# Investigation of the agricultural reuse potential of urban wastewater and other resources derived by using membrane bioreactor technology within the circular economy framework

**Laura Antiñolo Bermúdez[1*], Verónica Díaz Mendoza[1], Juan Carlos Leyva Díaz[1], Jaime Martín Pascual[1], María del Mar Muñio Martínez[2] and Jose Manuel Poyatos Capilla[1]**

[1]Department of Civil Engineering and Institute of Water Research, University of Granada, Granada, Spain

[2]Department of Chemical Engineering and Institute of Water Research, University of Granada, Granada, Spain

*Corresponding author

*lantinolo@ugr.es; vdiaz@ugr.es; jcleyva@ugr.es; jmpascual@ugr.es; mmunio@ugr.es; jpoyatos@ugr.es*

## Abstract

The European Union, as delineated in Regulation (EU) 2020/741, sets forth minimum criteria for the reuse of wastewater. Directive 86/278/CEE sets the regulations for the reuse of sewage sludge in agriculture. This study aimed to investigate the treated water derived from a pilot plant situated in Granada, Spain, that utilizes membrane bioreactor technology to process real urban wastewater with the quality standards necessary for agricultural reuse. Additionally, the study evaluated the utilization potential of other resources generated during wastewater treatment, including biogas and biostabilized sludge. The pilot plant incorporated a membrane bioreactor featuring four ultrafiltration membranes operating continuously alongside a sludge treatment line operating in batch mode. The pilot plant operated during four cycles, each with distinct hydraulic retention times (6 hours and 12 hours) and variable mixed liquor-suspended solids concentrations (ranging from 2688 mg $L^{-1}$ to 7542 mg $L^{-1}$). During these cycles, the plant was doped with increasing concentrations of emerging contamination compounds (diclofenac, ibuprofen, and erythromycin) to test their effect on the resources derived from the treatment. Subsequently, a tertiary treatment involving an advanced oxidation process was applied to the different water lines, which left the wastewater treatment plant for a period of 30 minutes and utilized varying concentrations of oxidant. The results indicate that the effluent obtained meets the required quality standards for agricultural use. Therefore, there is potential to use this waste as a resource, which is in line with the principles of the circular economy. Furthermore, the other resources generated during the treatment process, such as the biogas produced during the digestion process and the biostabilized sludge, have the potential to be used as resources according to the circular economy indicators.

**Keywords:** circular economy; membrane bioreactor; pharmaceutical compounds; reuse; urban wastewater treatment.

## 1. Introduction

The identification of emerging contaminant compounds, notably pharmaceutical substances, has become evident in global water systems (Garduño-Jiménez et al., 2023; Kookana et al., 2020). The introduction of such compounds into these facilities has the potential to disrupt their functionality, resulting in possible inadequate wastewater treatment processes. Furthermore, it should be noted that climatic events in recent years have caused water scarcity in regions not historically affected and exacerbating existing shortages in areas already grappling with inadequate water resources (Duque-Acevedo et al., 2020). Additionally, in recent decades, the global population has exhibited a sustained period of growth. The consumption of water by the general population, in conjunction with the various industrial production activities that are associated with human activity, has resulted in the generation of substantial and progressively increasing volumes of urban and industrial wastewater (Rajesh Banu et al., 2020). In this context, the circular economy emerges as a solution based on the idea of reducing waste and extending the useful life of resources, focusing on efficiency and reducing consumption of raw materials and pollution (Lehmann et al., 2022). This necessitates a comprehensive study of treated water reuse for agricultural applications. Within this context, the European Union (EU), through Regulation (EU) 2020/741, delineates minimum criteria for wastewater reuse for agricultural purposes. The directive emphasizes the interest in promoting the circular economy principles, imposes stringent quality standards for reused water in agriculture, and concurrently diminishes the reliance on fertilizer applications. In addition, wastewater treatment plants also produce other wastes that need to be treated, such as those produced in the sludge line. The European Parliament's Waste Framework Directive (EU) 850/2018 focuses on the management, reduction, and effective recovery of economically valuable waste. Directive 86/278/CEE sets regulations for the reuse of sewage sludge in agriculture.

Membrane bioreactors are a technology that is proving effective against contaminants that cannot be removed by conventional treatment technologies. This technology, which is commonly used to filter pathogens, has great potential to reduce emerging organic and microbial contaminants (Verlicchi et al., 2023). It is also presented in some cases as a technology with removal efficiencies of around 100% due to its longer cell retention time (Kundan et al., 2022). Wastewater treatment plants (WWTPs) that use membrane bioreactor technology demonstrate the attainment of high-quality effluents (Bonetta et al., 2022). The integration of membrane bioreactors with tertiary chemical treatments, such as advanced oxidation processes (AOPs), is currently being investigated. This tertiary treatment can rapidly oxidize and completely degrade organic pollutants (Gopalakrishnan et al., 2023). One of the most studied AOPs for wastewater treatment is the $H_2O_2$/UV process. An $H_2O_2$/UV system can completely mineralize any organic compound, reducing it to $CO_2$ and water (Antiñolo Bermúdez et al., 2021). The combined use of AOPs as a tertiary treatment in wastewater treatment plants can provide mechanisms for the biodegradation of contaminants, thus preventing their release into the environment.

Throughout the treatment regimen, valuable resources are concurrently generated, including biogas from sludge digestion and biostabilized sludge. The biostabilized sludge can be used as fertilizer or an agricultural soil conditioner. In addition, the volume of activated sludge from wastewater treatment plants is expected to increase significantly in the coming years due to the large-scale construction of wastewater treatment plants (Lu et al., 2023), making the study and optimization of this process of particular interest. This approach underscores the potential for resource recovery and sustainable practices within wastewater treatment.

The EU, like most governments around the world, focuses on the quality of its resources. Directive 2008/105/EC, which includes emerging pharmaceutical compounds such as anti-inflammatories and antibiotics, monitors substances that are not currently subject to phase-out legislation. Nevertheless, these substances have been the subject of investigation and have been demonstrated to be present in rivers, lakes, aquifers, and natural environments. Consequently, they may present a certain risk in the long term. Therefore, the study of their elimination is essential to prevent their entry into ecosystems.

The aim of this investigation was to evaluate the efficiency of a MBR-AOP system in generating high-quality effluent with the potential to be reused in agricultural applications. This study also examined the potential of other generated wastes to be utilized as resources, such as biogas and biostabilized sludge. To this end, the recoverable resources generated by a semi-technical pilot plant with membrane bioreactor technology fed with real urban wastewater, which was also subjected to different pharmaceutical doping, were evaluated. In pursuit of this aim, an assessment was conducted on the effluent quality and potential utilizable resources, employing circular economy indicators. The plant was doped with increasing concentrations of three pharmaceutical compounds of emerging concern, namely ibuprofen, erythromycin, and diclofenac, under a range of operational conditions. These conditions included four operating cycles, each with two hydraulic retention times (HRT) of 6 and 12 hours, as well as different mixed liquor-suspended solids (MLSS) concentrations. Under these conditions, the quality of the water intended for use, the potential of the excess sludge, and its energy potential in the digestion of the sludge line will be evaluated with circular economy indicators.

## 2. Materials and methods

## 2.1 Pilot plant

The pilot-scale urban wastewater treatment plant employing membrane bioreactor technology was located at the Los Vados WWTP (Granada, Spain). This plant treated urban wastewater from the primary settling. The system comprises a cylindrical mixing tank equipped with mechanical stirring, linked to a rectangular bioreactor with an 85 L capacity. The bioreactor contains four ultrafiltration membrane modules with a total filtration surface area of 3.72 $m^2$. Each membrane module has an individual surface area of 0.93 $m^2$ and a pore size of 0.04 µm (ZW-10 from Zenon). The membranes are constructed from polyvinylidene fluoride (PVDF) and feature an outside/in hollow-fiber configuration. Each module has a drained weight of 1.9 kg and a wet weight of 2.1 kg, with a permeate hold-up volume of 0.13 L. The plant was operated for four cycles under the specified operating conditions, as outlined in Table 1.

**Table 1.** Operation conditions of mixed liquor suspended solids (MLSS), hydraulic retention time (HRT), and solids retention time (SRT) in each cycle for the steady state.

| Cycle | HRT (h) | MLSS (mg $L^{-1}$) | SRT (day) |
|---|---|---|---|
| 1 | 6 | 5940 ± 515 | 22.3 |
| 2 | 6 | 7542 ± 1730 | 10.7 |
| 3 | 12 | 5967 ± 485 | 38.5 |
| 4 | 12 | 2688 ± 744 | 36.5 |

The typical operational transmembrane pressure (TMP) ranges from 10 kPa to 50 kPa, with a maximum TMP of 62 kPa. The flow rate during operation was 4.25 L $m^{-2}$ $h^{-1}$ for cycles 1 and 2 and 2.12 L $m^{-2}$ $h^{-1}$ for cycles 3 and 4. Filtration in these modules was conducted using a peristaltic pump in a combined cycle of 9 minutes and 35 seconds of filtration, followed by 25 seconds of backwashing. The filtration process was initiated by drawing fluid from the external surface of the membrane into the internal compartment via a suction mechanism. The membrane tank was continuously aerated to mechanically clean the membrane surfaces, maintain aerobic conditions, and ensure the homogenization of the mixed liquor. The air flow rate was 226.52 L $min^{-1}$ (56.63 L $min^{-1}$ per membrane module), with a dissolved oxygen set point of 1.5 mg $L^{-1}$. Once the set point was reached, aeration ceased and resumed when the dissolved oxygen level dropped below half of the set point. The system included a recirculation stream rate that was 50% higher than the effluent current from the membrane tank to the mixing tank, which ensured a constant MLSS concentration. Figure 1 shows a diagram of the pilot plant and the sludge line.

