOPs as a final stage of disinfection and cleaning after biological treatment, but they can also be employed as a pre-treatment step to promote further biological treatment.
- c. Membrane technologies are considered the main and key technology for advanced wastewater reclamation and reuse strategies which allow reliable advanced treatment. Their advantages include the need for less space, being a physical barrier against particle material, and efficiency at retaining microorganisms without causing resistance or byproduct formation. Unless membrane treatment in the form of reverse osmosis (RO) is already applied, an additional disinfection unit may be needed for safe wastewater reuse. Further details on membrane technologies are provided in Annex I.
- d. Disinfection, which includes chlorination, UV radiation and ozonation, etc., is usually the final step to be applied to water reclamation in most of WWTPs, of course this depending on the final use of reclaimed water.

22. Selection of the appropriate treatment technology should consider the intended final use of reclaimed water (i.e., potable water, irrigation water, use in city parks, etc.) as well as the applicability of reclamation technologies for removal of pollutants and their suitability for reclamation and treatment as indicated in Table 1.

23. The main disinfection technologies for wastewater treatment and water reuse and their variations are presented in Table 2. Disinfection is applied in order to ensure that reclaimed water is in compliance with national/local standards and regulations. The Regional Plans on Urban Wastewater Treatment and Sewage Sludge Management adopted in Decision IG.25/8 (COP 22, 7-10 December 2021, Antalya, Türkiye) provide guidance on this aspect as part of their measures.

24. It is important to consider, for water reclamation purposes, the implementation of risk management systems such as the Sanitation Safety Planning (SSP)[4](#page-9-0) system when public health is at stake. Predicted risks and their impacts should be considered as part of the inputs to be used in Decision Support Systems (DSS) which are explained later in this Guidance document

25. In addition to available wastewater technologies in this Guidance document, among others, there are two newly emerging treatment technologies which are currently under development regarding water reclamation. (i) Microalgal wastewater treatment (MWWT); and (ii) Microbial fuel cells (MFCs) for wastewater treatment. The utilization of microalgae-based wastewater treatment systems has gained considerable attention from the research community, and in collaboration with industry, a variety of wastewater technologies and methods have been created to meet the sector's specific needs. Microbial fuel cells are most effective for biodegrading the organic materials in wastewater and for lowering the chemical oxygen demand (COD). This method promotes environmental sustainability, low energy consumption, and cost by eliminating effluent disposal. These two treatment technologies are presented in Annex III, Part I. Additionally, two examples of green technologies based on biotechnology and the potential use of nature-based solutions that can be applied for material recovery and water reclamation are also presented.

## **Case-Study 1: Example of Good Practice**

As a best practice, the recharge-reclamation process in Shafdan, Israel is based on intermittent flooding and drying of the spreading basins, followed by pumping the reclaimed water from wells surrounding the recharge area. This method is known as Soil Aquifer Treatment (SAT). In the SAT process, suspended particles, nitrogen, and dissolved organic matter are removed primarily in the unsaturated zone by a combination of biological, chemical, and physical processes. When land space is available and an in-depth understanding of the hydrogeology of the area is present, SAT is a viable solution for wastewater treatment and reuse. About 120,5 million  $m<sup>3</sup>$  of secondary treated effluent are recharged annually in the Shafdan infiltration basin. After 300-400 days of retention, the surplus treated water is removed from the aquifer to prevent contamination of the drinking water. This water is transferred for irrigation purposes to the western Negev. Between 1974 and 2009, 2 billion m<sup>3</sup> of reclaimed water were treated and distributed, with just 4% of the treated plant effluent being discharged into the sea via Soreq stream (El Gohary et al., 2013).

#### **Case-Study 2: Example of Good Practice**

In Brasil, Royal Blue condominium complex, which was the first to install a greywater reuse system, the system has produced a substantial surplus of water for reuse. The consumption (91 litres per day) accounts for around 32% of the available water, leaving a surplus of approximately 68% in the building. The possibility for additional reuse could result in even greater future water savings. Currently, untreated greywater is discharged into the public sewage via a bypass system. The system generates a net monthly water savings of 432 m<sup>3</sup>. Regular expenses for the greywater treatment plant include those for operations and maintenance, electricity, sludge removal, and laboratory analysis. The monthly operating and maintenance cost for a 30 unit complex is roughly US\$260. The cash flow based on costs and revenues from the installation and operation of the reuse of greywater system becomes positive in 103 months, indicating that the investment will be recouped in 8.5 years based on current operation practices (Andersson, 2016).

<span id="page-9-0"></span><sup>4</sup> Sanitation Safety Planning (SSP) is a step-by-step risk-based approach developed by the World Health Organization (WHO) to assist in the implementation of local level risk assessment and management for the sanitation service chain - from containment, conveyance, treatment and end use of disposal.

Main disinfection technologies used for the reclamation/reuse systems						
<i>Type</i>	Technology	Comments/Indications				
Physical	Ultraviolet radiation (UV)	Multiple lamp systems are recommended for wastewater disinfection. The lamps should be changed after the end of their theoretical lifespan. Not useful with high turbidity.				
	Membrane-based technologies	Several types. The pore diameter defines the disinfection capacity. Ultrafiltration and nanofiltration as well as reverse osmosis are the main technologies quoted.				
Chemical	Chlorination	The most common technology. Residual action is its most important feature. Also used in combination with other technologies, mainly UV. By-products are generated while reacting with organic matter and other pollutants.				
Other	Additional lagooning (maturation) systems	The natural UV radiation disinfects. Other processes are natural die-off, predation. It is necessary to eliminate algae after this treatment.				
	Constructed wetlands. infiltration-percolation	Use of soil/biofilms disinfection capacity as well as filtration capacity (organisms associated with the solids).				
Mixed- combination	Ultraviolet (UV) chlorination. Also, membranes and chlorination	UV acts eliminating pathogens, and chlorine is used for final elimination and for maintaining a residual disinfection capacity.				

*Table 2: Main disinfection technologies for wastewater treatment and water reuse and their variations (Salgot and Folch, 2018)*

#### <span id="page-10-0"></span>3.2 Energy recovery technologies for wastewater treatment plants

26. The energy intensity of wastewater treatment plants can be decreased by designing treatment processes with a focus on energy efficiency and recovery. Energy recovery from wastewater is achievable through the application of different technologies.

27. The chemical energy in a typical municipal wastewater treatment plant can be estimated at 17.8 kJ  $g^{-1}$  of COD. This is about five times the electrical energy needed to operate a conventional activated sludge (CAS) process; although in the latter, a significant fraction of the energy stored in the COD is lost as heat during microbial metabolism. Current configurations hardly achieve energy selfsufficiency, which is usually in the range of 30% to 50%, depending on country concerned. Main examples of energy recovery technologies for municipal wastewater treatment plants are shown in Figure 2.

#### <span id="page-10-1"></span>*3.2.1 Energy recovery from wastewater treatment processes*

28. Biogas is the most frequent form of energy produced in WWTPs further to the anaerobic digestion of sludge. Biogas consists of methane (50% to 70%), carbon dioxide (30% to 50%), and trace amounts of nitrogen, hydrogen, hydrogen sulfide, and water vapor (Manyuchi et al., 2018). Nevertheless, energy generated from the [anaerobic digestion](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/anaerobic-digestion) of wastewater [sludge](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/sludge) and [combined heat](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/combined-heat-and-power)  [and power](https://www.sciencedirect.com/topics/earth-and-planetary-sciences/combined-heat-and-power) technologies is still limited. Barriers to widespread implementation of anaerobic digestion and combined heat and power are primarily associated with costs, (e.g., infrastructure or equipment capital costs) (Pfluger et al., 2018).

29. Nitrogenous compounds can also be recovered from wastewater. One route for this is the CANDO process which involves three steps: (i) nitrification of NH4<sup>+</sup> to NO<sup>2 −</sup>, (ii) partial anoxic reduction of  $NO^{2-}$  to N<sub>2</sub>O and (iii) chemical N<sub>2</sub>O conversion to N<sub>2</sub> with energy recovery. Another route recovers NH<sub>3</sub> directly from concentrated side streams in wastewater treatment plants, for example by stripping.  $NH_3$  can be burned to generate power or used as a transport fuel with the appropriate technology. A major issue with these routes is the nitrogen concentrations in municipal wastewater and whether this makes them feasible and economical to use (Kehrein, P. et al., 2020).



*Figure 2: Main examples of energy recovery technologies for municipal wastewater treatment plants*

30. Syngas can also be obtained from municipal sewage sludge using supercritical water treatment processes. Syngas or synthesis gas is a mixture of hydrogen and carbon monoxide, in various ratios. It is formed by the decomposition of organic matters in sewage sludge which is hydrolyzed into syngas. The gas often contains some carbon dioxide and methane. It is combustible and can be used as a fuel. The advantage over other sludge-handling technologies is that the sludge is converted into an energy carrier in much shorter residence times of only a few minutes. Moreover, excess sludge from WWTPs does not need to be dewatered before being fed to supercritical water reactors. In this regard, supercritical water technology has proved to be a promising treatment method for contaminated wastewater and sludge from a wide variety of industries including pulp and paper, pharmaceutical, textile, pesticides, dairy, petrochemical, explosives, and distillery.

