Resource recovery from sulphate-rich sewage through an innovative anaerobic-based water resource recovery facility (WRRF)

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ABSTRACT

This research work proposes an innovative water resource recovery facility (WRRF) for the recovery of energy, nutrients and reclaimed water from sewage, which represents a promising approach towards enhanced circular economy scenarios. To this aim, anaerobic technology, microalgae cultivation, and membrane technology were combined in a dedicated platform. The proposed platform produces a high-quality solid- and coliform-free effluent that can be directly discharged to receiving water bodies identified as sensitive areas. Specifically, the content of organic matter, nitrogen and phosphorus in the effluent was 45 mg $COD{\cdot}L^{-1}$, 14.9 mg $N{\cdot}L^{-1}$ and 0.5 mg $P{\cdot}L^{-1}$, respectively. Harvested solar energy and carbon dioxide biofixation in the form of microalgae biomass allowed remarkable methane yields (399 STP L $CH_4{\cdot}kg^{-1}$ COD_{inf}) to be achieved, equivalent to theoretical electricity productions of around 0.52 kWh per m^3 of wastewater entering the WRRF. Furthermore, 26.6% of total nitrogen influent load was recovered as ammonium sulphate, while nitrogen and phosphorus were recovered in the biosolids produced (650 ± 77 mg $N{\cdot}L^{-1}$ and 121.0 ± 7.2 mg $P{\cdot}L^{-1}$).

Key words | anaerobic digestion (AD), anaerobic membrane bioreactor (AnMBR), membrane photobioreactor (MPBR), resource recovery, sewage, water resource recovery facility (WRRF)

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INTRODUCTION

Sewage treatment is usually based on energy-intensive aerobic processes where the energy input for organic matter oxidation accounts for up to 50% of the total energy demand of the wastewater treatment plant (WWTP) (Sid *et al.* 2017). In addition, aerobic processes present a limited chance for nutrient recovery since nitrogen is usually released to the atmosphere via denitrification and phosphorus is usually stored as a metal salt within the sludge, preventing its possible reuse. Therefore, within an enhanced circular economy perspective, sewage treatment needs to shift towards new cost-effective, green alternatives allowing resource recovery from sewage, for example,

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energy, nutrients, reclaimed water, and biosolids to be maximised.

A new sewage treatment paradigm based on the so-called water resource recovery facility (WRRF) concept has emerged for waste-to-resource recovery within the scientific community (see e.g. Batstone *et al.* 2015). Within this paradigm, sewage is no longer considered as a waste but as a source of raw valuable resources, resulting in environmental and economic benefits (Puyol *et al.* 2017). To this aim, different platforms for resource recovery have been defined. For instance, Batstone *et al.* (2015) proposed two platforms mainly consisting of the following: (i) low energy mainstream, based on low strength anaerobic treatment; and (ii) uptake-release-recover, where nutrients and carbon are assimilated during biological uptake through either assimilation (i.e. growth) or accumulation by phototrophic or heterotrophic organisms, followed by anaerobic digestion (AD) of this biomass and nutrients and carbon recovery from the produced digestate.

The anaerobic membrane bioreactor (AnMBR) has emerged as a promising energy-effective technology for mainstream anaerobic treatment of low-strength wastewater (Pretel *et al.* 2016). AnMBRs have an intrinsic advantage compared to conventional AD: the use of membranes for decoupling the sludge retention time (SRT) from the hydraulic retention time (HRT). Therefore, AnMBRs can treat high flow rates with relatively low footprints since biomass washout is avoided by membrane filtration. Moreover, the reduced growth rates of anaerobic organisms at low temperature is offset by the biomass retention, promoting the application of anaerobic biotechnology to a wider range of environmental conditions (Giménez *et al.* 2012).

Some bottlenecks that prevent the widespread application of AnMBR still remain, such as the loss of dissolved methane in the effluent (which increases as the operating temperature decreases) and the competition between sulphate-reducing organisms (SRO) and methanogens for the available substrate when treating wastewaters with low organic matter to sulphate ratios (COD:SO_4-S) (Giménez *et al.* 2012). According to this, Pretel *et al.* (2016) showed that the anaerobic treatment of sulphate-rich wastewater at ambient temperature could be enhanced by including a primary settling stage prior to an AnMBR. This combination results in a WRRF where methane is produced in a sidestream AD, where the operating temperature of the unit can be increased using the heat generated in a combined heat and power (CHP) system fuelled with the biogas produced in the system. Moreover, when treating sulphate-rich wastewaters, since the COD:SO_4-S ratio entering the sidestream AD is much higher than the one entering the mainstream AnMBR, the growth of methanogens is favoured, therefore increasing the methane production of the whole WRRF. In this treatment scheme, methane is not produced in the mainstream AnMBR, which operates at ambient temperature and high flow rates, and it is possible to drastically reduce the loss of methane dissolved in the WRRF effluent.

The methane dissolved in the effluent of an anaerobic process should still be recovered for further enhancing the environmental and economic feasibility of the WRRF. To this aim, vacuum degasification non-porous membranes have been reported as a promising technology to replace traditional methods for dissolved methane recovery (Cookney *et al.* 2016). These membranes allow direct demethanisation of anaerobic streams with positive energy balances of the separation process (Cookney *et al.* 2016).

As for water reclamation, AnMBR equipped with ultrafiltration membranes produces a high quality permeate that is (partially) disinfected (Bair *et al.* 2015). Moreover, this effluent contains certain nitrogen and phosphorus concentrations (Giménez *et al.* 2011) thus representing a valuable water source for fertigation purposes. However, when fertigation is not possible, these concentrations of nutrients could prevent AnMBR effluent from direct emission to different receiving water bodies. In such cases, these nutrients can be recovered by different techniques, such as the cultivation of phototrophic organisms (Viruela *et al.* 2016).

Within the uptake-release-recover concept, membrane photobioreactor (MPBR) for autotrophic microalgae cultivation has been reported as an interesting approach for nutrient recovery (Bilad *et al.* 2014), presenting lower footprints than other microalgae cultivation systems (Viruela *et al.* 2016). Autotrophic microalgae use light energy, inorganic carbon and high amounts of inorganic compounds such as ammonium (NH_4^+) and phosphate (PO_4^{3-}) for growth. Hence, nutrients and solar energy are harvested in the form of microalgae biomass while biofixing carbon dioxide.