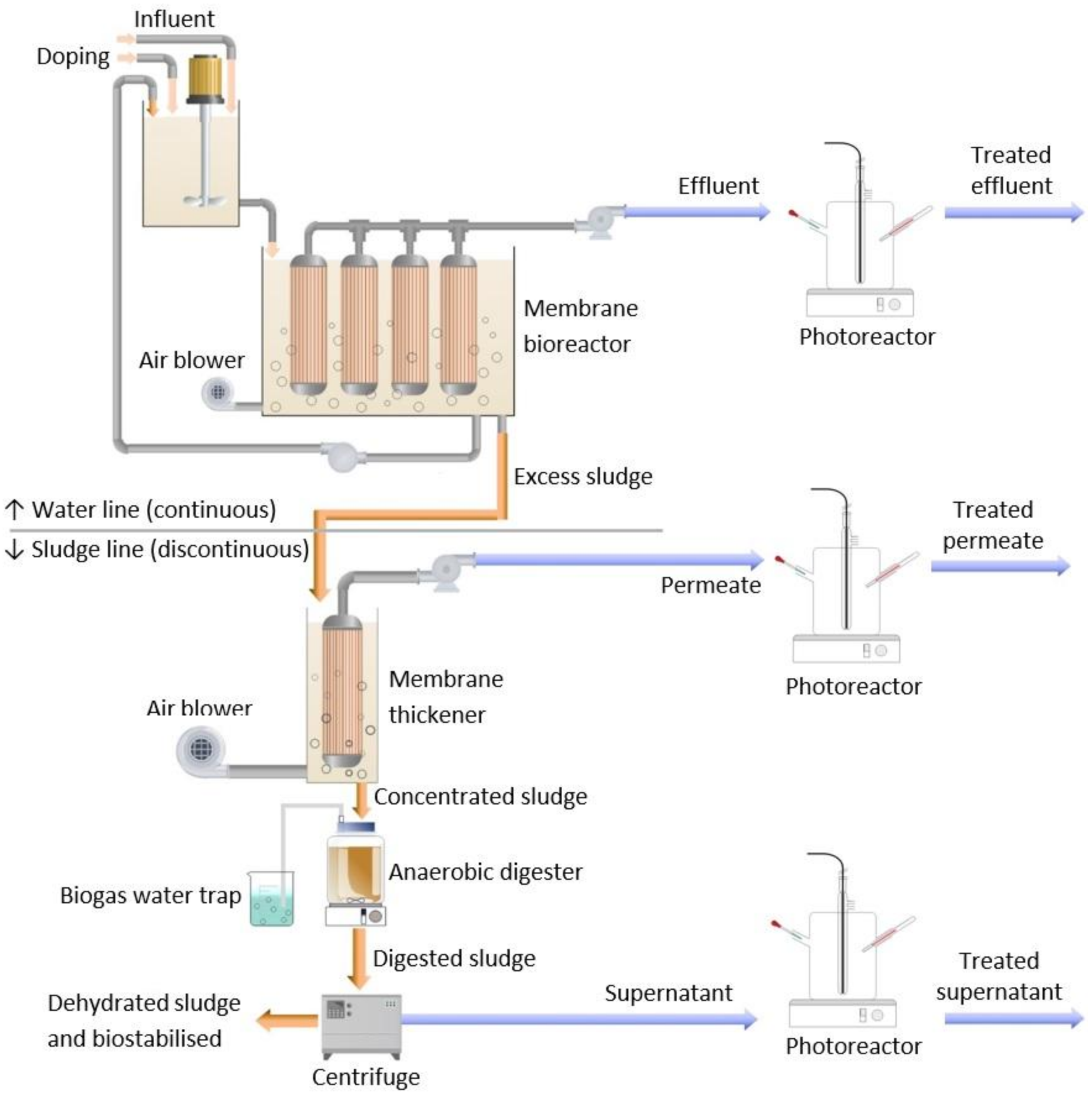


**Figure 1.** Diagram of the pilot plant that used membrane bioreactor technology.

Once a stable state had been achieved, a purge flow was initiated to extract waste sludge from the system. The pilot plant representing the water line was operated continuously across four cycles with modified operational parameters, specifically the MLSS concentration and the HRT.

The sludge line operated with daily sludge purged from the water line in batch mode. The sludge was concentrated in a membrane thickener, resulting in a concentration of 20.0% (v/v). The thickening process occurred in a vertically oriented, aerated circular tank with a total volume of 6.7 L and an effective volume of 4.32 L. A hollow-fiber microfiltration membrane with an overall surface area of 0.10 $m^2$ was immersed in the aforementioned tank. The membrane operated in a series of cycles of suction and backwashing, with each cycle optimized according to the ideal TMP (10–50 kPa). The hollow fibers of the membrane were composed of PVDF with an internal support made of braided polyester. Subsequently, the thickened sludge was transferred to a laboratory-scale digester, which was housed in a thermostatically controlled refrigerator for digestion. The digester was agitated under anaerobic conditions and included a water trap to capture the biogas produced. The temperature was maintained at a constant 32.5°C using a controller situated within the thermostatic refrigerator. The digestion process was allowed to continue for a period of 28 days to ensure that the sludge was completely degraded. Subsequently, centrifugation was employed to separate the liquid and solid phases of the digestate, which had been produced following digestion. This semi-technical scale pilot plant refers to a fully autonomous and functional plant that is a reduced-scale industrial plant located outdoors, just like an industrial scale plant. This scaling will provide data that is closer to reality than the laboratory-scale plant would provide. A similar study was carried out by analyzing a plant with the same characteristics but scaled up to a larger plant. The results showed that the removal rates of chemical oxygen demand (COD), fifth-day biological oxygen demand ($BOD_5$), and total suspended solids (TSS) parameters were maintained. Furthermore, from a kinetic point of view, there was an improvement in the heterotrophic biomass present in the membrane bioreactor. A significant increase in cell retention time in the system was also observed (Leyva-Díaz et al., 2013).

The samples subjected to advanced oxidation processes in each cycle were effluent, supernatant, and centrifuge reject water, thereby encompassing all water outlets of the integrated water treatment process.

**2.2 Dosage of pharmaceuticals in cycles**

The pharmaceuticals chosen for this study were diclofenac, ibuprofen, and erythromycin. The selection criteria included the nature of the compounds, ensuring that only one antibiotic was included. A single antibiotic was selected for investigation to identify the potential effects it may have on the plant and to differentiate its effects from those of anti-inflammatory compounds. Erythromycin was selected for analysis due to its inclusion on the second 2018 List of Priority Substances in the field of water policy (Directive 2008/105/EC), derived from Directive 2013/39/EU. Ibuprofen and diclofenac were selected for examination because of their high prevalence and widespread usage. Wastewater treatment plants that employ conventional methods achieve an average removal efficiency of 65.6% for erythromycin (Ping et al., 2022). Nonsteroidal anti-inflammatory pharmaceuticals, such as diclofenac and ibuprofen, are the pharmaceuticals most frequently detected in water sources (Wijaya et al., 2020; Antiñolo Bermúdez et al., 2023). The dosing criteria for diclofenac and erythromycin were selected based on their water solubility. Once the steady state was reached, three dosing cycles were performed in each cycle. The first cycle was conducted at a concentration 2.5 times lower than the solubility value, the second at a concentration equal to the solubility value, and the third at a concentration four times the solubility value. In the case of ibuprofen, due to its high water solubility, it was deemed unnecessary to utilize water solubility to establish the dosing criteria. Consequently, the dosage values were based on the highest concentration of ibuprofen recorded in wastewater worldwide, as determined by previous research (Tayo et al., 2018). A continuous dosage regimen was maintained throughout the development of the cycles in the pilot plant, with regard to pharmaceuticals. Table 2 shows the concentrations of pharmaceutical products for each dosing in each cycle.

**Table 2.** Concentration of pharmaceutical compounds for each dosing.

| | Ibuprofen | Diclofenac | Erythromycin |
|---|---|---|---|
| Dosing 1 (mg $L^{-1}$) | 0.06 | 0.95 | 0.58 |
| Dosing 2 (mg $L^{-1}$) | 0.13 | 2.37 | 1.44 |
| Dosing 3 (mg $L^{-1}$) | 0.56 | 9.48 | 5.76 |

Water solubility (25ºC) of erythromycin: 1.44 mg $L^{-1}$. Water solubility (25ºC) of diclofenac: 2.37 mg $L^{-1}$.

To ensure the correct dissolution of the pharmaceuticals, they were initially dissolved in 100 mL of water, where they were vortexed for 5 minutes. They were then brought to a volume of 30 L, which were dosed together with the effluent in a mixing tank at the flow rate set for each cycle according to the established HRT.

## 2.3 Analytical methods

During the operation of the plant in the four cycles studied and its different doping phases, samples of influent, effluent, and bioreactor were taken daily from the pilot plant (continuous water line) to characterize the wastewater and the operation. The following parameters were tested: COD, $BOD_5$, TSS, pH, conductivity, temperature, color analysis, and turbidity. Control analyses for $BOD_5$, COD and TSS were carried out according to Standard Methods (Metcalf et al., 2004). Turbidity measurements were conducted in accordance with the specifications outlined in the UNE-EN ISO 7027-1:2016 standard. Temperature and conductivity measurements were obtained with a

Crison CM 35® meter (Barcelona, Spain). The pH was determined using a Crison pH 25® meter (Barcelona, Spain). Absorbance measurements were conducted at various wavelengths on a Thermo Helios Gamma 9423 UVG 1002E spectrophotometer. Color measurements were conducted in accordance with the methodology outlined in Method B of the UNE-EN ISO 7887:2012 standard.