#### **Case-Study 3: Example of Good Practice**

The viability of an AnMBR demonstration plant treating urban wastewater (UWW) at temperatures of 25-30 °C during a 350-day experimental period was evaluated in Spain. The system, which was installed at the fullscale WWTP in Alcázar de San Juan, Spain, primarily comprises of a 40 m<sup>3</sup> anaerobic reactor (AnR) connected to three 0.8 m<sup>3</sup> membrane tanks (MT) (0.7 m<sup>3</sup> working volume + 0.1 m<sup>3</sup> headspace). The effluent from the pre-treatment of a full-scale municipal wastewater treatment facility was used to feed the plant. This effluent had high amounts of COD as well as sulfate. System operation contributed to a 36-58% decrease in sludge generation relative to theoretical aerobic sludge productions. Positive net energy productions were achieved by the system, and approximately zero net greenhouse gas emissions were produced as a result. The obtained findings show the feasibility of UWW treatment in AnMBR under mild and warm climates (Robles et al., 2020).

31. Biodiesel is another fuel that can be derived from sludge. Harvesting lipid-rich biomass by simply skimming the surface of wastewater treatment reactors could provide feedstock for high-yield biodiesel production. The use of phototrophic microalgae that treat the wastewater in high-rate ponds is a well-studied production route for biodiesel. However, the performance of phototrophic organisms depends on climatic conditions that are not available all year round in countries that have a winter season. In addition, land use for this type of biodiesel production is high, as are the costs of photobioreactors and algae harvesting (Kehrein *et al.* 2020).

32. Heat pumps are designed to use electricity to extract low-temperature thermal energy from the wastewater. They usually provide 3 to 4 units of heat energy per unit of electrical energy consumed. Considering that the temperature of the effluent shows relatively small seasonal variations by comparison with atmospheric temperatures, this can serve as a stable source of heat that is recoverable using heat pumps. Wastewater temperature can be used for heating or cooling buildings. Sludge temperature also offers a potentially interesting thermal energy resource for recovery on-site use during sludge drying (W. Mo and Q. Zhang, 2013).

#### **Case-Study 4: Example of Good Practice**

The wastewater treatment plant in Marrakech, Morocco was constructed with the purpose of protecting the environment, sustaining tourism and urban development, and meeting the water needs (24,000 m3/day) of 17 golf courses and city landscape. State and RADEEMA contributed 70% of the cost (125 million US dollars), while the private sector contributed the remaining 30%. The plant uses activated sludge for secondary treatment and sand filtration and ultraviolet lights for tertiary treatment. Energy recovery from biogas reduces greenhouse gas emissions and provides 45 percent of the plant's electrical energy needs (El Gohary et al., 2013).

## <span id="page-12-0"></span>*3.2.2 Energy recovery from sewage sludge in energy plants*

33. Treated sewage sludge can be co-incinerated in existing power plants. Co-incineration takes place mainly in coal-fired power plants, waste incineration plants and cement works.

34. Co-incineration in coal-fired power plants: Coal fired power plants are being replaced by gas powered plants. Nevertheless, sewage sludge can be co-incinerated in both lignite and hard coal fired power plants. Pulverized-fuel or circulating-fluidized bed are the main operating furnace systems.

35. Generally, only stabilized (i.e. digested) sewage sludge is burned. The use of raw sludge would cause great difficulties in handling and storage and is not suitable due to its high water content and especially due to its poor dewaterability and gas and odor generation. Technically, both the incineration of dried sewage sludge and that of simply dewatered sewage sludge is possible. Currently, dewatered sewage sludge having a dry substance content of about 25% to 35% dry mass is burnt in most co-incinerating power plants. Some power plants only use fully dried sewage sludge. In others, it is mixed with dewatered sewage sludge and added back to the incineration process.

36. When using dewatered sewage sludge, integrated drying of the sludge generally takes place prior to incineration. In power plants using pulverized fuel (PF) firing, the sewage sludge is usually introduced in the process via the coal mill and dried and crushed together with the coal. The drying capacity of the coal mills is often the limiting factor; reducing the use of dewatered sewage sludge to a low percentage. This is especially true for hard coal-fired power plants where only limited drying capacity is available due to the low water content of hard coal. In most coal-fired power plants, the proven sewage sludge content is up to 5% of the fuel mass.

37. Compared to coal, sewage sludge has a relatively high proportion of mineral components of about 40% to 50%. Correspondingly high is the ash content, which must be separated after incineration, while low is the calorific value related to the total solids content. The calorific value of sewage sludge is 9 to 12 MJ/kg in the fully dried condition. Lignite has a comparable calorific value at about 50% water content. Hard coal is extracted with a water content of 7% to 11% and has a calorific value of 27 to 30 MJ/kg in this condition.

38. Sewage sludge is a sink for several pollutants. When sewage sludge is co-incinerated in coalfired power plants, the additional input of heavy metals – particularly highly volatile substances such as mercury – becomes noticeable in the emission values. This is one of the reasons why the sewage sludge amount co-incinerated in power plants remains limited to a small percentage. It is recommended to use risk-based assessments for assessing undesired impacts of air emissions stemming from co-incineration of sludge in coal-fired plants.

39. Co-incineration in waste incineration plants: Municipal sewage sludge is disposed of in different degrees of drying in a number of waste incineration plants; the procedural principle of which is mostly based on grate firing technology. The admixture rate should not exceed 20% and the moist sludge should be well mixed with the rest of the material to avoid lumping. This is often achieved by so-called strewers in the waste bunker or through centrifugal devices for feeding the combustion chamber. If dried sewage sludge is co-incinerated, there is a risk that the sludge will fall through the grate without being sufficiently burned out. When co-incineration takes place in waste incineration plants, it should be noted that the sewage sludge significantly affects the dust content of the exhaust gas and therefore the flue gas cleaning facilities must be designed for the required increased separation performance.

40. Co-incineration in cement works: Cement production is a very energy intensive process and has used surrogate fuels from waste for decades. For this purpose, dried sewage sludge (an average water content of 27% by weight) replace fossil fuels. In addition, the mineral content in sewage sludge can substitute the mineral raw materials such as sand or iron ore required in cement production.

41. The co-incineration of sewage sludge in cement works is advantageous in two respects. On the one hand, valuable raw materials and fuels can be saved and, on the other hand, the co-incineration of sewage sludge, which is considered to be largely climate-neutral, also contributes to  $CO<sub>2</sub>$  reduction. In addition to dried sewage sludge, mechanically dewatered sewage sludge is also used to a small extent. In this case, only a very small contribution to meeting the energy demand can be expected; the substitution of raw materials is much more important.

42. The heavy metal limit values of waste incineration also apply to the co-incineration of sewage sludge in cement works. Heavy metal input limits for sewage sludge are also particularly important to limit the heavy metals content.

## <span id="page-13-0"></span>3.3 Nutrient reclamation and recovery technologies

43. Wastewater is a rich source of phosphorus (P), nitrogen (N), magnesium (Mg) and potassium (K). These substances provide the basis for the composition of a number of commercial fertilizers. Therefore, attempts have been made to properly recover these substances from wastewater even though their recovery is not fully economical despite their high potential.

44. There are many operational or partially deployed phosphorus recovery systems from wastewater such as wet chemical leaching, wet oxidative processes, metallurgical, bioleaching, thermochemical, and wet chemical extraction. It is common knowledge that P and NH4-N naturally precipitate out of urine as struvite scale (Somathilake, 2009). Other technologies for nutrients recovery include chemical precipitation, membrane processes, enhanced biological phosphorus removal, adsorption processes, adsorption.

45. Recent efforts (Günther et al., 2018) to collect nutrients as struvite through various chemically based extraction techniques have been pioneered. Struvite which is a phosphate-rich organic substance containing high levels of  $Mg^{2+}$ ,  $PO<sub>4</sub><sup>3</sup>$ , and NH<sub>4</sub><sup>+</sup> offers numerous advantages over commercially available chemical fertilizers. This includes slow-release characteristics, soil conditioning, preventing surface run-off, and limited consumption over an extended period of time (Krishnamoorthy et al., 2021).

#### **Case-Study 5: Example of Good Practice**

The economic feasibility of implementing an ammonium and phosphate simultaneous recovery method based on the use of calcium activated synthetic zeolites in a large urban WWTP in the Barcelona Metropolitan Area is evaluated. After a benchmarking investigation, a calcium-activated synthetic zeolite was chosen for its ability to concurrently recover ammonium and phosphate through a combination mechanism of ion exchange for ammonium and development of an insoluble mineral phase for phosphate. Rich in ammonium and phosphate, the sorbent can be used as a slow-release fertilizer. Based on the reported payback period of 7.5 years and internal rate of return of 15%, which is higher than the discount rate evaluated, it can be concluded that incorporating this alternative technology into the Baix Llobregat WWTP is economically profitable (You et al., 2019).

46. Electrodialysis (ED) is another technology which is currently seen as a promising method for removing and recovering nutrients from wastewater. It is best described as an electromechanical separation technique that serves for the extraction of ions in solution, in addition to the extraction of hardness and organics from electrolytes, by using ion-exchange membranes within an electric field to encourage ionic separation (Lee et al., 2013). It should be noted that the electrodialysis process for nutrient recovery differs from the typical ED for desalination (Mohammadi et al., 2021).