The microalgae harvested from an MPBR can be used as carbon source in the sidestream AD system, enhancing the energy balance of the WRRF, whilst the produced AD effluent can be used for nutrient valorisation (Sialve *et al.* 2009). However, AD of microalgae presents several drawbacks, such as: (i) low biodegradability of the highly-recalcitrant microalgae cell walls; (ii) low carbon to nitrogen ratio (C:N) that results in high levels of free ammonia, which can inhibit the anaerobic process; and (iii) the need of cost-effective microalgae harvesting systems since biogas production from microalgae depends on biomass concentration (Giménez *et al.* 2018).

One alternative to improve the digestibility of microalgae and prevent the possible inhibition of the process by free ammonia is the AD of this microalgae biomass, with carbon-rich substrates available in municipalities (e.g. food waste or sewage sludge, among others). During the process, a high concentration of nutrients such as nitrogen can be released and recovered in the form of commercial products such as ammonium sulphate using, for instance, absorption-desorption, ion exchange with zeolites or synthetic resins or membrane contactors. The latter stands out as a promising recovery technology since it has been reported to achieve low energy requirements and high efficiency recovery yields (Norddahl *et al.* 2006).

All the above is proof that several attempts have been made by different authors to transform the classical WWTPs into more energy and environmental efficient facilities. Shifting from aerobic for anaerobic processes (Pretel *et al.* 2016), recovering nitrogen as ammonium sulphate using membrane contactors (Norddahl *et al.* 2006), or recovering phosphorus as struvite (Martí *et al.* 2017). However, to the best of authors' knowledge, there are no studies so far evaluating the resource recovery from wastewater streams in real conditions as a holistic approach.

The mainstream of the proposed WRRF platform consists of a primary settling step, an AnMBR as secondary treatment, and a MPBR as tertiary treatment. The combination of AnMBR and MPBR transforms the sewage into microalgae biomass (a source of energy and nutrients) and reclaimed water. The sidestream of this platform consists of an additional AnMBR, a non-porous degassing membrane, and a membrane contactor. The AD of sewage sludge and harvested microalgae biomass enhances biogas production. The non-porous degassing membrane and the membrane contactor enable recovery of the dissolved methane and nitrogen, respectively. This treatment platform is proposed for treating sulphate-rich sewage. However, when treating wastewaters with a low sulphate content, this platform would be significantly simplified since previous studies have demonstrated that the combination of AnMBR and MPBR is an interesting approach for resource recovery from sewage (see e.g. Pretel *et al.* 2015; González-Camejo *et al.* 2017).

The objective of this work is to provide a proof of concept and evaluation of the technical feasibility of the proposed novel WRRF platform proposed for the recovery of reclaimed water, nutrients and energy from (sulphate-rich) sewage, based on a circular economy perspective.

METHODS

WRRF platform

Figure 1 shows the flow diagram of the WRRF platform proposed in this study, which is located in the 'Conca del Carraixet' WWTP (Valencia, Spain).

Regarding the mainstream, the raw sewage pre-treatment consists of screening, degritter, and grease removal, after which the wastewater (sampling point #0) is introduced to a gravity-based primary clarifier for continuous removal of solids. Effluent from this primary clarifier is fed to a secondary treatment consisting of an AnMBR unit, where soluble organics are biologically removed and solids are physically retained. Moreover, the nitrogen and phosphorus content in the organic forms are mineralised, becoming available for recovery in the MPBR pilot unit.

The solids-free permeate from the AnMBR is fed to a tertiary treatment consisting of a MPBR for microalgae cultivation, where solar energy is harvested, inorganic nutrients are biologically assimilated, and carbon dioxide is biofixed as microalgae biomass. In addition, the MPBR system produces reclaimed water.

Concerning the sidestream, the sewage sludge and the harvested microalgae biomass are concentrated and fed to an AD process based on AnMBR technology ($AnMBR_{AD}$, i.e. sidestream AnMBR). This system valorises the organic matter in the form of biogas. Moreover, a nutrient-rich permeate and biosolids are produced, which could be used for nutrient valorisation. Specifically, the biosolids can be used for agricultural purposes, while the produced permeate is firstly treated in a non-porous membrane for dissolved methane recovery, and subsequently introduced to a membrane contactor for nitrogen recovery.

Description of the pilot units

AnMBR pilot unit

The AnMBR pilot unit mainly consists of an anaerobic reactor with a total volume of 1,300 L (900 L working volume) connected to two membrane tanks, each one with a total volume of 800 L (600 L working volume). Each membrane tank is equipped with one industrial-scale hollow-fibre ultrafiltration membrane unit composed of nine membrane bundles (PURON® KMS PUR-PSH31, 0.03 μm pores) with a total filtration area of 31 m^2. Gas-assisted membrane-scouring was used to minimise cake layer formation.