For the anaerobic digestion of the sludge produced in the pilot plant in the four cycles of operation, four digesters were used per cycle, corresponding to the reference (digestor 1), doping 1 (digestor 2), doping 2 (digestor 3), and doping 3 (digestor 4). Throughout the digestion process, all digesters were subjected to a series of tests for COD, TSS, pH, conductivity, temperature, alkalinity, and volatile fatty acids. The methodologies delineated by the American Public Health Association (APHA) (Association et al., 2022) were employed to determine volatile fatty acids and alkalinity.

The permeate from the thickening phase of the activated sludge prior to digestion, as well as the rejects from the centrifugation phase following digestion of the sludge, were subjected to a color test. The color test was used to ascertain the evolution of the color of the sample following the AOP, so the sample was measured both before and after the AOP test. A series of spot tests for *Escherichia coli* was conducted using the membrane filtration method outlined in the DifcoTM manual (Gómez Nieto & Hontoria García, 2003). The method entails the filtration of the sample through a 0.45 µm membrane and subsequent incubation at 44°C on plates with Endo Agar as the culture medium. Furthermore, chromatographic detection of nitrogen and phosphorus was also carried out. Two ion chromatographs were employed in this study: a Metrohom ECO IC plus 919 IC ion chromatograph with autosampler and a Metrohom Compact IC

761 ion chromatograph. The analytical method employed was high-performance liquid chromatography (HPLC) with a triple quadrupole mass spectrometry detector.

The advanced oxidation process was conducted using a UV-Consulting Peschl® photochemical reactor (Mainz, Germany). The reactor has a capacity of 0.8 L. The photoirradiation source is a medium-pressure mercury vapor lamp with an emission spectrum in the ultraviolet range above 190 nm and a power output of 150 W. The reactor is equipped with stirring to ensure thorough mixing and is insulated by a cylindrical quartz tube surrounded by a cooling jacket. The cooling system, which employed a cold-water bath, ensured that the photoreactor operated at a constant temperature of 20°C. The samples underwent $H_2O_2$/UV treatments, each lasting 30 minutes, utilizing three progressively higher concentrations of $H_2O_2$: 25 mg/L, 50 mg/L, and 100 mg/L. During these experiments, aliquots were collected at specific time intervals of 0 minutes, 10 minutes, 20 minutes, and 30 minutes to monitor the reaction progression.

Furthermore, tests were conducted to ascertain the nitrogen and phosphorus concentrations present in the plant effluent across the different operational cycles. The influent and effluent samples were analyzed using a Metrohm ECO IC autosampler ion chromatograph coupled with a 919 IC and a Metrohm Compact IC 761 ion chromatograph. The analytical method employed was HPLC equipped with a triple-quadrupole mass spectrometry detector (Monteoliva-García et al., 2019b).

### 2.4 Circular economy indicators

To provide a comprehensive evaluation of the wastewater treatment process, a series of indicators were established to assess the quality of the water, the quality of the sludge, and the production of biogas. Once the results from the circular economy indicators were calculated and analyzed, the suitability of the treated water for reuse in agricultural irrigation, in terms of resource recovery, was assessed at various stages of the treatment process. The potential of the biostabilized sludge produced was also assessed.

#### 2.4.1 Circular economy indicators for water

Indicator of reducing matter removal efficiency ($I_{RECOD}$)

Although this indicator does not refer to the circular economy as such, it does indicate the overall efficiency of the wastewater treatment plant. This indicator is calculated using Equation 1 (Bermúdez et al., 2022):

$$I_{RECOD} = \frac{Q_w(COD_{in} - COD_{eff})}{10^6}\left(\frac{Kg\ O_2}{day}\right) \quad [1]$$

Where $Q_w$: wastewater flow rate (L $day^{-1}$)
$COD_{in}$: chemical oxygen demand concentration in the influent (mg $L^{-1}$).
$COD_{eff}$: chemical oxygen demand concentration in the effluent (mg $L^{-1}$).

Indicator of recovery of water in the treatment process ($I_{W,R}$):

This indicator analyses the percentage of water that is recovered in the entire water treatment process, including the water line and the sludge line. This indicator is calculated using Equation 2 (Bermúdez et al., 2022):

$$I_{W,R} = \frac{Q_{eff} + Q_p + Q_s}{Q_w} \cdot 100\ (\%) \quad [2]$$

Where $Q_{eff}$: effluent flow rate in water line (L $day^{-1}$).
$Q_p$: flow rate permeate from the sludge thickener (L $day^{-1}$).

$Q_s$: flow rate supernatant from digester sludge centrifugation (L day$^{-1}$).

Indicator of effluent inorganic content for nitrogen ($I_{EIC(N)}$) and for phosphorus ($I_{EIC(P)}$):

Wastewater contains significant concentrations of nutrients such as nitrogen and phosphorus, which, if discharged into the environment, can lead to excessive algal growth, known as eutrophication. This results in adverse effects such as poorer water quality habitats and food sources, as well as reduced concentrations of dissolved oxygen and its availability for aquatic life (Cao et al., 2022). Given their capacity to exert a significant impact on the environment, the discharge concentration of these substances is subject to legislative regulation (Directive 98/15/CE). Nevertheless, they are a valuable compound in agriculture, and the potential for reuse of these compounds in the recovery of treated water is a significant benefit. These indicators are calculated using Equation 3 and 4 (Preisner et al., 2020)(Bermúdez et al., 2022):

$$I_{EIC(N)} = N_{eff} \cdot Q_{eff} \ \left(\frac{mg}{day}\right) \qquad [3]$$

$$I_{EIC(P)} = P_{eff} \cdot Q_{eff} \ \left(\frac{mg}{day}\right) \qquad [4]$$

Where $N_{eff}$: inorganic nitrogen concentration in the effluent (mg L$^{-1}$).

$P_{eff}$: inorganic phosphorus concentration in the effluent (mg L$^{-1}$).

### 2.4.2 Circular economy indicators for sludge

Indicator of the amount of sludge recovered as a function of sludge produced ($I_{SG,\%R}$):

This indicator is employed to ascertain the proportion of biostabilized sludge recovered at the conclusion of the treatment process in the sludge line in relation to the total quantity generated in the water line during the water treatment process. It is calculated using Equation 5 (Molina-Sánchez et al., 2018):

$$I_{SG,\%R}(\%) = \frac{m_{SG,R}}{m_{SG,T}} \cdot 100 \qquad [5]$$

Where $m_{SG,R}$: sludge flow rate recovered during the water treatment process (kg day$^{-1}$).
$m_{SG,T}$: sludge flow rate produced during the water treatment process (kg day$^{-1}$).

Indicator of technological nutrient performance for recovered sludge ($I_{SG,R}$):

This indicator differs from the previous one in that it shows the quantity of sludge recovered during the treatment of wastewater in relation to the volume of wastewater treated. It is calculated using Equation 6 (Bermúdez et al., 2022):

$$I_{SG,R} = \frac{m_{SG,R}}{Q_{eff}} \quad \left(\frac{kg}{L}\right) \qquad [6]$$

Where $m_{SG,R}$: sludge flow rate recovered during the water treatment process (kg day$^{-1}$).

### 2.4.3 Circular economy for biogas produced

The COD of the digester is monitored to calculate the biogas produced during digestion. For anaerobic digestion systems in general, the methane production in relation to the COD removed is 4 mg COD removed per mg methane (i.e. 1 mg methane is produced for every 4 mg COD removed). The mass of methane is one-quarter of the mass of COD removed in the process (35°C and 760 mm Hg) (Gobernment of Spain, 2007). The maximum daily $CH_4$ (L biogas Kg$^{-1}$ sludge day$^{-1}$) was calculated from the daily quantity of COD removed per kilogram of sludge digested.

Biogas indicator of biogas generation potential in relation to sludge mass flow rate ($I_{MDP}$):

This indicator is employed to ascertain the potential of the sludge to generate biogas during anaerobic digestion. The result provides information about the maximum daily production of biogas. It is calculated using Equation 7:

$$I_{MDP} = \frac{0.35 \cdot COD_R}{\rho_{sludge}} \quad \left(\frac{\text{L } CH_4}{\text{Kg Sludge}}\right) \qquad [7]$$

Where $COD_R$: chemical oxygen demand per day during the anaerobic digestion.

$\rho_{sludge}$: sludge density in anaerobic digestion (by default 1)

Efficiency of biogas transformation into electric energy ($E_b$):

During the anaerobic digestion process, biogas is produced, which is a resource that can be utilized to generate electrical energy that can then be employed in internal combustion engines. Approximately 6.5 kWh of energy is produced from one $m^3$ of biogas, with an estimated 35% biogas conversion efficiency (Salguero-Puerta et al., 2019). This indicator is calculated using Equation 8:

$$E_b = 6.5 \cdot q_b \cdot 0.35 \quad \left(\frac{\text{kWh}}{\text{day}}\right) \qquad [8]$$

Where $E_b$: energy obtained from biogas (kWh $day^{-1}$).

$q_b$: volumetric flow of biogas obtained by the anaerobic digestion ($m^3$ biogas $day^{-1}$).

## 3. Results and discussion

### 3.1 Pilot plant reuse options

The pilot plant´s operating efficiency data for the different duty cycles and the doping carried out within them are shown in Table 3.