47. As discussed in the previous section, incineration of sewage sludge is a wastewater treatment method that serves to decrease sludge volume, odor, and to eliminate organic pollutants like pharmaceuticals and pathogens. Significant quantities of phosphorus contained in sewage sludge can be reused in agricultural or urban land application provided sludge characteristics meet national standards and regulations. But the presence of heavy metals is still the main obstacle to direct application of sewage sludge incineration ash on crop fields (Vogel et al., 2013).

#### **Case-Study 6: Example of Good Practice**

The potential benefits of reusing treated sewage wastewater to irrigate and fertilize crops on otherwise dry and infertile soils were demonstrated in a two-year experiment (2013-2015) at a farm outside the city of Gerga in Egypt, which helped to alleviate pressure on scarce water resources while also contributing in order to meet growing food demand. The investigated farm is located near the municipal WWTP in Gerga and is managed by the Cairo-based Holding Company for Water and Wastewater in cooperation with UNEP and the Italian Ministry of the Environment, Land, and Sea. Depending on water need, trees and crops were irrigated for up to 5.5 hours per day. The experimental farm's total water consumption was approximately 2.35 litres per second. The treated wastewater proved to be a viable alternative to fertilizers for the selected crops. The analysis revealed that root or bulb crops such as potatoes, sweet potatoes, carrots, turnips, onions, and garlic contained elevated levels of heavy metals. However, the Egyptian and European standards for irrigation of leaf or stem food crops were met (Andersson, 2016).

48. Examples of fertilizers/nutrient recovery technologies for municipal wastewater treatment is shown in Figure 3. It should be noted that sludge land applications and use of sludge as soil conditioner have been addressed in the Regional Plan for Sewage Sludge Management (Decision IG.25/8, COP22, Antalya, Türkiye).



*Figure 3: Main examples of fertilizers/nutrient recovery technologies for municipal wastewater treatment* 

## <span id="page-15-0"></span>3.4 Economic, environmental, health and social considerations for resource recovery from wastewater treatment processes

49. Before selecting a resource recovery route, the feasibility for water reclamation/recovery of materials and energy from wastewater treatment processes should be investigated beforehand to determine the associated economic costs in terms of extracting the required resource in feasible quantities and acceptable quality; their market value chain, competition and logistical aspects which impact cost; emissions and health risks; as well as social acceptance and availability legislations. These aspects should be considered as part of the inputs to be used in Decision Support Systems (DSS) which are explained later in this Guidance document.

50. The main economic, environmental, health and social considerations for recovery of water, energy and fertilizers (nutrients) from wastewater treatment processes are presented in Table 3. These aspects are considered the starting point for any design of wastewater treatment plants as well as selecting the appropriate technologies for resource recovery. Table 3 is clustered into three parts: (i) economy including value chain, (ii) pollution and health risks, and (iii) social acceptance and supporting policies.

51. The value chain is the key driving force for decision makers to select a certain technology to serve the purpose of material/energy recovery. Naturally it may vary based on the country needs and priorities. Comprehensive market research with a projection including logistical aspects should be prepared, especially for nutrient recovery.

52. Pollution and health-related considerations are directly related to the effect of discharges and production of unwanted harmful byproducts which are key elements for mitigating the risk of a selected resource recovery technology. For this reason, risk management systems should be considered in any scheme for materials recovery with the aim to alleviate any adverse impacts on human health.

53. Finally, social acceptance of recovered materials (e.g. reuse of reclaimed water) and related policies in place are crucial for the technologically successful and economically viable recovery of resources and materials from wastewater treatment processes.



## *Table 3: Main economic, environmental, health and social considerations for recovery of water, energy and nutrients from wastewater treatment processes (adapted from Kehrein, P. et al. 2020)*



<span id="page-17-0"></span>

## **4. Treatment Technologies for Contaminants of Emerging Concern in Wastewater Treatment Plants**

54. Contaminants of Emerging Concern (CEC) are natural or manmade chemicals and substances that can be found in water bodies. According to the Organisation for Economic Cooperation and Development (OECD) "Contaminants of emerging concern" (CECs) comprise a vast array of contaminants that have only recently appeared in water, or that are of recent concern because they have been detected at concentrations significantly higher than expected, or their risk to human and environmental health may not be fully understood. Examples include pharmaceuticals, industrial and household chemicals, personal care products, pesticides, manufactured nanomaterials, and their transformation products' (OECD, 2018). These contaminants have a high potential to be harmful to humans, aquatic life, and the environment. The presence of these contaminants becomes a significant cause for concern if they are not regulated. Contaminants of emerging concern frequently result in the production of by-products whose physicochemical characteristics are unknown. Exposure to contaminants of emerging concern has the potential to cause a wide variety of diseases in humans. Some emerging contaminants can act as endocrine disruptors due to their structural similarity to naturally occurring hormones, while others can induce mutagenic and carcinogenic effects, such as an increased risk of breast and prostate cancer (Prangya R. Rout et al., 2021).

## <span id="page-18-0"></span>4.1 Classification of Contaminants of Emerging Concern and their sources, occurrence and fate/transport

55. In accordance with their chemical and physical features, ECs fall into one of three broad categories: Particulate matter, organic compounds, and inorganic compounds as depicted in Figure 4. Approximately 70% of the CECs found in environmental samples are PhACs (pharmaceutically active compounds) and PCPs (personal care products), whereas the remaining 30% are industrial and agricultural compounds (Ouda et al., 2021).

56. Domestic wastewater, industrial effluents, hospital discharges, livestock farming, and agricultural runoff are just some of the sources of CECs that make their way into the aquatic and subsurface environment. Major sources of CECs in the environment come from pharmaceutical, PCP, biocide, and other chemical industrial effluents. PhACs and PCPs can be introduced to the environment from a variety of sources, but household discharge is a significant contributor. Drug conjugates, antibiotic-resistant bacteria and genes, pharmaceutical metabolites, radioactive elements, and so on are all found in hospital effluents and contribute significantly to CECs. Other significant sources of CECs include the runoff from animal farming and agricultural activities, particularly in the form of steroid hormones and pesticides used to increase crop yields. The biocides and insecticides employed, the nature of the surface water bodies, and the weather all play a role in how much CEC is contributed by these sources. Landfill leaching, irrigation with reclaimed water, aquaculture discharge, sewage treatment facility leaks, etc., are other sources of CECs in the environment. Figure 5 illustrates the principal sources and routes of CEC in aquatic and subsurface ecosystems.

57. Once CECs have entered the environment, they begin immediately to migrate to various aquatic environments by following a variety of distinct pathways; their concentrations varying greatly from one another in various aquatic environments. This is primarily the result of a number of factors, including, but not limited to, dilution, environmental persistency, treatment efficiency, and others (Luo et al., 2014). In most cases, the presence of CECs in aquatic environments was documented in a variety of distinct categories, including raw sewage, effluent treated wastewater from WWTPs, sewage sludge, surface water, groundwater, and drinking water.



*Figure 4: A streamlined classification method for CEC (Adapted from Ouda et al., 2021)*



<span id="page-19-0"></span>*Figure 5: Principal sources and routes of contaminants of emerging concern (CECs) in aquatic and subsurface ecosystems (Adapted from Prangya R. Rout et al., 2021)*

## 4.2 Treatment of Contaminants of Emerging Concern in WWTPs

58. The relatively low concentrations of CECs make them difficult to treat, which also suggests that detecting and monitoring CECs is a challenge. Although separation is a common method for concentrating samples in order to improve detection rates, this approach is not without its drawbacks. The most notable is the potential for loss of contaminants, damage to analytical instruments, and the difficulty of inline detection. CECs have highly variable physiochemical properties, which means that it is impossible to detect all types of CECs using the same analytical technique. As a result, there is a need for improved and advanced analytical and bioanalytical methods for the detection of ECs. Research is now being pursued for the creation of analytical methods for the detection and monitoring of Ecs that are both straightforward and economical (Ouda et al., 2021).

59. Conventional WWTPs are not specifically intended for the efficient removal of CECs. Depending on their persistence, the physicochemical features of CECs, applied treatment procedures, and the operational/environmental conditions, the removal effectiveness of CECs varies significantly. Generally, the basic primary treatment procedures applied in WWTPs are designed to remove suspended and colloidal materials. It is found that CECs are also removed to some degree, primarily through sorption onto the primary sludge, as shown in Figure 6.



*Figure 6: Mechanism of sorption of CECs to primary/secondary sludge*

60. During the secondary treatment phase in a WWTP which aims to remove organics or nutrients by biological decomposition, the CECs are susceptible to different processes, such as biodegradation, sorption, dispersion, dilution, photodegradation, and volatilization. However, biotransformation or biodegradation and sorption are the predominant mechanisms of CEC removal.

61. Similarly, the tertiary treatment procedures in WWTPs intended for the removal of nutrients, suspended particles, and pathogens have been shown to have a considerable EC removal efficiency, particularly for the resistant CECs by traditional oxidation techniques comparable to ozonation.

62. Generally, CECs removal efficiency during primary treatment ranges from 20% to 50%, whereas the removal efficiency during the subsequent treatment processes ranges from 30% to 70%. On the other hand, there are instances of negative removal of CECs in WWTPs in which their effluent concentrations exceed their influent concentrations. This is because the majority of CECs are

eliminated as a mixture of parent chemicals and conjugates via feces and urine. During biological treatment, conjugates can revert back to their parent compounds by enzymatic cleavage, leading to a rise in the concentration of the relevant CECs (Prangya R. Rout et al., 2021).