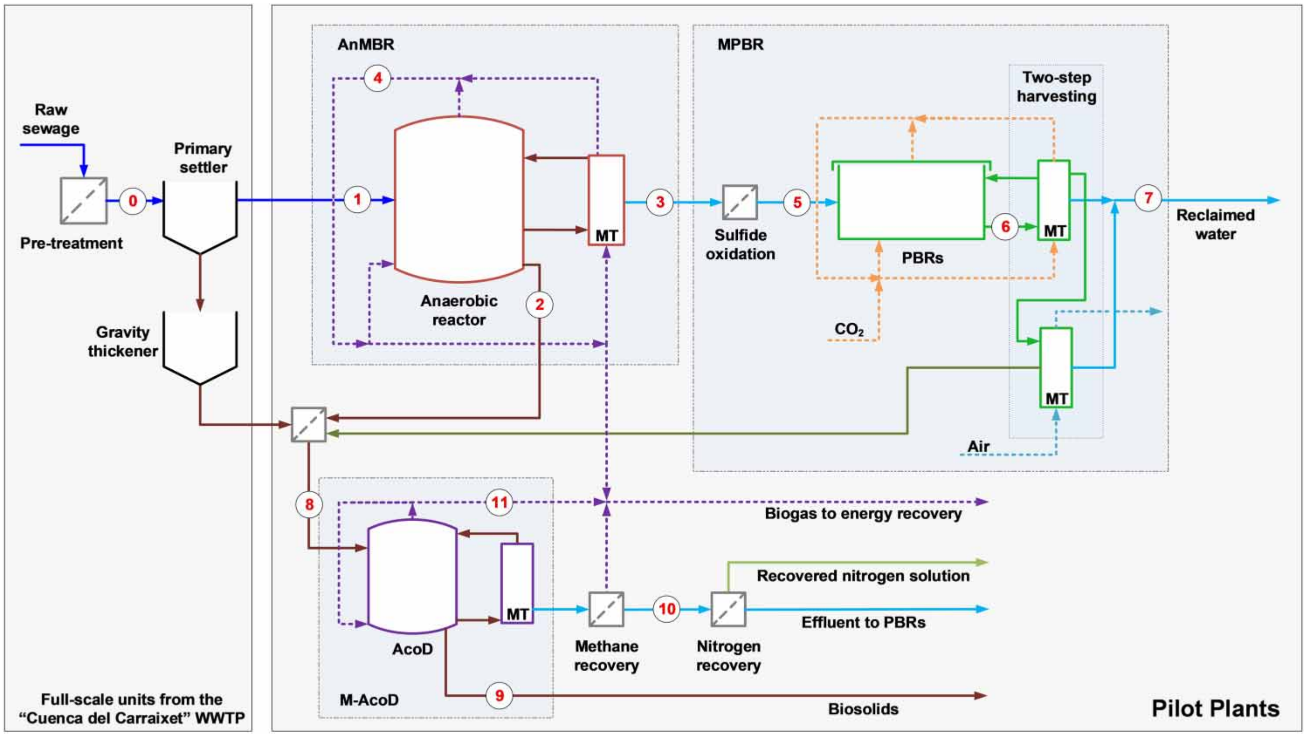

Figure 1 | Layout of the WRRF including the sampling points (1–11). AD, anaerobic digester; AnMBR, anaerobic membrane bioreactor; $AnMBR_{AD}$, sidestream anaerobic membrane bioreactor; MPBR, membrane photobioreactor; MT, membrane tank; PBR, photobioreactor.

MPBR pilot unit

The MPBR plant mainly consists of three 1.25-m height, 2-m width and 0.1-m depth methacrylate flat-plate photobioreactors (PBRs) with a total volume of 750 L (maximum working volume of 705 L). The PBRs are connected to a two-step harvesting system. Each filtration step consists of a membrane tank of 14 L that includes a hollow-fibre membrane bundle with a filtration area of 3.44 m^2. This bundle was obtained by modifying an industrial-scale hollow-fibre ultrafiltration membrane unit (PURON® KMS PUR-PSH31, 0.03 μm pores). The PBRs were continuously stirred by gas sparging, enabling proper mixing of the culture and preventing wall fouling. Membrane scouring by gas sparging was used to minimise cake layer formation in both filtration steps.

$AnMBR_{AD}$ pilot unit

The $AnMBR_{AD}$ plant consists of an AD with a total volume of 1,000 L (maximum working volume of 900 L) and a 1-L membrane tank fitted with a 0.42-m^2 hollow-fibre ultrafiltration membrane unit (PURON® KMS, 0.03 μm pores). An equalisation tank of 125 L is used to mix the different co-substrates prior to being fed to the system. To improve the mixing conditions in the AD and to favour the stripping of the produced gases from the liquid phase, a fraction of the produced biogas was recycled to the bottom of the digester. Biogas-assisted membrane-scouring was used to minimise cake layer formation.

Dissolved methane and nitrogen membrane-based recovery systems

The proposed WRRF platform was equipped with a polydimethylsiloxane (PDMS) membrane module provided by PermSelect® (MedArray Inc., USA) with a total filtration area of 2.1 m^2, which was used as a final polishing step for desorption and recovery of dissolved methane. Furthermore, a microporous polypropylene (PP) membrane contactor of 1.4 m^2 provided by Liqui-Cel® (model 2.5 × 8 Extra Flow X50) was used for the recovery of free ammonia as ammonium sulphate.

Operating conditions of the pilot units

The operational conditions of the AnMBR, MPBR and $AnMBR_{AD}$ pilot units within the experimental period of this work are shown in Table 1. The pilot units were

Table 1 | Operating conditions of the AnMBR, MPBR and $AnMBR_{AD}$ pilot units

	SRT (d)	HRT (d)	Temperature (°C)	Working volume (L)	Light PAR (μmol·m^{-2} s^{-1})	OLR (g COD·L^{-1}·d^{-1})
AnMBR	70.0 ± 3.7	1.1 ± 0.2	24.9 ± 0.5	2,100	–	0.22 ± 0.07
MPBR	5.4 ± 0.3	2.1 ± 0.1	23.8 ± 1.1	705	273 ± 118	0.04 ± 0.01
$AnMBR_{AD}$	69.7 ± 0.3	30.0 ± 0.3	55.0 ± 0.9	500	–	0.56 ± 0.05

SRT, sludge retention time; HRT, hydraulic retention time; PAR, photoactive radiation; OLR, organic loading rate.

operated continuously for 3 months. This study shows the data obtained under steady-state conditions. Steady-state conditions were related to stable suspended solids concentrations in the bioreactors. A 30-day period of steady-state data is shown in this paper. Table 2 shows the average characteristics of the different streams of the WRRF (Figure 1) during the steady-state period.

The AnMBR and the MPBR units were operated outdoors at ambient temperature. In addition, the MPBR system was operated at variable light intensity due to the dynamics of the environmental conditions. It is worth pointing out that due to operating volume restrictions, only a fraction of the produced AnMBR effluent was fed to the MPBR. The pH of the MPBR was controlled at 7.5 by the addition of pure CO_2 into the aeration system to avoid undesirable chemical processes such as phosphate precipitation and free ammonia stripping.

Primary sludge coming from the full-scale WWTP thickener, digestate from the AnMBR pilot unit, and microalgae biomass harvested from the MPBR pilot unit were digested in the $AnMBR_{AD}$ pilot unit. The final composition of the blending fed to the $AnMBR_{AD}$ was the following: 34, 13, and 53% of total solids for primary sludge, AnMBR digestate, and harvested microalgae, respectively. The contribution of each tributary stream was chosen based on experimental data from previous research and new simulation data using an extended version of the mathematical model BNRM2 (data not shown) (Barat *et al.* 2013).

As for the dissolved methane recovery system, the PDMS membrane was operated on the shell side, collecting the permeate gas into the lumen side. Vacuum was used to generate the driving force, resulting in a transmembrane pressure of 0.8 bars in order to maximise the partial pressure gradient, thus improving methane recovery.

Concerning the nitrogen recovery system, the PP membrane contactor was operated also on the shell side, recovering the nitrogen in the lumen side in the form of ammonium sulphate. To this aim, the nitrogen was concentrated in a sulphate acid solution of 0.05 M at a pH of up to 9. This solution was circulated through the inner section of the membranes at a flow rate of around 0.2 L·min^{-1}.