**Table 3.** Operation efficiencies data for the different cycles.

| Cycle | | Influent $BOD_5$ ($mgO_2\,L^{-1}$) | Influent COD ($mgO_2\,L^{-1}$) | Influent TSS ($mg\,L^{-1}$) | Effluent $BOD_5$ ($mgO_2\,L^{-1}$) | Effluent COD ($mgO_2\,L^{-1}$) | Effluent TSS ($mg\,L^{-1}$) | $BOD_5$ Removal (%) | COD Removal (%) | TSS Removal (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Dosing 1 | 228 ± 43 | 415 ±67 | 89 ± 24 | 2 ± 2 | 25 ± 15 | 4 ± 3 | 99.0 ± 1.0 | 93.5 ± 4.9 | 94.4 ± 6.0 |
| | Dosing 2 | 342 ± 50 | 575 ± 100 | 121 ± 33 | 3 ± 1 | 23 ± 18 | 3 ± 1 | 99.0 ± 0.2 | 95.6 ± 3.7 | 97.2 ± 1.4 |
| | Dosing 3 | 254 ± 29 | 488 ± 31 | 98 ± 2 | 1 ± 1 | 21 ± 13 | 2 ± 1 | 99.6 ± 0.4 | 95.8 ± 2.5 | 98.0 ± 1.3 |
| 2 | Dosing 1 | 282 ± 18 | 535 ± 120 | 107 ± 34 | 8 ± 5 | 63 ± 37 | 7 ± 7 | 97.0 ± 2.1 | 88.2 ± 5.4 | 94.0 ± 4.1 |
| | Dosing 2 | 242 ± 44 | 476 ± 73 | 80 ± 6 | 7 ± 5 | 58 ± 17 | 2 ± 2 | 97.0 ± 2.1 | 87.7 ± 3.1 | 97.0 ± 2.7 |
| | Dosing 3 | 242 ± 22 | 458 ± 24 | 89 ± 9 | 5 ± 3 | 50 ± 20 | 5 ± 3 | 97.9 ± 2.0 | 89.1 ± 3.9 | 94.3 ± 3.4 |
| 3 | Dosing 1 | 244 ± 27 | 552 ± 128 | 87 ± 8 | 2 ± 1 | 33 ± 32 | 2 ± 2 | 99.3 ± 0.3 | 92.7 ± 8.6 | 97.7 ± 2.4 |
| | Dosing 2 | 236 ± 60 | 502 ± 254 | 80 ± 11 | 3 ± 2 | 21 ± 26 | 6 ± 3 | 98.9 ± 0.9 | 96.6 ± 4.4 | 92.8 ± 2.9 |
| | Dosing 3 | 300 ± 27 | 497 ± 30 | 91 ± 11 | 2 ± 1 | 37 ± 29 | 2 ± 2 | 99.2 ± 0.5 | 92.5 ± 6.0 | 97.6 ± 1.9 |
| 4 | Dosing 1 | 383 ± 78 | 589 ± 72 | 134 ± 46 | 11 ± 6 | 42 ± 38 | 2 ± 1 | 97.4 ± 1.2 | 93.3 ± 7.9 | 98.0 ± 1.4 |
| | Dosing 2 | 396 ± 69 | 638 ± 115 | 126 ± 13 | 21 ± 11 | 41 ± 36 | 3 ± 2 | 94.4 ± 3.3 | 94.7 ± 5.9 | 98.2 ± 2.5 |
| | Dosing 3 | 400 ± 22 | 571 ± 41 | 118 ± 7 | 28 ± 7 | 48 ± 13 | 2 ± 1 | 93.0 ± 2.1 | 91.6 ± 2.5 | 98.3 ± 0.9 |

Cycle 1: 6 hours of hydraulic retention time (HRT) and 5940 ± 515 $mgL^{-1}$ of mixed liquor suspended solids (MLSS); cycle 2: 6 hours of HRT and 7542 ± 1730 $mgL^{-1}$ of MLSS; cycle 3: 12 hours of HRT and 5967 ± 485 $mgL^{-1}$ of MLSS; cycle 4: 12 hours of HRT and 2688 ± 744 $mgL^{-1}$ of MLSS).

The operating cycles lasted 61 days for cycle 1, 81 days for cycle 2, 69 days for cycle 3 and 61 days for cycle 4. The data pertaining to this section were subjected to a comparative analysis with the data obtained from the study of the cycles without pharmaceutical doping (Bermúdez et al., 2022). Regulation (EU) 2020/741 classifies reclaimed water for agricultural irrigation (quality A, B, C, and D) according to quality requirements that control *E. Coli*, $BOD_5$, TSS and turbidity, with the highest quality being category A in cycles 1, 2 and 3. In the case of cycle 4, the $BOD_5$ value must be ≤10 $mg\,L^{-1}$ for the limits established by the legislation, so that according to Regulation (EU) 2020/741 (Table 2, annex I) it would be in category B, which corresponds to that established by Directive 91/271/EEC. From the perspective of the reuse of treated water, the levels of total suspended solids comply with the most restrictive legislation in all cycles with their respective doping phases. In addition, the water can be discharged into the watercourse as it complies with current legislation Directive 91/271/CEE. Furthermore, the limits for TSS of ≤35 $mg\,L^{-1}$ and a removal rate of 90.0 % have been established. This study has demonstrated that the water in question largely meets these limits, as evidenced by the data presented in Table 3. Additionally, the minimum discharge concentrations for $BOD_5$ are ≤25 mg $O_2$ $L^{-1}$, and the removal rates are 70.0 - 90.0 % removal. For COD, the minimum requirements are 75.0 % and ≤125 mg $O_2$ $L^{-1}$. The pilot plant has demonstrated that these plant performance requirements can be met even at the highest dosages, with removal rates exceeding 93% for $BOD_5$ and 87.7% for COD. Other studies have demonstrated comparable removal rates, thereby substantiating the potential of MBR as a promising technology for effective wastewater treatment (Calero-Díaz et al., 2017; Do & Chu, 2022; Monteoliva-García et al., 2019b, 2019a). Pharmaceutical removal performance in all operating cycles, irrespective of the doping phase, was over 94% for ibuprofen, 76% for diclofenac, and 85% for erythromycin. This highlights the good performance of membrane bioreactor technology against this type of contaminant.

In addition, influent and effluent samples from the pilot plant were analyzed in order to ascertain the amount of total nitrogen and total phosphorus present. The plant is unable to remove these nutrients due to the absence of anoxic and anaerobic zones. This is due to the fact that the technology employed in the pilot plant in this research is designed in such a way that no removal of nitrogen and phosphorus occurs, and the treated water contains these nutrients, thereby making a positive contribution to the receiving environment in agriculture.

The results of the turbidity values obtained for the effluent in the different cycles demonstrate that they are in compliance with the minimum requirements for water reuse in agriculture (cycle 1: <4.3 NTU; cycle 2 <6.3 NTU; cycle 3 <8.5 NTU; cycle 4 <10.7

NTU). In the case of cycle 1, the reclaimed water would comply with quality value A (Annex I; Table 1; Table 2), the most restrictive one that allows direct irrigation of the feed. Consequently, the water from the other cycles would have a quality B for having turbidity values higher than 5 NTU. For values above 5 NTU, it is established that it can be used for irrigation without the feed being in direct contact with the water. The membranes utilized in this study were five years old, which may account for the observed turbidity values exceeding the anticipated levels for ultrafiltration membranes, given that their integrity may have been compromised by prolonged use. These membranes were previously employed in a study with lower turbidity results (<1 NTU) (Monteoliva-García et al., 2020).

For the *E. Coli* tests, all the cycles studied, with their respective doping, meet the requirements for maximum quality A (Table 1, Annex I), as defined in Regulation (EU) 2020/741, with values below 10 CFU (cycle 1: <6.62 CFU; cycle 2 <7.3 CFU; cycle 3 <7.1 CFU; cycle 4 <6.2 CFU). Recycled water of this quality can be used to irrigate raw food crops.

During the four operating cycles studied and the examination of the various parameters required by legislation, the treated water could be used for irrigation in agriculture in all four cycles. In the case of cycles one, two and three, it would be possible to irrigate crops that are consumed raw and the edible part is in direct contact with the reclaimed water, as the maximum quality of reuse has been obtained. In the case of cycle 4, the treated water is suitable for irrigation of food crops that are consumed raw and the edible part is not in contact with the treated water, as well as processed food crops and non-food crops.

## 3.2 Advanced oxidation processes

### 3.2.1 Water line

The data pertaining to this section are subjected to a comparative analysis with the data obtained from the study of the cycles without pharmaceutical doping (Bermúdez et al., 2022). When the AOPs were applied to the effluent of the different cycles in their different phases, in the cases where ibuprofen was detected (cycles 1 and 2), complete elimination was achieved with the application of the lowest concentration of 25 mg $L^{-1}$ $H_2O_2$. Furthermore, other authors have verified that a nearly complete removal of 99% of the ibuprofen present in wastewater can be achieved after 30 minutes of treatment with the same dose of hydrogen peroxide (Afonso-Olivares et al., 2016). A further study demonstrated that ibuprofen was completely degraded after 40 minutes of treatment at this concentration, with the same result achieved in only 10 minutes of treatment at a 50 mg $L^{-1}$ $H_2O_2$ concentration (Monteoliva-García et al., 2019b). The rapid photolysis of ibuprofen at low oxidant concentrations indicates a rapid elimination of the pharmaceutical with an effective photodecomposition of $H_2O_2$ and that was verified by another study utilizing a similar lamp and where practically all the ibuprofen was consumed (Adityosulindro et al., 2022).

The pharmaceutical diclofenac was identified in the effluents of all cycles. When treated with AOP at a concentration of 25 mg $L^{-1}$ of $H_2O_2$, the compound was removed with an efficiency of over 83% in all cycles. This increased to 99% when the concentration of the oxidant was increased to 100 mg $L^{-1}$. In another study, similar results were obtained, with the removal of over 80% attributed to direct photodegradation (Lekkerkerker-Teunissen et al., 2012).

In the case of erythromycin, where it was detected in the effluents of cycles 1, 2, and 4, it was found that the treatment with AOPs had limitations. While the treatment was effective, removal efficiencies ranging from 19.9% to 73.4% in all cycles were achieved for the highest oxidant concentration of 100 mg $L^{-1}$ applied. These yields are lower than those of the pharmaceuticals ibuprofen and diclofenac. This phenomenon appears to be related to the nature of the compound in question (an antibiotic), whereas the other pharmaceuticals are anti-inflammatory. A similar range of removal was observed in another study despite the use of longer treatment times of up to 45 minutes, with removals ranging from 34% to 76% (Afonso-Olivares et al., 2016).