63. Effects of use of primary, secondary and tertiary treatment technologies on CEC removal are further elaborated in Annex II to this Guideline, including removal of CECs in the activated sludge process and membrane bioreactors under secondary treatment, as well as removal of CECs by means of ozonation, and activated carbon adsorption under tertiary treatment. According to the proposal for revision the Urban Wastewater Treatment Directive, under Article 17, and 75 Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) Member States were requested to monitor, among others, contaminants of emerging concern.

## <span id="page-21-0"></span>**5. Microplastics in Wastewater Treatment Plants: Occurrence, Detection and Removal**

64. Microplastics, also defined as plastic particles with a size smaller than 5 millimeters (Thompson, 2015) can either be generated directly (primary microplastics) or formed indirectly (secondary microplastics) by the erosion of large plastic debris as a result of exposure to environmental stressors such water, wind, and sunlight. Microplastics are found throughout the aquatic environment, from rivers and lakes to estuaries and coastlines to marine ecosystems, due to the widespread use of plastic items and the inadequate management of plastic waste disposal. There is growing concern about the threats that microplastics bring to aquatic life and human health. Microplastics' presence and deposition in the environment raise significant environmental and ecological problems (Sun et al., 2019). Their absorption can also contribute to the spread of micropollutants.

65. Controlling microplastics requires a thorough understanding of their occurrence and fate in WWTPs, as well as an efficient detection method (Sun et al., 2019). This section is aimed to provide guidance on microplastics removal in wastewater treatment plants with the aim to help facility operators to achieve sustainable operation of WWTPs.

## <span id="page-21-1"></span>5.1 Occurrence of microplastic in wastewater treatment plants

66. Microplastics originating from industrial and urban activities can be transported to WWTPs via the sewerage system. These include numerous personal care and cosmetic products such as lotions, soaps, facial and body scrubs and toothpaste. Even though these facilities are capable of removing more than 90% of microplastics from wastewater, millions of microplastics are still released into the environment each day via treated wastewater (Sol et al., 2020).

67. The concentration of microplastics typically ranges between 6.10 x  $10<sup>2</sup>$  and 3.14 x  $10<sup>4</sup>$ particles/L in influent and between 0.01 and 2.97 x  $10^2$  particles/L in the effluent, despite a wide range of reported data variability (Ali et al., 2021). Microplastic concentrations may vary from one treatment plant to another due to many factors, including catchment area, population served, land use in the near area, the presence or absence of a combined sewer system, the type of wastewater being treated (domestic, commercial, industrial), and so on. As the major proportion of microplastics in wastewater are derived from residential discharges, human activities in the served catchment, such as the preference of residents for wearing synthetic clothing or using plastic products, may directly affect the concentration of microplastics in wastewater (Sun et al., 2019).

## <span id="page-21-2"></span>5.2 Techniques for microplastic detection in wastewater treatment plants

68. As depicted in Figure 7, the detection of microplastics in WWTPs typically involves three steps: sample collection; sample pretreatment; and microplastic characterization/quantification; yet, the methodologies utilized for each step are not yet standardized. Since microplastics can be found in both wastewater and sewage sludge, several approaches may be applied depending on sample properties (Sun et al., 2019). Microplastics in wastewater can be collected in a variety of ways, the most common of which are container collection, autosampler collection, separate pumping and

filtration, and surface filtration. For the pretreatment of microplastics in WWTPs, various techniques are used to purify and remove microplastics from their original matrices, as samples obtained from WWTPs (especially sludge samples) may contain a high concentration of organic matter or inorganic particles. Wet (catalytic) peroxidation is a frequent technique for removing organic materials from WWTP samples (WPO). Enzymatic degradation is a relatively recent technique being explored for the purification of microplastics contaminated with organic material. Technical enzymes such as lipase, amylase, proteinase, chitinase, and cellulase are used in the degradation process by dissolving microplastic samples. Alkaline and acid treatment are alternate techniques for removing organic materials from wastewater and sludge samples. On the other hand, inorganic particles in wastewater and sludge samples are typically extracted using density separation and salt solution. As the last step of the detection of microplastics in WWTPs, microplastics analysis can be divided into two categories: physical characterization and chemical characterization. Characterizing the size distribution of microplastics as well as analyzing other physical parameters such as shape and color is the primary focus of physical characterization. Besides, chemical characterization is essentially used to investigate the microplastics' chemical composition (Sun et al., 2019).



*Figure 7: Process flow diagram for microplastic detection in wastewater treatment plants (Sun et al., 2019)*

# <span id="page-22-0"></span>5.3 Removal of microplastic in wastewater treatment plants

69. The removal effectiveness of microplastics during preliminary, primary, secondary, and tertiary treatment is depicted in Figure 8 by the estimated particle flow of microplastics based on literature-reported value ranges. The majority of microplastics in wastewater can be efficiently removed by preliminary and primary treatment (pre-treatment). It is reported that between 35% and 59% of the microplastics could be eliminated during the preliminary treatment and between 50% and 98% of the microplastics could be eliminated during the primary treatment. As a result of its ability to efficiently remove microplastics of larger size, pre-treatment has the greatest effect on the size distribution of microplastics. Microplastics in wastewater were reduced to 0.2% to 14% with secondary treatment, which typically includes biological treatment and clarification.



*Figure 8: Estimated particle flow of microplastics in a WWTP with primary, secondary, and tertiary treatment processes (Sun et al., 2019)*

70. As a result of the presence of sludge flocs or bacterial extracellular polymers in the aeration tank, the remaining plastic debris is likely to be accumulated and eventually deposited in the secondary clarification tank (Sun et al., 2019). In addition, chemicals used in secondary treatment, such as ferric sulfate or other flocculating agents, may have a beneficial effect on microplastic removal by causing the suspended particulate matter to aggregate together forming a "floc." (Murphy et al., 2016). On the other hand, potentially significant additional microplastic polishing may be provided by the tertiary treatment. After the tertiary treatment, the microplastic concentration in the effluent can be dropped to between 0.2 and 2% of the influent. The efficiency of microplastic removal depends on the applied treatment processes, with membrane-related technologies having the highest performance (Sun et al., 2019).

## <span id="page-23-0"></span>5.4 Measures to reduce inputs of microplastics into sewage sludge

71. Effective reduction of microplastics in sewage sludge can be achieved through enforcement of bans on single use of plastics and by prohibiting inputs of microplastics in personal care and cosmetic products. This action should be accompanied by a behavior change of the general public and campaigns to reduce the use of such products. Certain textile designs can be developed taking into consideration the need to reduce microfibre generation during washing. Household-based systems can be manufactured to prevent microplastics from being released into sewer lines or the environment.

72. Furthermore, the Amendments to the Regional Plan on Marine Litter Management in the Mediterranean which was adopted in Decision IG.25/9 by COP22 (7-10 December 2021, Antalya, Türkiye) provide a comprehensive legal framework for combatting microplastic with some robust measures to be implemented for reduction of the plastics reaching the Mediterranean environment.

## <span id="page-23-1"></span>**6. Decision Support System for Selection of Wastewater Treatment Technologies**

73. This section is aimed to provide guidelines on Decision Support Systems (DSS) to help policymakers/design engineers/facilities manager in implementing the best technology to achieve sustainable wastewater solutions in accordance with national/regional legal frameworks and regulations.

74. Wastewater treatment plants (WWTPs) are investigated globally in an effort to develop more environmentally friendly methods for their management. The design and operation of WWTPs are required to take into account a variety of complicated goals, such as reducing costs while successively developing installations that are both safe and operative and that offer entirely reliable wastewater treatment (Rodriguez-Roda et al., 2000).

75. To this aim, Decision Support Systems (DSS) have been employed as a helpful tool in solving complex and multi-scenario problems for WWTPs. They provide a systematic framework for the selection and design of water and wastewater treatment processes (M. A. Hamouda et al., 2009).

76. Decision Support Systems (DSS) allow not only for the integration of various aspects relevant to the sustainable operation of WWTPs, but also address external factors of economic, environmental, health and social nature. In this regard, risk-based management systems such as Sanitation Safety Planning (SSP) systems should be also considered. These systems provide a systematic analysis and prediction of risks and their impacts on human health which can be used as inputs in Decision Support Systems (DSS) for mitigating adverse impacts on public health.

## <span id="page-24-0"></span>6.1 Role of decision support systems for the selection of wastewater treatment technologies

77. A robust DSS should be (i) based on system analysis technique, (ii) capable of gathering, representing, and analyzing information relevant to the problem, (iii) adaptable and able to deal with insufficient data or uncertainty, (iv) user-friendly, (v) capable of producing results that are helpful. The complexity of the decision-making process, the immediacy with which a solution is required, the presence of relevant knowledge during application, and the specificity of the issue are all factors that should be taken into account when determining whether or not a DSS is necessary. General procedures for developing a DSS include: (i) problem analysis and interpretation, (ii) representation of knowledge and reasoning, (iii) progressive optimization of the design with the purpose of producing and assessing alternatives, and (iv) validation and confirmation of the DSS logic for better user engagement and usability (M. Hamouda et al., 2009).

## <span id="page-24-1"></span>6.2 Main types of DSS applied to WWTP issues

78. There are four approaches adopted by Decision Support Systems for implementation of wastewater treatment plants (G. Mannina et al., 2019) as illustrated in Figure 9. These are:

- a. Life Cycle Assessment (LCA).
- b. Mathematical Model (MM).
- c. Multi-Criteria Decision Making (MCDM).
- d. Intelligent DSS (IDSS).