Analytical methods

In order to evaluate the biological process performance, samples were collected three times a week from the sampling points numbered in Figure 1. Total Solids (TS), Volatile Solids (VS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Total and Soluble COD (TCOD and SCOD, respectively), Total Nitrogen (TN), Soluble Nitrogen (SN), Ammonium (NH_4-N), Nitrite (NO_2-N), Nitrate (NO_3-N), Total Phosphorus (TP), Soluble Phosphorus (SP), Phosphate (PO_4-P), Sulphide (S^{2-}) and Sulphate (SO_2^{-4}) were determined according to *Standard Methods* (APHA *et al.* 2012). Volatile Fatty Acids (VFA) and Alkalinity (Alk) were measured by titration in accordance with the methodology proposed by the South African Water Research Commission (Moosbrugger *et al.* 1992).

The presence of *Escherichia coli* and other coliform pathogens in permeates was quantitatively determined through positive β-glucuronidase assay using membrane filters, following the UNE-EN ISO 9308-1:2014 standard method.

The methane fraction of the biogas was measured three times a week using a gas chromatograph equipped with a Flame Ionisation Detector (GC-FID, Thermo Scientific). 1 mL of biogas was collected in a gas-tight syringe and injected into a 15 m × 0.53 mm × 1 μm TRACER column (Teknokroma) which was maintained at 40 °C. The carrier gas was helium at a flow-rate of 40 mL·min^{-1}. Pure CH_4 gas (99.9995%) was used as standard.

Process performance indicators

The removal or recovery rate and the removal or recovery efficiency for a given compound was calculated using Equations (1) and (2), respectively. The volumetric

Table 2 | Characterisation of the different WRRF streams during the steady-state period

Sampling point	0	1	2	3	4	5	6	7	8	9	10	11
pH	n.a.	7.9 ± 0.2	7.4 ± 0.1	n.a.	n.a.	n.a	7.4 ± 0.2	7.4 ± 0.2	n.a.	7.5 ± 0.1	n.a.	n.a.
ORP (mV)	n.a.	n.a	−467 ± 18	n.a	n.a	n.a	n.a	n.a	n.a	−522 ± 12	n.a	n.a
COD (mg COD·L^{-1})	444 ± 42	244 ± 36	4,902 ± 96	n.a	n.a	81 ± 14	1,434 ± 154	45 ± 10	16,737 ± 1,052	17,310 ± 401	n.a	n.a
SCOD (mg COD·L^{-1})	n.a.	98 ± 7	n.a	144 ± 11	n.a	81 ± 14	n.a	45 ± 10	1,597 ± 283	n.a	1,169 ± 64	n.a
TS (mg TS·L^{-1})	1,435 ± 78	n.a	5,278 ± 108	n.a	n.a	n.a	n.a	n.a	11,872 ± 1,048	14,013 ± 929	n.a	n.a
VS (%)	78.1 ± 5.7	n.a	59.3 ± 0.8	n.a	n.a	n.a	n.a	n.a	73.5 ± 4.3	67.7 ± 2.3	n.a	n.a
TSS (mg TSS·L^{-1})	238 ± 28	83 ± 8	4,213 ± 118	n.a	n.a	n.a	786 ± 69	n.a	9,797 ± 1,005	12,322 ± 202	n.a	n.a
VSS (%)	81.0 ± 6.1	80.7 ± 5.7	59.3 ± 0.2	n.a	n.a	n.a	93.8 ± 2.2	n.a	75.8 ± 7.1	69.6 ± 1.3	n.a	n.a
VFA (mg HAc·L^{-1})	n.a.	1.9 ± 0.1	n.a	0.6 ± 0.1	n.a	n.a	n.a	n.a	756 ± 171	n.a	523 ± 35	n.a
Alk (mg $CaCO_3$·L^{-1})	n.a.	469 ± 50	n.a	523 ± 35	n.a	n.a	n.a	n.a	417 ± 121	n.a	1,906 ± 67	n.a
CH_4 (%)	n.a	n.a	n.a	n.a	$<$D.L	n.a	n.a	n.a	n.a	n.a	n.a	62 ± 5
TN (mg N·L^{-1})	49.9 ± 8.4	45.6 ± 5.9	332 ± 14	44.9 ± 5.8	n.a	n.a	92 ± 8	14.9 ± 1.2	547 ± 105	650 ± 77	508 ± 20	n.a
SN (mg N·L^{-1})	n.a.	41.0 ± 4.8	n.a	44.9 ± 5.8	n.a	44.8 ± 5.3	n.a	14.9 ± 1.2	154.2 ± 44.9	n.a	508 ± 20	n.a
TP (mg P·L^{-1})	8.3 ± 1.9	5.7 ± 1.9	85.0 ± 1.6	3.9 ± 0.5	n.a	n.a	7.7 ± 1.1	0.5 ± 0.1	145.9 ± 18.9	121.0 ± 7.2	17.7 ± 1.4	n.a
PO_4-P (mg P·L^{-1})	n.a	3.3 ± 1.2	n.a	3.9 ± 0.5	n.a	3.8 ± 1.1	n.a	0.5 ± 0.1	37.3 ± 8.8	n.a	17.7 ± 1.4	n.a
S^{2-} (mg S·L^{-1})	n.a	n.a	n.a	52.3 ± 4.8	n.a	n.a	n.a	n.a	n.a	n.a	33.4 ± 1.7	n.a
SO_4 (mg SO_4·L^{-1})	n.a.	305.6 ± 45.5	n.a	132.7 ± 31.1	n.a	n.a	n.a	n.a	129.3 ± 32.4	n.a	n.a	n.a

Average and standard deviations of pH, Oxidation Redox Potential (ORP), Chemical Oxygen Demand (COD), Soluble COD (SCOD), Total Solids (TS), Volatile Solids (VS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Volatile Fatty Acids (VFA), Alkalinity (Alk), CH_4, and TN, SN, TP, PO_4-P, S^{2-} and SO_4^{2-} concentrations in the sampling points of the proposed WRRF (see Figure 1). n.a: not available. D.L: Detection Limit.

microalgae biomass productivity was calculated using Equation (3).

$$Removal\ or\ recovery\ rate\ (RR) = \frac{Q \cdot (C_I - C_F)}{V_R} \quad (1)$$

$$Removal\ or\ recovery\ efficiency\ (RE) = \frac{(C_I - C_F)}{C_I} \cdot 100 \quad (2)$$

$$Biomass\ productivity\ (BP) = \frac{Q_W \cdot X_{VSS}}{V_R} \quad (3)$$

where, C_I and C_F are the concentrations of a given compound in the influent and the effluent ($g \cdot m^{-3}$), respectively, Q is the treatment flow rate ($m^3 \cdot d^{-1}$), V_R is the volume of the reactor (m^3), Q_W is the flow rate of wasted biomass ($m^3 \cdot d^{-1}$) and X_{VSS} is the concentration of volatile suspended solids in the reactor ($g\ VSS \cdot m^{-3}$).