### 3.2.2 Sludge line

The data pertaining to this section were subject to a comparative analysis with the data obtained from the study of the cycles without pharmaceutical doping (Bermúdez et al., 2022). The treated sludge was subject to two stages of water removal. The first stage occurred during the thickening phase prior to digestion, while the second stage occurred during centrifugation of the digested sludge. The supernatant of the thickened activated sludge and the centrifugation water were subjected to the tertiary treatment of advanced UV/$H_2O_2$ oxidation during the four cycles of operation and in their different phases. After 30 min of treatment, the removal efficacy of the pharmaceuticals in both the supernatant water and the centrifuge water was found to be highly satisfactory.

In cases where ibuprofen was detected, it was completely eliminated in all cycles, which is in agreement with the results obtained by other authors. This demonstrates the efficacy of this treatment for this pharmaceutical (Afonso-Olivares et al., 2016). In the case of diclofenac, water disinfection is highly effective, with complete removal in many cases. The lowest concentration of oxidant (25 mg $L^{-1}$ $H_2O_2$) consistently yields removal efficiencies of over 82%, regardless of the concentration of 50 mg $L^{-1}$ and 100 mg $L^{-1}$ of $H_2O_2$ employed in all cycles for supernatant water and the centrifuge water. These exemplary removal efficiencies for diclofenac are also documented in the scientific literature to be in excess of 80% (Lekkerkerker-Teunissen et al., 2012). The same is true for erythromycin, which achieves very good elimination performances. For the concentration of 25 mg $L^{-1}$ of $H_2O_2$ in the supernatant water, the erythromycin removal yields were always higher than 39%, and for the centrifugate water at 40%. In the case of the high oxidant concentrations of 50 mg $L^{-1}$ and 100 mg $L^{-1}$ $H_2O_2$ studied, complete elimination was observed in all cycles for supernatant water and the centrifuge water.

### 3.2.3 Color analysis

Although color analysis is not explicitly included in the legislation as a determining factor in the use of treated water for agricultural purposes, it can be considered a quality parameter and was, therefore, measured. The results obtained for the effluent in the steady state in the different cycles demonstrate that following the AOP test, the color of the effluent is reduced by more than 77% in all cases, with some reaching 100%. In the case of cycle 3, the effluent of the water line in the three cases of doping carried out leaves the system without color in most cases. In those cases in which a very residual color does emerge, this is completely eliminated after being subjected to the AOP treatment. For supernatant in cycles 1, 2, and 3, a color removal of more than 80% is also achieved in most cases for the highest absorbance values (620 nm). In some instances, this is complete, but in others, it is more moderate at the lowest oxidant concentration. In the case of cycle 4 for the supernatant, color removal yields of over

90% are achieved and even complete for the 50 mg/L and 100 mg/L $H_2O_2$ treatments. Regarding the treatments applied to the water resulting from the centrifugation of the digested sludge in all cycles, as well as to the effluent and the supernatant, the color removal yields are moderate compared to the cases of the effluent and the supernatant, with removal yields ranging between 40% and 80% in all cycles.

### 3.3 Circular economy indicators

#### 3.3.1 Indicator of reducing matter removal efficiency ($I_{RECOD}$)

The temporal evolution of the circular economy indicator $I_{RECOD}$ is presented in Figure 2 below.

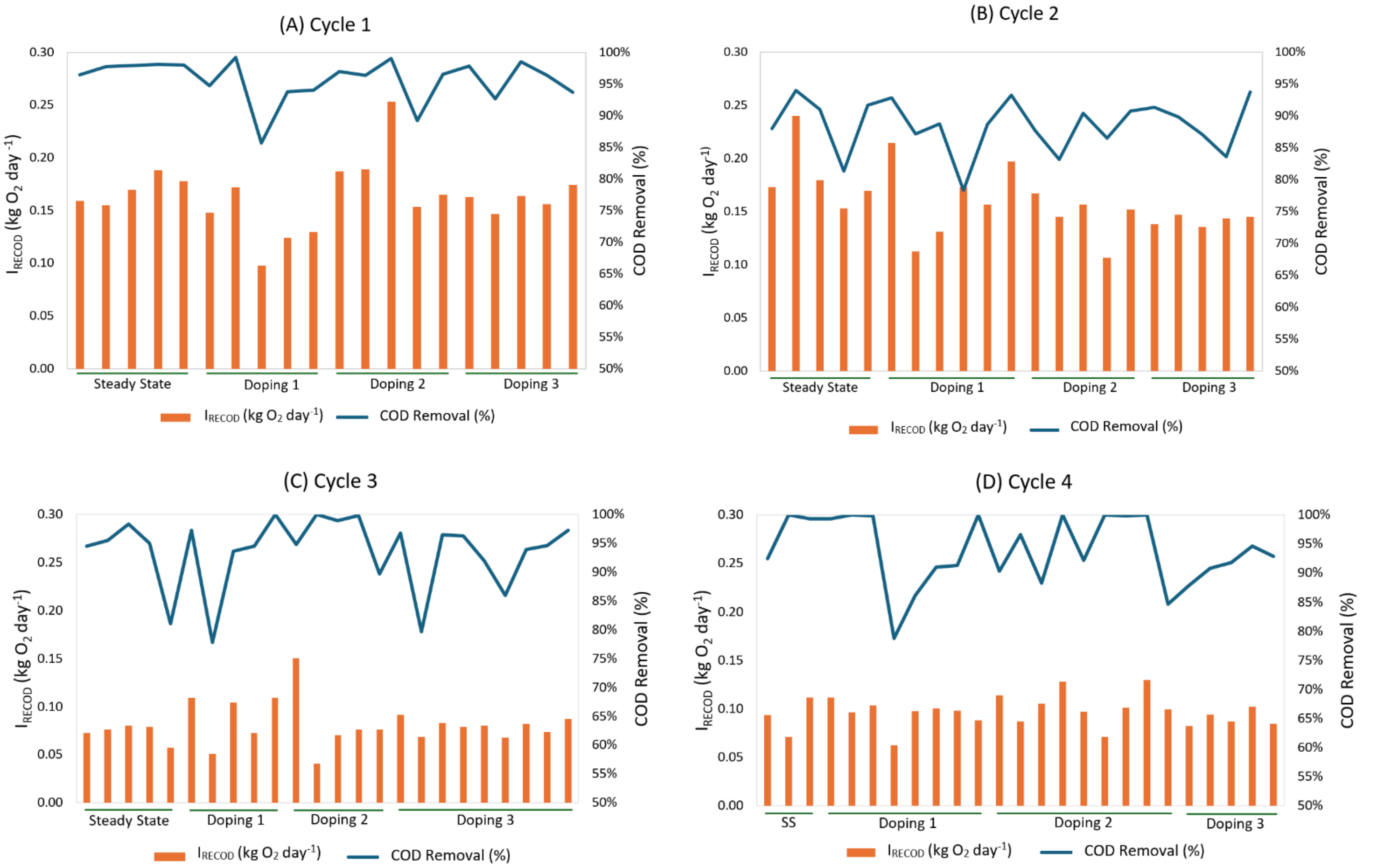

**Figure 2.** Temporal evolution of the circular economy indicator $I_{RECOD}$ in cycle 1 (A), 2 (B), 3 (C) and 4 (D). SS: Steady State.

The data pertaining to $I_{RECOD}$ were subjected to a comparative analysis with the data obtained from the study of the cycles without pharmaceutical doping (Bermúdez et al., 2022). This circular economy indicator is linked to legislation because it indirectly represents the COD evolution parameter. As illustrated in Figure 2, the disposal percentages, although fluctuating, are consistently within the parameters permitted by legislation throughout the various stages of the cycles. The reducing matter removal in kilograms of oxygen per day, as represented in the columns, illustrates the temporal evolution during the operation of the cycle phases. This discrepancy in organic matter removal efficiency is primarily attributable to the elevated HRT employed in cycles 3 and 4 and the largest SRT. Moreover, in the case of cycles 1 and 3, where the MLSS concentration is similar, the different HRT in cycle 3 appears to exert a greater influence on the observed behavior, which is comparable to that observed in cycle 4 with the same HRT but a lower MLSS concentration. This results in an increase in efficiency but a decrease in the removal rate of kg $BOD_5$ per day. The efficiencies observed across all cycles are comparable, offering insight into the system's behavior during different operational phases.

### 3.3.2 Circular economy indicators for water

Table 4 shows the circular economy indicators for water.