## <span id="page-24-2"></span>*6.2.1 Life Cycle Assessment (LCA)*

79. In the field of wastewater treatment, LCA has been increasingly applied to assess the environmental trade-offs of current technologies (Fang et al., 2016). Additionally, the environmental impact of WWTPs, including the efficiency of the processes and the services, can be assessed with cradle to grave approaches by utilization of LCA (Pasqualino et al., 2009). The main objective of LCA applications for WWTPs is to develop and quantify indicators for evaluating the global environmental consequences of WWTPs. Energy use, wastewater discharge, sludge disposal/reuse, and land occupation are the primary factors that affect the WWTP's environmental profile (Hospido et al., 2004).

80. The LCA is a standardized technique that is regulated by the ISO standards 14040 and 14044 (Lee & Jepson, 2021; Zhou et al., 2014). It is a tool that can be used to determine environmental impacts and potential consequences over the entire life cycle of a product's or system's life cycle, beginning with the raw materials and continuing all the way to disposal. Using the LCA method, decision-makers are able to locate environmentally sensitive areas and devise plans to lessen the severity of adverse effects on the surrounding environment (Lee & Jepson, 2021). Definition of goal and scope; life cycle inventory (LCI); life cycle impact assessment (LCIA); and interpretation, are the four stages that make up the LCA.



*Figure 9: Main focuses and decision support systems for WWTP (G. Mannina et al., 2019)*

81. One of the challenges of LCA is defining the system boundary because it varies greatly, with some studies covering the whole urban water system and others focusing solely on the WWTP (Corominas et al., 2013). Although plant performance can be affected by influent composition, plant size, and local climate (Lorenzo-Toja et al., 2016), the environmental performance of WWTPs is mostly based on effluent discharge and sludge application on land (Hospido et al., 2004). In addition, the sludge and solids stream of wastewater treatment accumulates substances that are both useful and hazardous, such as phosphorus and heavy metals, and these compounds need to be included in LCA analyses (Yoshida et al., 2014). Thus, any environmental assessment of a novel wastewater technology must incorporate life cycle boundaries that include the end-use of water and nutrients (Fang et al., 2016). Instead of being a measuring tool, LCA can also be used to help make decisions. The decisionmaker is provided with data from the DSS to help narrow down their alternatives (Pryshlakivsky & Searcy, 2021).

## **Example 1: Application of LCA**

The environmental impact of producing ammonium sulfate (AS) via the Haber Bosch process and recovering ammonia from the side stream of wastewater treatment plants (WWTPs) was compared using a decision support system (DSS) tool. A life cycle assessment (LCA) was applied to assess the environmental impact of ammonium sulfate (AS) fertilizer production by air-stripping ammonia from WWTP side streams with varied side stream nitrogen contents. The Intergovernmental Panel for Climate Change (IPCC) 100-year global warming potential (IPCC GWP 100a) was used to account for greenhouse gas. According to obtained results, implementing air-stripping technology at wastewater treatment plants to produce AS fertilizer has a significant potential for environmental mitigation and economic benefit. Compared to the hydrocarbon-based Haber-Bosch process, which is projected to produce 2.5 kg  $CO<sub>2</sub>e/kg AS$  in greenhouse gas emissions, air-stripping technology emits between  $0.2$  and  $0.5$  kg  $CO<sub>2</sub>e/kg$  AS (Kar et al., 2023).

# <span id="page-25-0"></span>*6.2.2 Mathematical Model (MM)*

82. Mathematical models serve as the foundation for the earliest documented DSSs. Due to the low cost of implementation, mathematical model-based DSSs are a promising tool for gaining a detailed understanding of WWTP characteristics (Mannina et al., 2016). Mathematical models may vary based on their level of complexity and details. The quantification of both direct and indirect GHG emissions (Kyung et al., 2015), as well as economic and social indicators (Gemar et al., 2018), are common components of these simplified models. When a more precise depiction of reality is needed, a detailed model should be used. However, mechanistic mathematical models (such as the activated

sludge model – ASM family) are rarely utilized because of their complexity and the need for extensive datasets (G. Mannina et al., 2019). Regarding this type of DSS, there are a number of advantages that can be highlighted. For instance, it is possible that MMs can be used to validate lab data at a proportional rate and to offer reliable estimates for commercial-scale operations (Zuthi et al., 2012) by providing a variety of potential solutions for consideration during the decision-making process (Mannina & Cosenza, 2013). In brief, stakeholders may be able to save time and money by using DSSs based on mathematical modeling to test out several approaches to a problem before implementing them at the site (G. Mannina et al., 2019).

# **Example 2: Application of MM**

A comprehensive membrane bioreactor (MBR) mathematical model, which quantifies the primary physical and biological processes was applied for wastewater treatment. The model explains the biological elimination of organic matter, nitrogen, and phosphorus, as well as greenhouse gases (carbon dioxide, CO2 and nitrous oxide,  $N_2O$ ). All of the following novel elements are taken into consideration by the model: soluble microbial product (SMP) formation/degradation due to microbial growth and endogenous respiration; interlink between SMP and membrane fouling; two-step nitrification process; N2O formation due to ammonia-oxidizing bacteria as a product of the hydroxylamine oxidation ( $NH<sub>2</sub>OH$ ) and of the nitrite ( $NO<sub>2</sub>$ ) reduction. The model was calibrated using a comprehensive calibration methodology and data from an MBR pilot plant at the University of Cape Town (UCT) (Mannina et al, 2018).

# <span id="page-26-0"></span>*6.2.3 Multi-Criteria Decision Making (MCDM)*

The Multi-Criteria Decision Making-based DSS is a combination of various criteria/methods designed with the goal of optimizing the behavior of a WWTP that employs multiple technologies and focuses attention on multiple optimization goals (Torregrossa et al., 2017). Application of MCDM-based DSS to the WWTP context is suggested when multi-objective solutions are required for more effective management of t



*Figure 9: Main focuses and decision support systems for WWTP (G. Mannina et al., 2019)*

83. he entire facility (Jiang et al., 2018). When it comes to pursuing the optimization of WWTPs, the MCDM technique in particular is one of the most powerful DSS.

84. In addition, MCDM-based DSSs are frequently combined with other DSSs to provide a more holistic solution to treatment problems (de Faria et al., 2015). For instance, Mannina et al. (2019) optimized the behavior of a membrane bioreactor pilot plant by coupling an integrated mathematical model with the Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) technique (G. Mannina et al., 2019). In order to determine the best treatment method and the most robust solution under influent uncertainties and stricter effluent limits, Castillo et al. (2016) combined a multi-criteria analysis (MCA) with an integrated mathematical model. This was done to generate a ranked shortlist of feasible treatments for three different scenarios, each of which involved a unique method of wastewater treatment (Castillo et al., 2016).

## **Example 3: Application of MCDM**

As a DSS application, alternative wastewater treatment plants (WWTPs) located in the southeast of Spain involving the two most common technologies (MBR and CAS) were evaluated by using a MCDM method. The efficiency of eleven different options for removing four pharmaceutical activated compounds (PhAC)– carbamazepine (CBZ), ketoprofen (KTP), diclofenac (DCF), and naproxen (NPX)—according to a predetermined list of seven criteria were evaluated. The TOPSIS method has been used to conduct MCDM and evaluate the available alternatives. In the evaluation of the removal efficiency of PhAC, the most relevant criteria were found as C1 (hydraulic retention time), C2 (annual mean temperature), and C3 (treatment capacity), whereas criteria C4 (technology), C5 (TSS efficiency), C6 (COD efficiency), and C7 (BOD efficiency) were less relevant, indicating that the criterion technology (C4) was not as important for the possibility of reusing wastewater. The results of the multi-criteria problem revealed a number of the most influential factors for eliminating PhAC and their significance in the design of WWTPs with clean technologies that support the circular economy, hence ensuring the correct utilization of wastewater (Fernández-López et al., 2021).

## <span id="page-27-0"></span>*6.2.4 Intelligent DSS (IDSS)*

85. The IDSS is a tool that integrates multiple methodologies, some from the Artificial Intelligence (AI) discipline and others from the fields of Statistics and Control Theory, to enhance the complicated decisions made by the final users of a WWTP. For instance, in order to avoid the adoption of sophisticated physical, chemical, and biological models, Nadiri et al. (2018) developed an IDSS that utilized supervised committee of fuzzy logic (SCFL) models as alternatives for the WWTP modeling. The fuzzy logic (FL) model predicts water quality parameters based on measurements derived from influent quality data, including pH, temperature, chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS). The SCFL model combines the water quality forecasts of individual FL models by using an Artificial Neural Network (ANN) (Nadiri et al., 2018).