The carbon dioxide biofixation ratio in the MPBR was calculated using the equation described by de Morais & Costa (2007):

$$R_{CO_2} = m_{cbm} P \left(\frac{M_{CO_2}}{M_C} \right) \quad (4)$$

where, m_{cbm} is the fraction of carbon in the microalgae biomass (w/w), which was calculated from the biomass composition obtained by atomic spectroscopy, P is the biomass productivity ($g \cdot L^{-1} \cdot d^{-1}$), and M_{CO2} and M_C are the molecular weights of CO_2 and carbon (C), respectively.

The anaerobic process efficiency was evaluated in terms of biodegradability percentage and methane yield using Equations (5) and (6), respectively.

$$\%\ Biodegradability = \frac{CH_4 - COD + H_2S - COD}{COD_{influent}} \cdot 100 \quad (5)$$

$$Y^{CH_4} = \frac{CH_4 - V}{COD_{influent}} \cdot 100 \quad (6)$$

where, $COD_{influent}$ ($g\ COD \cdot d^{-1}$) is the COD of the influent, $CH_4 - COD$ is the COD of the produced methane (biogas methane and methane dissolved in the effluent) ($g\ COD \cdot d^{-1}$), $H_2S - COD$ is the COD consumed by SRO for sulphate reduction ($g\ COD \cdot d^{-1}$) and CH_4 - V is the production of methane (biogas methane and methane dissolved in the effluent) (L).

Mass balances were carried out for COD, nitrogen and phosphorus. Appendix 1 (available with the online version of this paper) shows the data used in mass balance calculations.

Energy and economic balance of the WRRF

In order to assess the performance of the proposed WRRF platform, mass, energy and economic balances were performed. The energy and economic balance has been carried out following the model proposed by Pretel et al. (2016). The following items were considered: pumping requirements, mixing, membrane scouring, $AnMBR_{AD}$ heating needs, energy recovery from methane, and operating and maintenance of the membrane modules (reagents for membrane cleaning and replacements). Appendix 2 (available with the online version of this paper) shows the main assumptions considered for energy and economic balance calculations.

RESULTS AND DISCUSSION

The performance of the proposed WRRF platform was evaluated in terms of reclaimed water production, nutrient recovery and energy recovery. The characteristics of the sewage used in this study (sampling point #0 in Figure 1) as well as the characteristics of the different streams of the WRRF (sampling points #1 to #11 in Figure 1) are shown in Table 2.

It is important to highlight the significant sulphate concentration in the influent ($305.6 \pm 45.5\ mg\ SO_4 \cdot L^{-1}$) in comparison with typical domestic wastewaters (around $90\ mg\ SO_4 \cdot L^{-1}$). This high sulphate influent concentration, typical in some geographical areas like the one in this study, resulted in a low $COD:SO_4$-S ratio in the mainstream, favouring the proliferation of SRO (Giménez et al. 2012), thus degrading the soluble COD via sulphate-reducing processes and hampering the methanogens' development. To mitigate this issue, a primary clarifier was incorporated in the layout of the system for maximising energy recovery through the anaerobic partition and digestion of particulate organics in the sidestream, favouring methanogen growth in the sidestream due to an increased $COD:SO_4$-S ratio.

Reclaimed water production

As Figure 1 shows, water recovery was carried out in three consecutive steps within the mainstream.

In the primary treatment, particulate organics were partially removed through classical gravity clarification, reducing the concentration of TSS entering the AnMBR from 238 to $83\ mg \cdot L^{-1}$ (see sampling point #0 and #1 in Table 2). This reduced solid load to the AnMBR allows reducing the footprint of the system since smaller reaction volumes can be projected for a given treatment flow rate. On the other hand, when operating at low mixed liquor suspended solids concentrations, both OPEX and CAPEX can be reduced because of: (i) a reduction in the membrane fouling propensity; and (ii) the possibility of increasing the operating transmembrane flux, decreasing the required membrane filtration area.

The particulate organics recovered as primary sludge were valorised in the sidestream AD, where the high COD:SO_4-S ratio hinders the growth of SRO. In fact, the COD:SO_4-S ratio in the influent of the sidestream $AnMBR_{AD}$ was 164.1 kg COD·kg^{-1} S. As a result, the lower proportion of SO_4 limited the growth of SRO.

During the secondary treatment (AnMBR step), solids were physically retained, organic nutrients were mineralised and soluble organics were biologically removed via sulphate-reducing processes, since after the primary settling step, the COD:SO_4-S ratio in the mainstream decreased to around 2.4 kg COD·kg^{-1} S. This low COD:SO_4-S ratio resulted in a negligible methane production in the AnMBR unit because SRO outcompeted methanogens for the available substrate. Therefore, this degradation of organics in the mainstream via sulphate-reducing processes can be considered, in combination with the previous primary settling step, an attractive approach when treating sulphate-rich wastewaters.

The reduced COD:SO_4-S ratio in the influent to the AnMBR unit avoided methane production in the mainline. The absence of dissolved methane in the effluent from the AnMBR avoids any global warming potential impact associated to emissions to the atmosphere of this compound mainstream. On the other hand, it is important to note that most of the particulate organic matter was valorised via methanisation in the sidestream AD system, where the treatment flow would allow the operating temperature to be increased using the heat energy generated in a CHP system using the producing biogas as fuel.

Additionally, sulphate allowed the oxidation of soluble organic matter in the mainstream, therefore avoiding the energy input for organic matter removal required in aerobic processes. However, the presence of sulphide in the effluent entails some drawbacks that can hinder downstream operations, such as microalgae cultivation (González-Camejo *et al.* 2017). In order to avoid these possible drawbacks, a sulphide oxidation step was included in the WRRF after the AnMBR unit (Figure 1).

The effluent of the AnMBR unit (see sampling point #3 in Table 2) featured negligible suspended solids and low COD concentrations. Moreover, COD levels were further reduced after the sulphide oxidation step (see sampling point #5 in Table 2). However, direct discharge of the effluent from the AnMBR to different receiving water bodies is not always possible since it contains significant amounts of nitrogen and phosphorus. Nonetheless, this nutrient-rich effluent from the AnMBR system is a suitable growth medium for microalgae cultivation in a tertiary treatment based on MPBR technology.