**Table 4.** Indicator of recovery of water in the treatment process ($I_{W,R}$), effluent inorganic content for nitrogen ($I_{EIC(N)}$) and effluent inorganic content for phosphorous ($I_{EIC(P)}$).

| Cycle | | $I_{W,R}$ (%) | $I_{EIC(N)}$ (mg day$^{-1}$) | $I_{EIC(P)}$ (mg day$^{-1}$) |
|---|---|---|---|---|
| 1 | Dosing 1 | 99.99 | 4454.0 | 14660.8 |
| | Dosing 2 | | 4352.0 | 14232.4 |
| | Dosing 3 | | 4386.0 | 13712.2 |
| 2 | Dosing 1 | 99.98 | 2754.0 | 12465.4 |
| | Dosing 2 | | 2597.6 | 12088.4 |
| | Dosing 3 | | 2522.8 | 12165.2 |
| 3 | Dosing 1 | 99.99 | 13814.2 | 1042.1 |
| | Dosing 2 | | 12535.8 | 955.4 |
| | Dosing 3 | | 12945.5 | 906.1 |
| 4 | Dosing 1 | 99.99 | 15830.4 | 7954.3 |
| | Dosing 2 | | 16631.1 | 7505.5 |
| | Dosing 3 | | 16337.0 | 7758.8 |

The percentage of water recovered during the treatment process, as represented by the $I_{W,R}$ indicator, is highly satisfactory. The vast majority of the water that undergoes treatment is recovered and is also potentially suitable for reuse because no restrictions for these nutrients are specified in the legislation. The elevated data are a consequence of the centrifugation applied to the digested sludge and the fact that the purged sludge flow rate is markedly inferior to the water line effluent flow rate. This process enables the production of such high yields, although these are not viable on an industrial scale. This percentage is considerably higher than that achieved in other studies, where 47.0% is recovered in wastewater from the pig farming industry (Molina-Moreno et al., 2017) and approximately 85% is obtained from paper industry waters (Molina-Sánchez et al., 2018). For the indicators $I_{EIC(N)}$ and $I_{EIC(P)}$, significant mass fluxes of mg day$^{-1}$ were obtained. The maximum production of nitrogen is obtained in cycle 4 for doping 2, with $I_{EIC(N)}$ of 16631.1 mg N day$^{-1}$ and the maximum production of phosphorus in cycle 1 for doping 1 with $I_{EIC(P)}$ of 14660.8 mg P day$^{-1}$. The amounts obtained per cycle as the amount of doping increases are approximate, so it seems that the amount of nutrients (nitrogen and phosphorus) is not affected. The influence of the HRT on the amount of nutrients is remarkable because, when the HRT is lower (6 hours, cycles 1 and 2), the minimum amounts of total nitrogen and the maximum amounts of phosphorus are obtained. When the HRT is higher (12 hours, cycles 3 and 4), the behavior is reversed, and the minimum amount of total phosphorus and the maximum amount of total nitrogen are obtained. The inorganic content of the effluent represents an added value for the reuse of water in agriculture due to its nutrient load. This type of biostabilized sludge can be used as a soil conditioner or fertilizer due to the organic fraction contained in these nutrients (Kaszycki et al., 2021). A number of countries, including Sweden and Switzerland, have already initiated the recovery of phosphorus in order to lay the groundwork for the wider recovery of phosphorus. This represents a viable opportunity with the potential to replace 15% of the world's phosphorus demand (Som Gupta & Khatiwada, 2024). This study does not meet the standards set for the discharge of treated water for the new EU directive proposal approved in April 2024, which will include nutrient removal restrictions for member states with long-term targets. However, it should be noted that the co-concentration of these nutrients could be beneficial from the point of view of the potential use of this water in agriculture. In order to adapt the pilot plant to the standards of the new EU directive (April 2024), the pilot plant will be adapted by adding two modules before the membrane bioreactor, where anaerobic and anoxic conditions are present, which would allow the elimination of phosphorus and nitrogen nutrients.

### 3.4 Circular economy indicators for sludge

The amount of sludge concentrate recovered was estimated on the basis of the sludge produced in the plant. During the four operating cycles studied, the amount of sludge recovered, represented by the indicator ($I_{SG,\%R}$), was 0.68% during the doping, the same as for the steady state (Bermúdez et al., 2022). The sludge treatment line operates discontinuously, so this result is always similar in terms of sludge recovery per liter of sludge produced in the water line.

Table 5 shows the values of the sludge flow rate recovered during the water treatment process, the sludge flow rate produced during the wastewater treatment process, the sludge recovery indicator ($I_{SG,R}$) and the effective sludge flow rate per day. The values of these indicators are the same for all doping levels, as they depend on the flow of water treated in the plant and the flow of sludge produced.

**Table 5.** Performance of parameters of circular economy indicators for activated sludge. $m_{SG,R}$: sludge flow rate recovered during the water treatment process (kg day$^{-1}$); $m_{SG,T}$: sludge flow rate produced during the water treatment process (kg day$^{-1}$); Qeff: flow rate (L day$^{-1}$); $I_{SG,R}$: indicator of technological nutrient performance for recovered sludge.

| **Cycle** | $m_{SG,R}$ (Kg day$^{-1}$) | $m_{SG,T}$ (Kg day$^{-1}$) | Qeff (L day$^{-1}$) | $I_{SG,R}$ (Kg L$^{-1}$) |
|---|---|---|---|---|
| 1 | 0.026 | 3.80 | 343,80 | $7.55 \cdot 10^{-5}$ |
| 2 | 0.054 | 7.98 | 347.98 | $1.56 \cdot 10^{-4}$ |
| 3 | 0.015 | 2.21 | 172.21 | $7.75 \cdot 10^{-5}$ |
| 4 | 0.016 | 2.33 | 172.33 | $9.22 \cdot 10^{-5}$ |

In this study, a pilot-scale plant was used. Therefore, the $I_{SG,R}$ indicator data are very small as they are given as a function of the treated water flow. If we consider scaling-up this plant to industrial size, it has the potential to produce a significant amount of biostabilized sludge that can be reused in agriculture. Other studies have achieved higher percentages of biostabilized sludge of 4% (Molina-Moreno et al., 2017; Molina-Sánchez et al., 2018), but a lower percentage of treated water is recovered. Other studies have reported overall recovery rates of 2% sludge in urban wastewater treatment plants (Kaszycki et al., 2021). Other authors also highlight the energy potential of sewage sludge, which can also be efficiently converted into heat, electricity, and biofuels, although this line of research is still under development (Castellanos et al., 2024). The residual concentration of the emerging contaminant pharmaceuticals studied in this research and retained in the biostabilized sludge does not currently represent a limitation for the reuse of biostabilized sludge, as no concentration of these compounds is included in Directive 86/278/EEC on the reuse of sewage sludge in agriculture.

It should also be noted that anaerobic treatment of urban wastewater and sludge is very important because, in addition to the benefits of energy production and agricultural use, it reduces greenhouse gas emissions (Gupta & Khatiwada, 2024).

### 3.5 Circular economy indicator for biogas produced

During the anaerobic digestion process, organic substances were decomposed, and biogas was generated. In this context, micro-organisms engage in metabolic activity in an environment characterized by a lack of oxygen, namely an anaerobic environment (Molina-Moreno et al., 2017; Salguero-Puerta et al., 2019). The calculation of the volumetric flow rate of biogas generated was obtained by an indirect method. This involved the use of stoichiometric calculations and the evaluation of COD reduction throughout the digestion process.

Table 6 presents the maximum daily biogas production per liter of activated sludge during the digestion phase in the different cycles, as well as the cumulative biogas production over the entire digestion period.

**Table 6**. Biogas produced during the anaerobic digestion process. $I_{MDP}$: Biogas indicator of biogas generation potential in relation to sludge mass flow rate.

| Cycle | Digester | Biogas produced ($mg\ CH_4\ L^{-1}$) | $I_{MDP}$ ($L$ biogas $Kg^{-1}$ sludge) | Total volume $CH_4$ ($L\ Kg^{-1}$ sludge throughout the digestion) |
|---|---|---|---|---|
| 1 | Digester 1 | 675.0 | 0.134 | 0.945 |
| | Digester 2 | 591.6 | 0.088 | 0.735 |
| | Digester 3 | 583.5 | 0.099 | 0.817 |
| 2 | Digester 1 | 1233.3 | 0.257 | 1.727 |
| | Digester 2 | 1950.8 | 0.210 | 2.731 |
| | Digester 3 | 2033.3 | 0.443 | 2.847 |
| 3 | Digester 1 | 2233.3 | 0.642 | 3.127 |
| | Digester 2 | 1016.8 | 0.222 | 1.423 |
| | Digester 3 | 1450.0 | 0.303 | 1.937 |
| 4 | Digester 1 | 793.4 | 0.117 | 1.111 |
| | Digester 2 | 641.7 | 0.077 | 0.898 |
| | Digester 3 | 540.0 | 0.128 | 0.756 |

Digester 1: dosage of pharmaceuticals with concentration 1. Digester 2: dosage of pharmaceuticals with concentration 2. Digester 3: dosage of pharmaceuticals with concentration 3.

The maximum daily production of methane ($CH_4$) occurs in cycle 2 in digester 0 (0.793 L biogas $Kg^{-1}$ sludge $day^{-1}$), which corresponds to the steady state of the cycle (Bermúdez et al., 2022). This is due to the fact that in cycle 2 the SRT (10.7 days) is much lower than in cycle 3 (38.5 days). This means that in cycle 2 the microorganisms have more biodegradable matter available and their consumption rate is much higher than that of the sludge with longer cell retention time, which would be more stabilized.

With regard to digester 0 for cycles 3 and 4 (Bermúdez et al., 2022), which exhibit the lowest daily production rates (0.198 L biogas $Kg^{-1}$ sludge $day^{-1}$ for cycle 3 and 0.117 L biogas $Kg^{-1}$ sludge $day^{-1}$ for cycle 4) and operate at the same HRT, the maximum daily production rate of methane is observed in cycle 3 with 0.642 L biogas $Kg^{-1}$ sludge $day^{-1}$ in doping 1 (Table 6), accompanied by a higher total methane production. However, cycle 3 exhibits the highest SRT. This higher production is favored by a higher MLSS concentration compared to cycle 4. A comparison of cycles 3 and 4 (12 h HRT) with cycle 1 (6 h HRT) indicates that a more adapted aerobic biocommunity does not necessarily imply that the sludge from which it originates has a higher biogas potential under anaerobic conditions. This may be attributed to the longer HRT of cycle 3 in comparison to cycle 1. This indicates that the microorganisms are more adapted to the conditions, which in turn facilitates digestion and consequently results in a higher total final methane production.

The results are comparable to those of previous studies conducted at lower temperatures, indicating that the methane production rate in this study was low relative to expectations during digestion (Zhang et al., 2018). The low methane production may be attributed to the scaling-up of the anaerobic digester, which has likely significantly influenced the biological digestion process by inhibiting it to a minimum.