#### **Example 3: Application of IDSS**

erformance is very possible (Antwi et al., 2019). Two novel feed forward back propagation Artificial Neural Networks (ANN)-based-models (8:NH:1 and 7:NH:1) combined with Box-Behnken design of experiments methodology were developed to model NH4+and Total Nitrogen (TN) removal within an upflow-sludge-bed (USB) reactor treating nitrogen-rich wastewater via Single-stage Nitrogen removal using Anammox and Partial nitrification (SNAP) process. ANN were developed by applying the response surface methodology to the process of optimizing the parameters of network design. The computational findings demonstrated that the response surface-optimized ANN architecture improved the performance of the ANN-based models. In addition, the overall performance of the generated ANN-based models demonstrated that modeling complex biological systems (such as SNAP) using ANN-based models to increase removal efficiencies, construct process management techniques, and maximize

<span id="page-27-1"></span>86. Decision Support Systems for implementation of wastewater treatment plants offer several advantages when compared with traditional strategies. Figure 10 provides a schematic comparison between the two approaches: conventional versus DSS solutions. In principle, conventional solutions exhibit several limitations including (Giorgio Mannina et al., 2019):

a. Challenges in managing the great complexity of WWTPs owing to the interaction of different components and elements (biological, chemical, physical, mechanical, etc.);

- b. Inadequate control, automation, and instrumentation in WWTPs to accommodate their dynamic nature;
- c. Lack of a thorough analysis of all possible alternatives;
- d. No prediction capability for probable alternative decision assessment; and
- e. Inability to undertake extensive application of data-based models.



*Figure 10: Decision support system for the selection of wastewater treatment technologies – conventional versus DSS solutions (Giorgio Mannina et al., 2019)*

87. The four approaches adopted by the Decision Support Systems for implementation of wastewater treatment plants, namely life cycle assessment (LCA), mathematical model (MM), Multi-Criteria Decision Making (MCDM), and Intelligent DSS (IDSS) all have their own advantages and limitations which should be accounted for prior to selection for decision making. These aspects are manifested in the ability of these individual approaches to support decision-making in terms of quality, operational, design, energy, and sustainability issues. Specific advantages and limitations of each of the four approaches are illustrated in Table 4.







88. As can be inferred, DSS can be applied as a reliable tool for selecting appropriate treatment technologies in wastewater treatment plants. It can be equally employed in conjunction with the economic, environmental, health and social considerations for recovery of water, energy and nutrients from wastewater treatment processes as tabulated in Table 3. All four DSS approaches provide for the systematic development of alternatives and support alternative analysis forecasting capacities. However, only the life cycle assessment approach allows the consideration of findings of environmental impact assessment and for making comparisons of plant layouts. On the other hand, intelligent decision support systems allow for application of data and model driven methodologies as well as artificial intelligence/statistical control methods.

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**Annex I Membrane treatment technologies**

# **Introduction**

1. Membrane technologies are considered the main and key technology for advanced wastewater reclamation and reuse strategies which allows reliable advanced treatment. Existing membranes can be classified as organic, inorganic, and inorganic-organic hybrid membranes based on the composition of the membrane materials. Examples of these organic, inorganic, and inorganic-organic hybrid membranes materials is presented in Figure A.1.



*Figure A.1: Classification of membranes based on composition of membrane materials*

2. Additionally, membranes could be also classified as isotropic and anisotropic membranes. Moreover, depending on the geometry of the membrane, it is possible to categorize the membranes as either flat sheet, tubular, capillary, or hollow fiber membranes. Each of these types of membranes is designed to be used for a specific engineering application.

3. Membrane technologies can be classified depending on their driving forces, which include osmotic pressure gradients, electrical potential, temperature, and hydraulic pressure. Wastewater is typically reclaimed and reused by the use of pressure-driven membrane separation technologies such microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) as explained below. Characteristics of pressure driven membrane processes are presented in Table A.1.

<b>Membrane</b> process	<b>MWCO</b> (kPa)	<b>Rejected</b> size $(\mu m)$	<b>Pressure</b> requirement (bar)	Average permeability (L/m <sup>2</sup> h bar)	<b>Rejected components</b>
MF	100-500	$10^{-1} - 10$	$0.5 - 3$	500	Bacteria, fat, oil, grease, colloids, organics, microparticles
UF	$20 - 150$	$10^{-3} - 1$	$2 - 5$	150	Proteins, pigments, oils, sugar, organics, microplastics
<b>NF</b>	$2 - 20$	$10^{-3} - 10^{-2}$	$5 - 15$	$10-20$	Pigments, sulfates, divalent cations, divalent anions, lactose, sucrose, sodium chloride
R <sub>O</sub>	$0.2 - 2.$	$10^{-4} - 10^{-3}$	$15 - 75$	$5-10$	All contaminants including monovalent ions

*Table A.1: Characteristics of pressure driven membrane processes (Adapted from Singh & Hankins, 2016)*

#### **Microfiltration**

4. MF membranes are of average pore radius 0.1-10 μm where transport in the process is driven by convective forces, and the target pollutants are separated by a sieving mechanism. Due to the large size of the pores, this membrane is used for rough separation of fine components with sizes between 0.025 and 10.0 μm. Therefore, in membrane-based separation and purification plants, MF is generally used as preliminary treatment stage. Although MF is frequently employed to decrease the load on UF, NF, or RO, the potential of fouling on this membrane is also quite significant. When an MF membrane module for wastewater treatment is implemented, residual macromolecules produce fouling through partial and total pore blockage (Pal, 2020).

5. The effect of membrane material on fouling is significant. Ceramic membranes are more susceptible to fouling than polymeric membranes. Again, the degree of fouling varies based on the polymer type among polymeric membranes. PES membranes are subject to more fouling than polyamide membranes. Ceramic MF membranes are superior to their polymeric equivalents when it comes to ease of cleaning, mechanical strength, disinfection, and service life. However, it is easier to fabricate polymeric membranes of various diameters for different modules than ceramic membranes. In cleaning and disinfection, ceramic membranes have a significant advantage over polymeric membranes because they are resistant to morphological change during chemical cleaning and thermal sterilization (Pal, 2020).

## **Ultrafiltration**

6. Compared to MF, UF is utilized extensively in water treatment. Almost all kinds of water contaminants can be removed from water using UF, although to various degrees, if the pollutants' diameters fall within the range of 10-50 nm. This asymmetric membrane is characterized by a value known as the MWCO, which stands for the minimum molecular weight (in Dalton) of the molecules that are maintained by the membrane at a rate of 90%.

7. Concentration polarization is a significant challenge that arises when using UF membrane. In UF, the concentration polarization effect on flux demands the application of increasing pressure in order to maintain a constant flux. Manufacturers suggest acid-base cleaning cycles and back washing to help with membrane fouling. Even while ceramic UF membranes are simpler to clean and disinfect, polymeric UF membranes have fewer problems with fouling.

#### **Nanofiltration**

8. NF membranes are a fairly new technology that fills a gap between two well-known separation processes: reverse osmosis and ultrafiltration. One of the most interesting things about NF membranes is that they are capable of letting monovalent ions, like sodium chloride, pass through while preventing divalent and multivalent ions, like sodium sulfate. In order to reduce costs and enhance the environmental impact of wastewaters, NF could play a significant role in separating valuable compounds or removing a dangerous and undesired pollutant from liquid streams (Zhao et al., 2005). NF can be applied to the removal of dissolved minerals including hardness components, sulfates, nitrates, As, Ni, Cr, F, Fe, Mn, micro-inorganic and organic pollutants, pesticides, contaminants of emerging concerns, and disinfection by-products.

#### **Reverse Osmosis**

9. RO is well-known among pressure-driven membrane processes for its up to 99.5% separating small particles including microorganisms and monovalent ions such as sodium ions and chloride ions. RO has long been at the forefront of water reclamation through the treatment of wastewater. Pollution of reused wastewater RO membrane is more challenging than RO membrane used for seawater desalination because of the dissolved organic matter in secondary effluent, which is made when biological wastewater is performed (Tang et al., 2014).

10. Tang et al. searched at the organic and inorganic forms of the deposits at different RO elements in full-scale municipal wastewater reclamation plants. On the surface of the RO membrane, the most commonly found elements were Fe, Ca, and Mg. Ca and Mg scaling could be prevented if the right antiscalants were injected. The reduction of certain specific fractions in the pre-treatment of the RO process may be beneficial in reducing membrane fouling (Tang et al., 2016).

## **Forward osmosis**

11. Forward osmosis (FO) is a membrane separation technique that is neither pressure nor temperature driven. Under osmotic pressure, FO-based technology mimics the natural osmotic transport. When water contaminants cannot be easily removed from water due to their complicated nature, it is preferable to separate the water from the contaminants. Consideration has been given to the utilization of FO to reduce wastewater discharge for wastewater reuse and zero liquid discharge technologies. Furthermore, the utilization of FO to wastewater reclamation faces several key issues, including internal concentration polarization, reverse salt flux, concentration polarization, and membrane fouling (Jung et al., 2020).

## **Integrated Membrane Processes**

12. Various combinations of these pressure-driven membrane technologies have been implemented in various wastewater treatment applications. This is applied to minimize fouling of the RO membrane and improve continuous flux maintenance. In addition, this functions as a multi-barrier treatment for removing pollutants from wastewater. In the majority of applications, MF, UF, and NF perform as RO pre-treatment phases. Rodriguez-Mozaz et al. studied on the performance of a pilot wastewater treatment system based on a MF–RO system that processed effluents of an urban wastewater treatment plant on-site (Rodriguez-Mozaz et al., 2015). The primary purpose of this work was to evaluate the viability of the MF–RO system for the removal efficiency of these contaminants, as well as to evaluate the suitability of the resulting water for numerous reuse applications.