Finally, within the tertiary treatment (MPBR step), nutrients were removed via microalgae cultivation. The MPBR unit showed nitrogen and phosphorus removal efficiencies of 66.7% and 85.7%, respectively, obtaining an effluent with a nutrient content lower than the requirements established in European Directive 91/271/CEE for discharges to sensitive areas from urban WWTPs with treatment capacities between 10,000 and 100,000 PE (see sampling point #7 in Table 2). Moreover, as commented before, microalgae cultivation enabled not only nutrient uptake but also solar energy harvesting and carbon dioxide biofixation in the form of new microalgal biomass, which served as feedstock for the sidestream $AnMBR_{AD}$ unit.

Apart from the requirements established in the European Directive 91/271/CEE for COD, solids and nutrients, the concentration of pathogens in the effluent from the proposed WRRF needs to be monitored based on the subsequent use of the produced water. For instance, non-faecal coliform colony-forming units (cfu) per 100 mL can be discharged to the environment according to the Spanish water quality regulation. As a result of using ultrafiltration membrane units with a mean pore size of 0.03 μm, neither *E.coli* cfu per 100 mL nor helminthic eggs were detected in the final treated water. Reclaimed water was therefore produced in the proposed WRRF platform, which could be used for different purposes; that is, agricultural irrigation, aquifer recharge, urban or industrial uses, or for recreational areas.

Nutrient recovery

After mineralisation of the organic forms in the AnMBR unit, inorganic nutrient uptake occurred in the MPBR unit. Specifically, the nitrogen uptake rate by microalgae resulted in 20 ± 3 mg N·L^{-1}·d^{-1}, while the nitrogen content in the microalgae biomass was 124 ± 25 mg N·g^{-1} VSS. On the other hand, both the harvested microalgae biomass and the sewage sludge were fed to the sidestream $AnMBR_{AD}$ unit, where the organic forms of nitrogen and phosphorus were also mineralised. This mineralisation led to ammonium concentrations in the $AnMBR_{AD}$ permeate of 508 ± 20 mg N ·L^{-1}.

Based on this nitrogen content, a membrane contactor was used for ammonium recovery in the form of ammonium sulphate, removing 100% of the ammonium content in the permeate from the $AnMBR_{AD}$. These results are similar to those obtained by Norddahl *et al.* (2006) at a pH over 9. However, maximum nitrogen recovery efficiencies of 83% were achieved. Ammonia stripping was identified as the main reason for this ammonium loss. Nevertheless, these losses could be easily minimised at industrial scale by working in a closed system.

Regarding phosphorus, the phosphorus uptake rate in the MPBR unit resulted in 2.2 ± 0.6 mg PO_4-P·L^{-1}·d^{-1}, while the phosphorus content in the microalgae biomass was 10.4 ± 4.2 mg P·g^{-1} VSS. The phosphorus loading rate of the $AnMBR_{AD}$ was 57% higher than the amount determined in both permeate (17.7 ± 1.4 mg PO_4-P·L^{-1}) and waste streams. These results suggest that uncontrolled chemical precipitation occurred in the $AnMBR_{AD}$. Further research is therefore needed in order to prevent this uncontrolled precipitation and to improve the recovery of phosphorus in the sidestream AD system.

Nutrients were also recovered in the biosolids fraction. The production of biosolids in the WRRF was about 0.205 kg VSS per m^3 of treated water (0.461 kg VSS·kg^{-1} COD). The nutrient content in the biosolids accounted for 650 ± 77 mg N·L^{-1} and 121.0 ± 7.2 mg P·L^{-1} (see sampling point #9 in Table 2). These levels of nutrients make these biosolids eligible to be used as fertiliser. For instance, the recent literature review of Sharma *et al.* (2017) highlights the benefits of using nutrient-rich biosolids (a source of carbon and inorganic nutrients) as fertiliser in the Mediterranean area, where a carbon deficiency in soil is commonly found. Moreover, the operating temperature set in the $AnMBR_{AD}$ (55 °C) is reported to be effective in terms of pathogen removal (Carrington 2001). However, further research is needed to evaluate the potential of the produced biosolids for direct farmland application or composting.

Energy recovery

As previously mentioned, a negligible methane production was observed in the mainstream, since SRO outcompeted methanogens in the AnMBR unit. Since sulphate-reducers consume 2 mg of biodegradable organic matter per mg of SO_4-S (Giménez *et al.* 2012), a 57% reduction of sulphate in the effluent was observed. Thus, it can be assumed that sulphate reduction was the major pathway for organic matter removal.

Nevertheless, due to the biofixation of CO_2 in the form of microalgae biomass, an overall methane yield of 399 STP L CH_4·kg^{-1} COD_{inf} was achieved in the proposed WRRF platform under the evaluated operating conditions. Specifically, methane production in the $AnMBR_{AD}$ unit resulted in 85.5 L_{CH4}·d^{-1} on average. The methane content in the produced biogas was 62 ± 5%. This methane production represents a theoretical electricity production in a CHP system of around 0.44 kWh per m^3 of wastewater entering the WRRF.

Additionally, the membrane-based system for dissolved methane recovery from the effluent of the $AnMBR_{AD}$ reached an average methane recovery of 96%, reducing the loss of methane dissolved in the $AnMBR_{AD}$ effluent to levels below 0.34 mg CH_4·L^{-1}.

Mass, energy and economic balance

Figure 2 shows the overall COD, nitrogen and phosphorus mass balances of the evaluated WRRF platform. Total COD output was 116% higher than the COD input (see Figure 2(a)) due to CO_2 biofixation through microalgae growth being around 0.31 g COD·L^{-1}·d^{-1}. Overall, the resultant influent COD removal efficiency was 90.4%. Figure 2(b) shows a significant efficiency for nitrogen recovery in the form of ammonium sulphate of 26.7% of total N in the influent. However, 8.6% is lost due to stripping processes and the use of NO_3-N as the electron acceptor during AD in the $AnMBR_{AD}$. As for the phosphorus mass balance, 34.8% of TP was recovered in the biosolids (see Figure 2(c)). However, this figure illustrates that 55.9% of the total phosphorus content entering the WRRF was likely to be chemically precipitated in the system.