With regard to the evolution of the digesters in the presence of doping, there is a generalized decrease with respect to digester 0 (Bermúdez et al., 2022), with the exception of cycle 3, where there is an increase in the $I_{MDP}$ (maximum daily methane produced) in doping 1. This decrease is more pronounced in digester 2, with a slight recovery in digester 3. This phenomenon appears to be linked to the fact that the system, which has a higher concentration of pharmaceuticals, is more stimulated, leading to greater microbial activity in an attempt to counteract the effect of the toxic substance. This results in peaks of activity, during which methane production increases. This behavior does not occur in cycle 4, which has the lowest concentration of micro-organisms, so the effect of the peak activity observed in the other cycles does not seem to be significant in this case, although the $I_{MDP}$ occurs in cycle 3. Therefore, it appears that the concentration of micro-organisms in the system and the effect of increased doping are the variables that most affect the digesters in the production of biogas.

Figure 3 illustrates the theoretical total energy production from the biogas produced per kg of sludge in the anaerobic digestion process, calculated by Equation 7. This value is derived from the maximum methane production observed per day during the entire 28 days anaerobic digestion period.

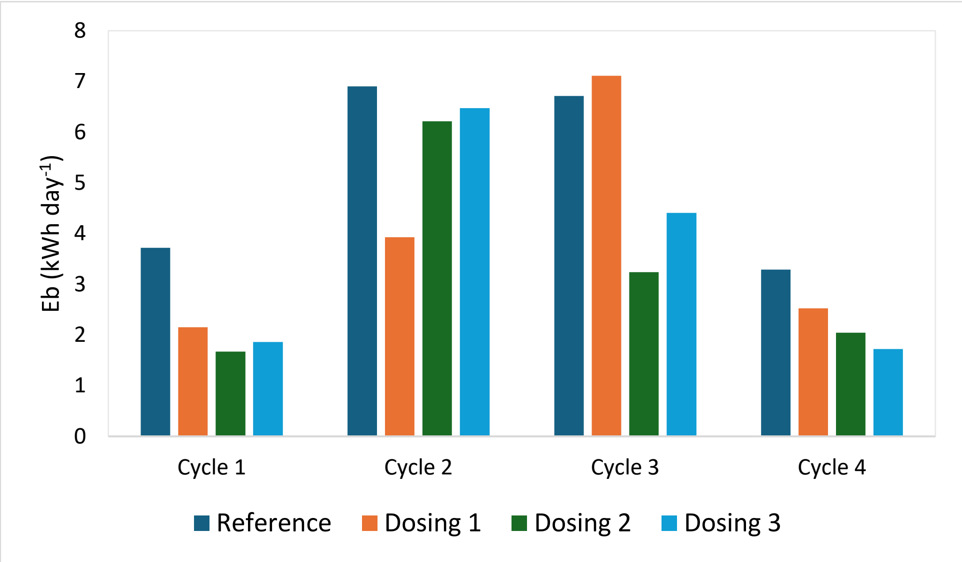


**Figure 3.** Theoretical energy produced per kilogram of sludge generated during anaerobic digestion.

In the steady state, during the 28 day process, the cycle with the highest potential energy production from $E_b$, the highest output is achieved when the system remains unaltered reaching a total value of 6.92 kWh day$^{-1}$ in cycle 2 during the reference phase (Bermúdez et al., 2022). This is indicative of the highest biogas production in this cycle, which can be attributed to the fact that cycle 2 has the highest MLSS concentration, the lowest HRT and the lowest SRT so the potential for methane production was at its maximum. The findings indicate that the introduction of doping into the principal system is associated with a reduction in biogas production. However, biogas production tends to recover with an increase in the concentration of pharmaceuticals added in cycles 1, 2 and 3. This is because the system becomes more excited and produces more biogas, resulting in more electricity. Consequently, the greatest electrical energy production is consistently observed when the system is not subjected to alterations due to the doping of the pharmaceuticals (Bermúdez et al., 2022). Subsequently, the addition of doping results in a reduction in biogas production, accompanied by a tendency for recovery at higher concentrations of pharmaceuticals in cycles 1, 2 and 3. In cycle 4, where the MLSS concentration is lowest and the HRT concentration is highest, it always decreases.

These theoretical energy results estimated using the circular economy indicators look promising. There are several energetically and economically viable wastewater treatment plants around the world that successfully recover biogas (Gupta & Khatiwada, 2024).

## 4. Conclusions

The present study examined four operational cycles in which the HRT and MLSS concentration were varied during the operation of a pilot plant utilizing membrane bioreactor technology (cycle 1 with 6 h of HRT and 5940 ± 515 of MLSS; cycle 2 with 6 h of HRT and 7542 ± 1730 of MLSS; cycle 3 with 12 h of HRT and 5967 ± 485 of MLSS; cycle 4 with 12 h of HRT and 2688 ± 744 of MLSS). The system performs the integrated treatment of real urban wastewater, including the water line and sludge line. In various cycles, the plant was subjected to different doping methods, such as increasing concentrations of the pharmaceuticals diclofenac, ibuprofen, and erythromycin. Furthermore, the various outlet water lines of the system, both in the water line and in the sludge line, were subjected to advanced oxidation treatments. A variety of circular economy indicators were employed to evaluate the plant's resource recovery. The following conclusions were reached:

- In accordance with the regulations established in legislation, the parameters of TSS, turbidity, *E. Coli,* and $BOD_5$ were satisfied. This allows the treated water to be reused in cycles 1, 2, and 3 for the irrigation of raw food and with irrigation that allows direct contact of the treated water with the edible part of the food. This complies with the maximum quality established in legislation (A). In the case of cycle 4, the second-best quality (B) was obtained. This allows the use of treated water for irrigation in instances where the edible part of the food is not in direct contact with the irrigation. This is in accordance with the principles of circularity, thereby facilitating the complete integration of treated water into the agricultural process.
- The employment of circular economy indicators for the resources generated during integrated wastewater treatment has yielded encouraging outcomes. The indicators demonstrate that the treated water can be utilized almost entirely in agriculture, thereby indicating the integration of this waste as a resource. Moreover, the treated water presents throughout the four cycles studied valuable nutrients in agriculture, including nitrogen and phosphorus. It is possible to select the nitrogen present in a higher concentration in the case of the 12 hours of HRT or the phosphorus in the case of the 6 hours of HRT, according to the needs of the agricultural reuse.
- The proportion of sludge recovered is markedly low in comparison to the volume of water treated. Nevertheless, during the anaerobic digestion of activated sludge, high-value resources such as biogas are produced, which has the potential to be used for the production of electricity. The best results are obtained in the case of the cycles with the highest concentration of MLSS and a

lower SRT in the bioreactor so the higher methane production potential results from the presence of more biodegradable biomass in the anaerobic reactor in the sludge line.

**Acknowledgements**

Grant PID2021-124740NB-I00 funded by MICIU/AEI/10.13039/501100011033 and by ERDF, EU.

**REFERENCES**

Adityosulindro, S., Julcour, C., Riboul, D., & Barthe, L. (2022). Degradation of ibuprofen by photo-based advanced oxidation processes: exploring methods of activation and related reaction routes. *International Journal of Environmental Science and Technology*, *19*(4), 3247–3260. https://doi.org/10.1007/S13762-021-03372-5/TABLES/3

Afonso-Olivares, C., Fernández-Rodríguez, C., Ojeda-González, R. J., Sosa-Ferrera, Z., Santana-Rodríguez, J. J., & Rodríguez, J. M. D. (2016). Estimation of kinetic parameters and UV doses necessary to remove twenty-three pharmaceuticals from pre-treated urban wastewater by UV/$H_2O_2$. *Journal of Photochemistry and Photobiology A: Chemistry*, *329*, 130–138. https://doi.org/10.1016/J.JPHOTOCHEM.2016.06.018

Antiñolo Bermúdez, L., Díaz Mendoza, V., Poyatos Capilla, J. M., Muñío Martínez, M. del M., & Martín Pascual, J. (2023). Effect of Pharmaceutical Compounds (Diclofenac, Ibuprofen, and Erythromycin) on the Heterotrophic Behaviors of Biomass of a

Membrane Bioreactor to Treat Urban Wastewater. *Environments 2023, Vol. 10, Page 198*, *10*(12), 198. https://doi.org/10.3390/ENVIRONMENTS10120198

Antiñolo Bermúdez, L., Pascual, J. M., Del Mar Muñio Martínez, M., Manuel, J., & Capilla, P. (2021). *Effectiveness of Advanced Oxidation Processes in Wastewater Treatment: State of the Art*. https://doi.org/10.3390/w13152094

Association, A. P. H., Association, A. W. W., & Federation, W. E. (2022). *Standar Methods for examination of water and wastewater* (22nd ed.).