**Annex II**

**Effect of Wastewater Treatment Technologies on Removal of Contaminants of Emerging Concern (CEC)**

## **Effect of primary treatment technologies on CECs removal**

1. Because the efficiency of treating CECs using alternative physical processes, such as sedimentation and flocculation, has been reported to be less than 10%, the physicochemical process known as sorption has emerged as the major treatment technology of choice. The term "sorption" refers to the mechanisms of both the absorption of CECs onto the lipid fraction of the primary sludge through hydrophobic interactions and the adsorption of CECs onto the surface of sludge particles mostly via electrostatic interactions. Both of these mechanisms are included in the category of "sorption." Because sorption is a technology that changes phases, the CECs transfer from the liquid phase (wastewater) to the solid phase (sludge). As a result, it can only give a temporary reduction in risk, which is why it is crucial to remember that sorption is a phase changing technology. Because the CECs removal mechanisms are not entirely understood, these approaches need additional research. It is not known whether sorption comes before degradation or the other way around. On the one hand, sorption to biosolids may be a first stage in the biodegradation process; on the other hand, CECs may subsequently desorb upon achieving adsorption equilibrium and return to the liquid phase once biodegradation has begun.

2. The physicochemical properties of CECs, the features of the sorption medium, and the operating ambient conditions all play a role in how well CECs are absorbed by the sorption medium. The persistent CECs in sludge can leach out even more during sludge treatment and/or disposal, which is a big problem that requires a careful plan for sludge disposal. So, systems based on sorption can be combined with other treatment methods to get better results.

#### **Effect of secondary treatment technologies on CECs removal**

3. Biodegradation/biotransformation and sorption are the main mechanisms that CECs are removed by secondary treatment technologies. Other mechanisms, such as photodegradation and volatilization, don't have much of an effect on how well CECs are removed. Photodegradation-based CEC removal isn't very important during secondary treatment because the amount of light is small compared to the amount of wastewater being treated, and highly concentrated particles in the wastewater block the sun. In the same way, the removal of CECs through volatilization during secondary treatment is not very important. Most places around the world use secondary biological treatment methods to get rid of CECs. Most conventional WWTPs use activated sludge processes (ASP), which are a type of secondary biological process. Other high-rate secondary biological processes include constructed wetlands, membrane bioreactors (MBRs), trickling filters, biological aerated filters (BAF), rotating biological contactors, moving bed biological reactors (MBBRs), fungal bioreactors, microalgal bioreactors, oxidation ditches, etc. In the sections, we'll talk briefly about the most common processes, like ASP and MBRs, which remove CEC more effectively than other technologies.

## *Removal of CECs in Activated Sludge Process*

4. The ability of the activated biomass that is already present in the sludge to biodegrade and biotransform the CECs is essential to the functioning of the activated sludge process. The qualities of the CECs themselves (such as their structural complexity, bioavailability, and functional groups), the properties of the sludge (such as its age and biomass activity), and the operating circumstances all have a role in the biodegradation of CECs (redox potential, SRT, HRT). For instance, linear short chain unsaturated aliphatic compounds with electron-donating functional groups are more easily biodegradable than their counterparts, branched chain saturated polycyclic compounds with electronwithdrawing functional groups. This is because electrons are donated rather than withdrawn during the degradation process. In spite of the remarkable effectiveness with which CECs are removed by ASP, there are situations in which the toxicity of CECs toward microbes presents considerable obstacles, in particular when antibiotics are being administered. Since there is a knowledge gap in connection to the presence of CECs in the sludge due to the complex matrix and the lack of sensitive analytical techniques to monitor CECs in sludge samples, the management of the secondary sludge that is

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produced during ASP (activated sludge process) is also another important issue to deal with. It is necessary to investigate the identification, measurement, and routine monitoring of reaction intermediates and transformation products of parent compounds. This is because transformation products can occasionally appear to be more harmful than the parent compounds and can revert back to them. In addition, the problems caused by the washout of biomass fraction in effluent, which leads to a low active biomass concentration and a relatively short SRT, need to be addressed in order to further improve the performance efficiency of the system. Therefore, the application of ASP in conjunction with various other treatment technologies may result in an improvement in the CECs removal efficiency.

#### *Removal of CECs in membrane bioreactors*

5. In recent years, membrane bioreactors have become increasingly popular for removing CECs from wastewater by combining the principles of biological degradation with membrane separation. The MBRs, which have evolved as an alternative treatment method to address the shortcomings of ASP, are highly effective at removing a wide variety of CECs that are notably challenging to remove using ASP or other secondary treatment technologies. Differential characteristics of MBRs, such as a longer SRT (15-80 days compared to 7-20 days in ASP), a higher biomass concentration mediated by membrane detainment, and a more significant separation between SRT and HRT with membrane retention of biomass/sludge, contribute to the system's superior CEC removal efficiency. Physicochemical parameters of CECs (size, concentration, func- tional group, charge, polarity), operating conditions, and membrane characteristics (surface roughness, surface charge, hydrophobicity, and membrane ma- terial) all play a role in the removal of CECs in MBRs (SRT, pH, temperature, and redox condition). Size exclusion, adsorption onto the membrane surface via electrostatic contact, sorption onto the biofilm layer/fouling layer generated on the membrane surface, followed by biodegradation, and hydrophobic interaction with the membrane are the primary methods by which CECs are removed in MBRs. However, biodegradation is the dominating method for removing polar CECs, while size exclusion, adsorption onto the membrane surface, or onto the biofilm layer (primarily CECs with a size smaller than membrane pore) are the primary mechanisms for removing nonpolar CECs. Additionally, UF MBRs are more effective at removing polar and hydrophilic CECs like estrone and ketoprofen than they are at removing non-polar hydrophilic CECs like phthalate.

6. There is a key drawback to MBR application in that it simply supports a separation process in which the CECs are just phase-changed but not actually removed from the environment. Permeate, a more dilute phase produced by the treatment process, and rejected effluent, a more concentrated phase produced by the CECs, are the two phases that result from the process. The concentrated phase must be processed further before being discarded. Alternative, sustainable methods of treating membrane concentrates are currently the subject of research. Sequential coupling of ASP with membrane filtration, which produced very high CECs removal efficiency, is one example. In this setup, the microorganisms in the activated sludge removed the CECs that were rejected by the membrane. Integration of membrane technology with bioelectrochemical systems (BES), also known as electrochemical membrane bioreactors, is another method (EMBR). By utilizing a three-pronged approach to treating wastewater (membrane filtration, biodegradation, and bioelectrogenesis; electricity generation by the microorganisms), EMBRs are said to be more efficient at removing CECs than MBRs and ASPs while using less energy. Most of these cutting-edge technologies, however, are still in the research and development (R&D) phase, at the pilot plant level. In addition, for future extensive usage at full scale, some constraints of MBRs such membrane fouling, high energy demand, and expensive membrane materials need to be addressed.

#### **Effect of tertiary treatment technologies on CECs removal**

7. In order to create high-quality discharge water for reuse, most WWTPs employ the tertiary or advanced treatment technologies as polishing techniques. The primary methods for CEC removal during tertiary treatment include oxidation (which can further mineralize CECs and their byproducts to CO2, H2O, and simple inorganic ions) and activated carbon (AC)-based sorption of a broad variety of

CECs from secondary wastewater (de Oliveira et al., 2020). CECs can be oxidized using a variety of oxidation processes, including ozonation, ultraviolet (UV) treatment, chlorination, photocatalysis, etc. (Yang et al., 2017) Adsorption onto activated carbon, ozonation, and hybrids of these two processes are some of the most advanced methods for removing organic micropollutants (OMPs) from wastewater effluents (Guillossou et al., 2020).

## *Use of Ozonation for CEC removal*

8. Chemical oxidation of CECs using ozone (O3) gas is known as ozonation which is one of the most promising methods to significantly cut down on the CECs present in wastewater treatment plants (Hollender et al., 2009). It is possible for ozone to react with CECs in one of two ways: either directly, as a primary oxidant, or indirectly, via hydroxyl radicals (HO<sup>-</sup>) generated as a by-product of ozone's reactivity with a subset of effluent organic matter (EfOM) such phenols and amines. Oxidation byproduct formation is a major problem associated with ozonation. The mechanisms of ozonation, which inhibit the breakdown of CECs, are sensitive to pH, temperature, and ozone doses. Insufficient ozone dosages will result in the development of transformation products or oxidation by-products rather than full mineralization. In addition, it is necessary to consider drawbacks such as high energy consumption, the cost of the approach due to the short lifetime of ozone, and interference by HO• scavengers in wastewater (P. R. Rout et al., 2021).