The AD of sewage sludge and microalgal biomass in the $AnMBR_{AD}$ enhanced energy recovery in the form of biogas. Moreover, the dissolved methane loss was minimised. The obtained digestate represented a valuable source of biosolids. These biosolids can be used for agricultural practices, representing a promising approach towards circular economy scenarios. Further information about mass balances is shown in Appendix 1.

As Figure 3(a) shows, the most energy-demanding process is membrane scouring by biogas sparging, which represents about 58% of the total energy requirements. This highlights the importance of optimising the filtration performance in each membrane filtration process to enhance the feasibility of the proposed platform.

As Figure 3(b) shows, the operating and maintenance costs of the membrane units are the most relevant items, reaching about 78% of the total cost. It is important to

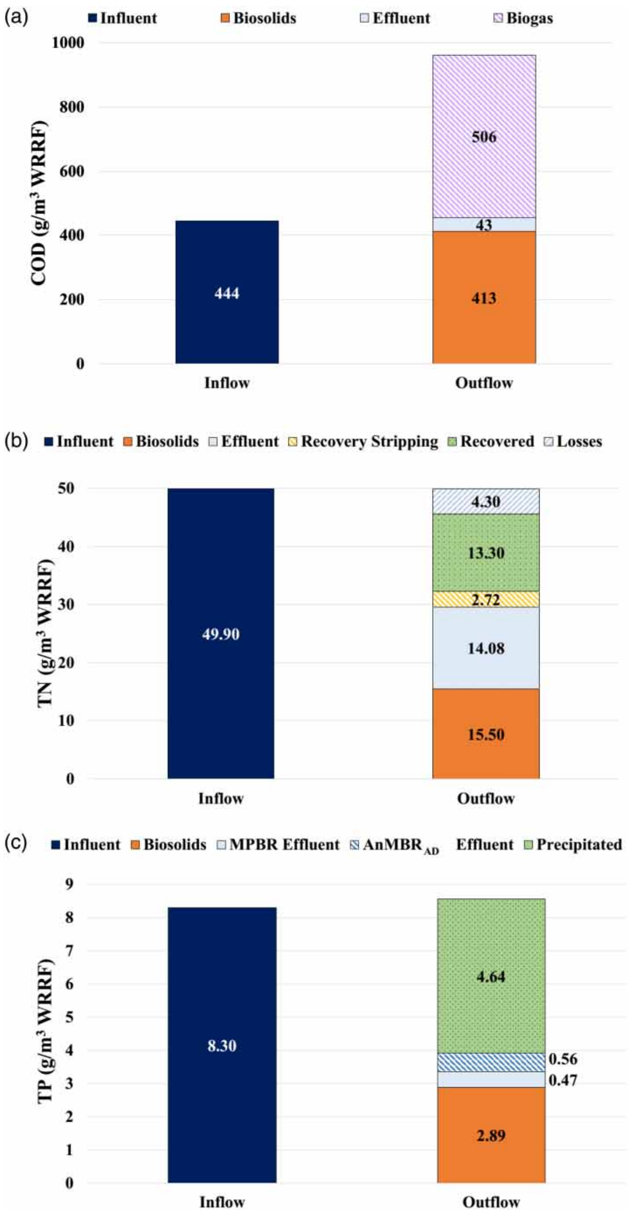

Figure 2 | WRRF mass balances for: (a) COD, (b) TN and (c) TP.

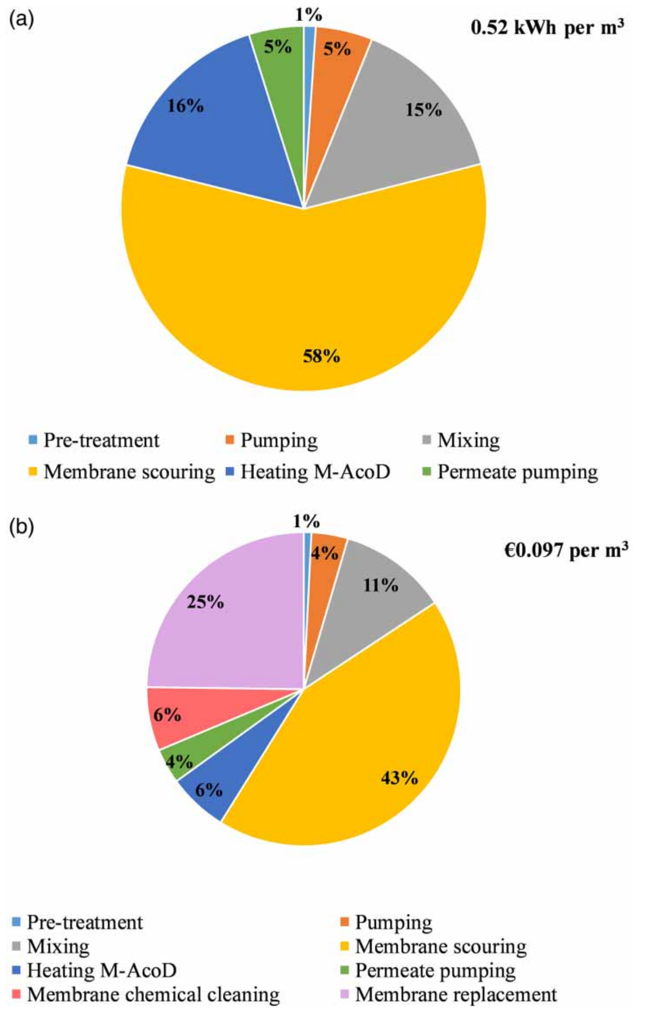

Figure 3 | (a) Energy and (b) economic balance of the WRRF platform.

highlight that capital expenses were not considered in this study. It must also be pointed out that nutrient recovery as commercial products, such as ammonium sulphate, struvite and amendments, were not considered in this economic study; these could have positive impacts on the economic balance.

Energy balance calculations resulted in a WRRF total energy demand of about 0.52 kWh per m^3 of treated water, from which 16% was related to heat requirements (i.e. 0.08 kWh per m^3). When biogas is used for energy recovery in a CHP system, 0.44 kWh per m^3 can be recovered as electricity. Hence, WRRF electricity requirements would be covered by the electricity recovered from the produced biogas. Regarding heat requirements, the recovered heat represents 0.03 kWh per m^3. Thus, WRRF heat energy requirements would be 0.053 kWh per m^3. Finally, this energy recovery entails a cost reduction from €0.097 to €0.036 per m^3 of treated water, which corresponds to a saving cost of €0.061 per m^3. The remaining costs are mainly due to membrane maintenance expenses.