Bermúdez, A., Díaz, L., Pascual, M., Martínez, M., Capilla, P., Stephen Inbaraj, B., Baglieri, A., Antiñolo Bermúdez, L., Carlos Leyva Díaz, J., Martín Pascual, J., del Mar Muñío Martínez, M., & Manuel Poyatos Capilla, J. (2022). Study of the Potential for Agricultural Reuse of Urban Wastewater with Membrane Bioreactor Technology in the Circular Economy Framework. *Agronomy 2022, Vol. 12, Page 1877*, *12*(8), 1877. https://doi.org/10.3390/AGRONOMY12081877

Bonetta, S., Pignata, C., Gasparro, E., Richiardi, L., Bonetta, S., & Carraro, E. (2022). *Impact of wastewater treatment plants on microbiological contamination for evaluating the risks of wastewater reuse*. https://doi.org/10.1186/s12302-022-00597-0

Calero-Díaz, G., Monteoliva-García, A., Leyva-Díaz, J. C., López-López, C., Martín-Pascual, J., Torres, J. C., & Poyatos, J. M. (2017). Impact of ciprofloxacin, carbamazepine and ibuprofen on a membrane bioreactor system: Kinetic study and biodegradation capacity. *Journal of Chemical Technology & Biotechnology*, *92*(12), 2944–2951. https://doi.org/10.1002/jctb.5316

Cao, M., Hu, A., Gad, M., Adyari, B., Qin, D., Zhang, L., Sun, Q., & Yu, C. P. (2022). Domestic wastewater causes nitrate pollution in an agricultural watershed, China. *Science of The Total Environment*, *823*, 153680. https://doi.org/10.1016/J.SCITOTENV.2022.153680

Castellanos, H. G., Aryanfar, Y., Keçebaş, A., Assad, M. E. H., Islam, S., Naveed, Q. N., & Lasisi, A. (2024). A new paradigm for mining energy from industrial sludge: A low-cost fuel. *Journal of Water Process Engineering*, *59*, 104987. https://doi.org/10.1016/J.JWPE.2024.104987

Do, K. U., & Chu, X. Q. (2022). Performances of membrane bioreactor technology for treating domestic wastewater operated at different sludge retention time. *Development in Wastewater Treatment Research and Processes: Removal of Emerging Contaminants from Wastewater through Bio-Nanotechnology*, 107–122. https://doi.org/10.1016/B978-0-323-85583-9.00010-7

Gobernment of Spain. (2007). *E N E R G Í A S R E N O V A B L E S Biomasa Digestores anaerobios Biomasa Digestores anaerobios Energía de la Biomasa GOBIERNO DE ESPAÑA MINISTERIO DE INDUSTRIA, TURISMO Y COMERCIO*. https://www.idae.es/sites/default/files/documentos/publicaciones_idae/documentos_10737_biomasa_digestores_anaerobios_a2007_0d62926d.pdf

Gómez Nieto, M. Á., & Hontoria García, E. (2003). *Técnicas analíticas en el control de la ingeniería ambiental* (M. Á. Gómez Nieto & E. Hontoria García, Eds.).

Gopalakrishnan, G., Jeyakumar, R. B., & Somanathan, A. (2023). Challenges and Emerging Trends in Advanced Oxidation Technologies and Integration of Advanced Oxidation

Processes with Biological Processes for Wastewater Treatment. *Sustainability 2023, Vol. 15, Page 4235*, *15*(5), 4235. https://doi.org/10.3390/SU15054235

Gupta, A. S., & Khatiwada, D. (2024). Investigating the sustainability of biogas recovery systems in wastewater treatment plants- A circular bioeconomy approach. *Renewable and Sustainable Energy Reviews*, *199*, 114447. https://doi.org/10.1016/J.RSER.2024.114447

Kaszycki, P., Głodniok, M., & Petryszak, P. (2021). Towards a bio-based circular economy in organic waste management and wastewater treatment – The Polish perspective. *New Biotechnology*, *61*, 80–89. https://doi.org/10.1016/J.NBT.2020.11.005

Kundan, S., Rupam, B., & Dash, R. R. (2022). Biological Treatment of Contaminants of Emerging Concern in Wastewater: A Review. *Journal of Hazardous, Toxic, and Radioactive Waste*, *26*(2), 4022002. https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000685

Lehmann, C., Cruz-Jesus, F., Oliveira, T., & Damásio, B. (2022). Leveraging the circular economy: Investment and innovation as drivers. *Journal of Cleaner Production*, *360*, 132146. https://doi.org/10.1016/J.JCLEPRO.2022.132146

Lekkerkerker-Teunissen, K., Benotti, M. J., Snyder, S. A., & van Dijk, H. C. (2012). Transformation of atrazine, carbamazepine, diclofenac and sulfamethoxazole by low and medium pressure UV and UV/H2O2 treatment. In *Separation and Purification Technology* (Vol. 96, pp. 33–43). https://doi.org/https://doi.org/10.1016/j.seppur.2012.04.018

Leyva-Díaz, J. C., Martín-Pascual, J., González-López, J., Hontoria, E., & Poyatos, J. M. (2013). Effects of scale-up on a hybrid moving bed biofilm reactor – membrane bioreactor for treating urban wastewater. *Chemical Engineering Science*, *104*, 808–816. https://doi.org/10.1016/J.CES.2013.10.004

Lu, Q., Wang, S., Ping, Q., & Li, Y. (2023). A novel approach to enhance methane production during anaerobic digestion of waste activated sludge by combined addition of trypsin, nano-zero-valent iron and activated carbon. *Chemosphere*, *341*, 140007. https://doi.org/10.1016/J.CHEMOSPHERE.2023.140007

Metcalf, L., Eddy, H. P., & Tchobanoglous, G. (2004). Wastewater energy: treatment and reuse. *McGraw-Hill*, 1819.

Molina-Moreno, V., Leyva-Díaz, J. C., Llorens-Montes, F. J., & Cortés-García, F. J. (2017). Design of Indicators of Circular Economy as Instruments for the Evaluation of Sustainability and Efficiency in Wastewater from Pig Farming Industry. *Water 2017, Vol. 9, Page 653*, *9*(9), 653. https://doi.org/10.3390/W9090653

Molina-Sánchez, E., Leyva-Díaz, J. C., Cortés-García, F. J., & Molina-Moreno, V. (2018). Proposal of Sustainability Indicators for the Waste Management from the Paper Industry within the Circular Economy Model. *Water 2018, Vol. 10, Page 1014*, *10*(8), 1014. https://doi.org/10.3390/W10081014

Monteoliva-García, A., Martín-Pascual, J. J., Muñío, M. M., & Poyatos, J. M. (2019a). Removal of a Pharmaceutical Mix from Urban Wastewater Coupling Membrane Bioreactor with Advanced Oxidation Processes. In *Journal of Environmental Engineering* (Vol. 145, Issue 9). https://doi.org/10.1061/(asce)ee.1943-7870.0001571

Monteoliva-García, A., Martín-Pascual, J., Muñío, M. M., & Poyatos, J. M. (2020). Effects of carrier addition on water quality and pharmaceutical removal capacity of a membrane bioreactor – Advanced oxidation process combined treatment. *Science of the Total Environment*, *708*, 135104. https://doi.org/10.1016/j.scitotenv.2019.135104

Monteoliva-García, A., Martín-Pascual, J., Muñío, M., & Poyatos, J. (2019b). Removal of carbamazepine, ciprofloxacin and ibuprofen in real urban wastewater by using light-driven advanced oxidation processes. *International Journal of Environmental Science and Technology*, *16*(10), 6005–6018. https://doi.org/10.1007/s13762-019-02365-9

Ping, Q., Zhang, Z., Ma, L., Yan, T., Wang, L., & Li, Y. (2022). The prevalence and removal of antibiotic resistance genes in full-scale wastewater treatment plants: Bacterial host, influencing factors and correlation with nitrogen metabolic pathway. *Science of The Total Environment*, *827*, 154154. https://doi.org/10.1016/J.SCITOTENV.2022.154154

Preisner, M., Neverova-Dziopak, E., & Kowalewski, Z. (2020). Analysis of eutrophication potential of municipal wastewater. *Water Science and Technology*, *81*(9), 1994–2003. https://doi.org/10.2166/WST.2020.254

Rajesh Banu, J., Kavitha, S., Yukesh Kannah, R., Bhosale, R. R., & Kumar, G. (2020). Industrial wastewater to biohydrogen: Possibilities towards successful biorefinery route. *Bioresource Technology*, *298*, 122378. https://doi.org/10.1016/J.BIORTECH.2019.122378

Salguero-Puerta, L., Leyva-Díaz, J. C., Cortés-García, F. J., & Molina-Moreno, V. (2019). Sustainability Indicators Concerning Waste Management for Implementation of the Circular Economy Model on the University of Lome (Togo) Campus. *International Journal of Environmental Research and Public Health 2019, Vol. 16, Page 2234*, *16*(12), 2234. https://doi.org/10.3390/IJERPH16122234

Som Gupta, A., & Khatiwada, D. (2024). Investigating the sustainability of biogas recovery systems in wastewater treatment plants-A circular bioeconomy approach. *Renewable and Sustainable Energy Reviews*, *199*, 114447. https://doi.org/10.1016/j.rser.2024.114447

Tayo, L. L., Caparanga, A. R., Doma, B. T., & Liao, C.-H. (2018). A Review on the Removal of Pharmaceutical and Personal Care Products (PPCPs) using Advanced Oxidation Processes. *Journal of Advanced Oxidation Technologies*, *21*(1), 196–214. https://doi.org/10.26802/jaots.2017.0079

Verlicchi, P., Grillini, V., Lacasa, E., Archer, E., Krzeminski, P., Gomes, A. I., Vilar, V. J. P., Rodrigo, M. A., Gäbler, J., & Schäfer, L. (2023). Selection of indicator contaminants of emerging concern when reusing reclaimed water for irrigation — A proposed methodology. *Science of The Total Environment*, *873*, 162359. https://doi.org/10.1016/J.SCITOTENV.2023.162359

Wijaya, L., Alyemeni, M., Ahmad, P., Alfarhan, A., Barcelo, D., El-Sheikh, M. A., & Pico, Y. (2020). *Ecotoxicological Effects of Ibuprofen on Plant Growth of Vigna unguiculata L*. https://doi.org/10.3390/plants9111473

Zhang, L., De Vrieze, J., Hendrickx, T. L. G., Wei, W., Temmink, H., Rijnaarts, H., & Zeeman, G. (2018). Anaerobic treatment of raw domestic wastewater in a UASB-digester at

10 °C and microbial community dynamics. *Chemical Engineering Journal*, *334*, 2088–2097. https://doi.org/10.1016/J.CEJ.2017.11.073