## *Use of Activated Carbon Adsorption for EC Removal*

9. Adsorption has also been widely explored for the removal of CECs due to its phase change mechanism, in which contaminants (adsorbates) transfer from the aqueous phase to the solid phase (adsorbent) (Rodriguez-Narvaez et al., 2017). Because of its high porosity, wide specific surface area, and, the high degree of surface contacts, active compounds (ACs) is the most commonly used adsorbent for a broad range CECs adsorption. Powder activated carbon (PAC) and granular activated carbon (GAC) are subcategories of AC based on particle size, whereas macroporous (50 nm), mesoporous  $(2-50 \text{ nm})$ , and microporous  $(>2 \text{ nm})$  are subcategories based on pore size. Effective removal of CECs from wastewater may be achieved using both PAC and GAC, although mesoporous AC was determined to be the most appropriate due to lower interference from the organic components for the adsorption active sites. The adsorption efficiency is influenced by the characteristics of CECs (molecular size, polarity, functional group, KOW, Kd, pKa), AC (particle size, surface area, pore diameter, mineral content), and environmental conditions (pH, temperature, wastewater type). Compared to ozonation, the AC-mediated adsorption of CECs has the benefits of no by-product generation and reduced WWTP energy usage. However, there is a significant requirement for primary energy in the creation of AC. Therefore, the long-term viability of AC manufacturing is a major concern. For AC manufacturing, small-scale kilns are typically used, and these have a high energy input requirement because of their low efficiency. If AC is to be produced on a large scale, it is crucial to determine the most cost-effective and environmentally friendly methods of doing so, as well as to calculate the carbon footprint of the production process. Additionally, the primary difficulty in this process is providing proper treatment and disposal for the used adsorbents that have become saturated with CECs. In order to increase the efficiency with which CECs are removed, it has been suggested that AC adsorption be used in combination with other treatments such as ultrafiltration and coagulation (P. R. Rout et al., 2021).]

**Annex III**

**Newly Emerging Treatment Technologies and Potential Green Treatment Technologies based on Nature Based Solutions**

# **PART I:**

# **Newly emerging treatment technologies which are currently under development regarding water reclamation**

# **1. Microalgal wastewater treatment (MWWT)**

Phytoremediation is a green technique that removes persistent contaminants from wastewater and makes it suitable for re-injection into the water supply system. The utilization of microalgae-based wastewater treatment systems has gained considerable attention from the research community, and in collaboration with industry, a variety of wastewater technologies and methods have been created to meet the sector's specific needs [1]. Additional technological needs for photobioreactor (PBR) systems are related with the utilization of microalgae in WWT. This is mostly due to photoautotrophic activities, for which a significant amount of light energy and CO2 is required. In general, PBRs for microalgae are classified as either open or closed systems. [2]. The optimization of growth factors such as operational (PBR, aeration), nutritional (carbon, nitrogen, and other nutrient sources), and environ-mental (light intensity, temperature, and day-night cycle) facilitated the growth of microalgae and municipal wastewater treatment. Recent advances in the comprehension of both remediation methods (director indirect) will aid in the development of large-scale municipal wastewater treatment technologies. Creating mutually supportive consortia with other organisms and immobilizing algal cells resulted in higher removal efficiency.

Since the 1960s, the use of algae for wastewater reclamation has been investigated, and circular blue bioeconomy concepts are becoming increasingly popular. Microalgae are utilized in the treatment of wastewater due to their ability to absorb organic and inorganic carbon, nitrogen, and phosphorus, while concurrently accumulating biomass and lowering N, P, and chemical oxygen demand (COD) in the wastewater. Microalgae are not yet utilized on a wide scale for the treatment of wastewater; nonetheless, there are significant examples of commercial systems that employ microalgae. Algae Systems LLC of the United States has a photo-bioreactor (PBR) designed to work with environmental light and CO2 to remove nutrients downstream of their source (Novoveská et al., 2016). Algal Enterprises (Australia) has developed a solution for a variety of wastewaters that consists of a closed PBR system paired with an anaerobic digestor to produce biogas. Utilizing open raceway ponds enriched with CO2 for the removal of nitrogen and phosphorus from municipal wastewater and the production of biomass for biofuels. These are examples of commercial systems based on microalgae cultures suspended in water. For the treatment of smaller volumes, immobilized systems are also commercially available. Companies such as HydroMentia, OneWater, and Gross-Wen Technologies market wastewater treatment solutions based on immobilized microalgae (or a combination of microalgae and bacteria) in various configurations [3]. However, microalgal-based wastewater reclamation presents problems, such as the selection of growing conditions (primarily light intensity, light time, and temperature) and the harvesting procedure. In any biotechnological application involving microalgae, harvesting remains one of the primary barriers that must be investigated further. Current harvesting approaches in wastewater treatment are either costly, time-consuming, or both, and could be improved based on the bioreactor or culture system selected for the wastewater treatment process. Despite the fact that microalgae can contribute to a circular bioeconomy, additional study and development are necessary to overcome the current obstacles [4].

# **2. Microbial fuel cells (MFCs) for wastewater treatment**

Conventional wastewater treatment technologies were burdened by high operational costs and energy consumption, as well as environmental contamination. Traditional wastewater treatment technologies are projected to cost approximately 3% of worldwide electricity demand, with effluent disposal (i.e.

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sludge disposal) accounting for 50% of the entire wastewater treatment cost. Ineffective conventional wastewater treatment also results in the emission of greenhouse gases and other toxic dissolved compounds, such as phosphates and ammonia. Microbial fuel cells are the most effective method for combating these issues. By biodegrading the organic materials in wastewater and lowering the chemical oxygen demand (COD), it promotes environmental sustainability, low energy consumption, and cost by eliminating effluent disposal. MFCs primarily consist of anodic and cathodic chambers separated by a proton exchange membrane (PEM) or salt bridge. As biocatalysts, microorganisms oxidize the organic substrate at the anode, sequestering protons and electrons. An external circuit directs electrons to the cathodic chamber, while the PEM delivers protons to the cathodic chamber. Therefore, the successful reduction reaction takes place in the cathodic chamber when protons and electrons combine with oxygen to produce water. Exoelectrogens are the name given to the microorganisms used as biocatalysts due to their outstanding properties. As they are capable of transferring electrons to the anode surface and catalyzing the reduction of electron acceptor (oxygen) at the cathode. Organic wastewater is one of the best substrates for bioremediation since it is nutrientrich and abundant throughout the year. It consists of effluents from municipal, industrial, and other sources, which are regarded as the primary energy source for power generation [5].

MFC applications in wastewater treatment offer numerous benefits, including long-term sustainability, utilization of renewable resources, degradation of organic and inorganic waste, bio-hydrogen production, and removal of chemicals such as nitrates, among others. To participate in large-scale implementation and exploitation of MFC technology for electricity production, the electrochemically active microbial community needs an in-depth understanding of its solution chemistry. These systems have generated power densities ranging from 2 to 20 mW/m2 in ideal laboratory circumstances. However, the amount of energy derived from biomass by microbial activities is extremely low. It has not yet attained its maximum performance in terms in pilot-scale units. In addition, it has been emphasized that the efficiency of specific MFC applications in wastewater treatment will be contingent on the amount and biodegradability of organic matter in the effluent, the temperature of the wastewater, and the lack of hazardous chemicals. Environmental pressure and the demand for renewable energy sources will continue to drive the development of this technology to the point where it can be used on a large scale. While highly effective MFCs on a large scale are not now available, the technology shows enormous promise, and engineers and scientists will certainly overcome important difficulties in the near future [6]. Recently, MFC-based hybrid technologies such as Sediment MFC (SMFC), Membrane-bioreactor MFC (MBR-MFC), constructed-wetland MFC (CW-MFC), MFCbased denitrification systems, Desalination MFC (DS-MFC), etc., have been developed. CW-MFC, SMFC, and DS-MFC offer different possibilities for waste-water treatment, whereas MBR-MFC can produce renewable electricity. Nonetheless, the greatest challenge is to improve them on a wider scale and minimize their cost while maximizing their production. Therefore, research must be conducted to improve the stability, performance, and power output of these hybrid technologies for them to soon be economically and practically feasible [5].

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# **PART II:**

**Potential green technologies based on biotechnology as well as potential use of nature-based solutions that can be applied for material recovery and water reclamation**

Even the low ammonium and hyposalinity tolerance of marine microalgae limits their usage in urban wastewater (UWW) treatment, a recent study shown that this challenge can be surmounted by introducing a zeolite-based adsorption phase to create an acceptable UWW stream utilizing the marine microalgae *Amphidinium carterae*. Secondary-treated urban wastewater was obtained from the "Bobar" sewage treatment plant in Almeria, Spain in this study. It is possible to use marine organisms such as *Amphidinium carterae* in a sustainable process to produce speciality metabolites (such as amphidinols, ca- rotenoids, and PUFAs) from the ammonium present in zeolite-treated UWW. By readjusting the salinity of the culture media using brine streams from saltwater desalination plants, regenerating the zeolites with NaCl, and using the desorbed ammonia as a fertilizer, this study demonstrates that the technique outlined here provide significant environmental benefits (López-Rosales et al., 2022).

The capacity of the central WWTP in the Italian municipality of Jesi is required to be increased from 15,000 to 60,000 people equivalents. At the Jesi WWTP, they used a natural-based solution that involved tertiary treatment using a free water surface (FWS) stage that covered 5 hectares. A sedimentation pond with a volume of  $5,000 \text{ m}^3$  and a subsurface horizontal-flow treatment wetland (HFTW) of 1 hectare were installed between the WWTP effluent and the FWS. Periodically, the collected sludge in the sedimentation basin is pumped into a wet woodland planted with Populous alba. The WWTP's performance data demonstrates that the WWTP has achieved the desired discharge levels for the Esino River for all parameters considered under Italian law (TSS 35 mg/L, COD 125 mg/L, BOD5 25 mg/L, ammonium 15 mg/L, nitrates 20 mg/L, nitrites 0.6 mg/L, total phosphorus 2 mg/L, chlorides 1,200 mg/L, sulphates 1,000 mg/L) (Kadlec and Wallace, 2009).

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