Overall discussion

The proposed WRRF pursues the recovery of reclaimed water, nutrients and energy contained in the wastewater. Conventional WWTPs are energy-intensive platforms where energy consumption for aeration represents above 40% of total WWTP energy demand (see e.g. Sid et al. 2017).

In the last few years, the process of activated sludge has been modified in order to reduce operating costs and to add technologies capable of carrying out the recovery of nutrients, mainly phosphorus. Sid *et al.* (2017) implemented a control of the aeration to decrease the cost of nitrification-denitrification processes (e.g. the Ludzack-Ettinger process) achieving a reduction of 10%, resulting in an overall cost of €0.1254 per m^3. In contrast, the energy consumption of the proposed WRRF is €0.0311 per m^3.

Regarding the recovery of phosphorus, slight modifications have been made in conventional WWTPs in order to replace chemical removal by struvite precipitation (Martí *et al.* 2017). Although this WRRF was designed to recover phosphorus, the uncontrolled precipitation of phosphate prevented the application of struvite precipitation processes. Nevertheless, an important fraction of phosphorus was recovered as biosolids (121.0 ± 7.2 mg $P \cdot L^{-1}$).

Nitrification-denitrification is the traditional process to remove nitrogen in activated sludge. Besides being an energy-intensive process, it does not allow the recovery of nitrogen, since it is released to the atmosphere in gaseous form. New technologies for nitrogen recovery have appeared but their coupling to a conventional WWTP is not easy, for example zeolites or electrochemical techniques. Regarding this, ammonia absorption-desorption is an alternative method, reaching removal values between 65–75% (Morales *et al.* 2013). In contrast, this WRRF layout allows considerable levels of nitrogen removal (100%) and recovery to be obtained, specifically 83% through the membrane contactor.

The proposed WRRF implies a new configuration for the holistic approach to wastewater treatment. Although it presents some advantages against traditional WWTPs such as lower energy costs and resource recovery, further research is needed to optimise it. Other researchers such as Batstone *et al.* (2015) have simulated new WRRF platforms looking to move forward with the paradigm shift. In any case, real data from these novel WRRF configurations are still lacking.

CONCLUSIONS

An alternative WRRF platform for sewage treatment has been presented and its performance has been evaluated. Results constitute the proof-of-concept of the system, exploring the feasibility of combining anaerobic technology, microalgae cultivation and membrane technology for resource recovery from sewage. The implementation of this alternative treatment solution allowed:

- The production of a stream with a content of 45 mg $COD \cdot L^{-1}$, 14.9 mg $N \cdot L^{-1}$ and 0.5 mg $P \cdot L^{-1}$ which can be discharged to environmental water flows according to European Directive 91/271/CEE.
- Different resources are recovered in the WRRF platform such as ammonia sulphate (28% of the incoming N) and biosolids with a content of 30% of the incoming N and 34% of the incoming P.
- The energy demand of the WRRF was 0.52 kWh per m^3 of water treated and the energy production of the WRRF was 0.47 kWh per m^3. WRRF total energy requirements could be covered, which represents a cost saving of €0.061 per m^3.

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REFERENCES

APHA/AWWA/WEF 2012 *Standard Methods for the Examination of Water and Wastewater*. Standard Methods, 541. American Public Health Association, Washington, DC, USA.

Bair, R. A., Ozcan, O. O., Calabria, J. L., Dick, G. H. & Yeh, D. H. 2015 Feasibility of anaerobic membrane bioreactors (AnMBR) for onsite sanitation and resource recovery (nutrients, energy and water) in urban slums. *Water Science and Technology* **72** (9), 1543–1551.

Barat, R., Serralta, J., Ruano, M. V., Jiménez, E., Ribes, J., Seco, A. & Ferrer, J. 2013 Biological nutrient removal model No. 2

(BNRM2): a general model for wastewater treatment plants. *Water Science and Technology* **67** (7), 1481–1489.

Batstone, D. J., Hülsen, T., Mehta, C. M. & Keller, J. 2015 Platforms for energy and nutrient recovery from domestic wastewater: a review. *Chemosphere* **140**, 2–11.

Bilad, M. R., Arafat, H. A. & Vankelecom, I. F. J. 2014 Membrane technology in microalgae cultivation and harvesting: a review. *Biotechnology Advances* **32** (7), 1283–1300.

Carrington, E.-G. 2001 *Evaluation of Sludge Treatments for Pathogen Reduction*. http://europa.eu.int/comm/environment/pubs/home.htm.

Cookney, J., McLeod, A., Mathioudakis, V., Ncube, P., Soares, A., Jefferson, B. & McAdam, E. J. 2016 Dissolved methane recovery from anaerobic effluents using hollow fibre membrane contactors. *Journal of Membrane Science* **502**, 141–150.

de Morais, M. G. & Costa, J. A. V. 2007 Biofixation of carbon dioxide by *Spirulina* sp. and *Scenedesmus obliquus* cultivated in a three-stage serial tubular photobioreactor. *Journal of Biotechnology* **129** (3), 439–445.

Giménez, J. B., Robles, A., Carretero, L., Duran, F., Ruano, M. V., Gatti, M. N., Ribes, J., Ferrer, J. & Seco, A. 2011 Experimental study of the anaerobic urban wastewater treatment in a submerged hollow-fiber membrane bioreactor at pilot scale. *Bioresource Technology* **102**, 8799–8806.

Giménez, J. B., Martí, N., Ferrer, J. & Seco, A. 2012 Methane recovery efficiency in a submerged anaerobic membrane bioreactor (SAnMBR) treating sulphate-rich urban wastewater: evaluation of methane losses with the effluent. *Bioresource Technology* **118**, 67–72.

Giménez, J. B., Bouzas, A., Carrere, H., Steyer, J.-P., Ferrer, J. & Seco, A. 2018 Assessment of cross-flow filtration as microalgae harvesting technique prior to anaerobic digestion: evaluation of biomass integrity and energy demand. *Bioresource Technology* **269**, 188–194.

González-Camejo, J., Serna-García, R., Viruela, A., Pachés, M., Durán, F., Robles, A., Ruano, M. V., Barat, R. & Seco, A. 2017 Short and long-term experiments on the effect of sulphide on microalgae cultivation in tertiary sewage treatment. *Bioresource Technology* **244**, 15–22.

Martí, N., Barat, R., Seco, A., Pastor, L. & Bouzas, A. 2017 Sludge management modeling to enhance P-recovery as struvite in wastewater treatment plants. *Journal of Environmental Management* **196**, 340–346.

Moosbrugger, R., Wentzel, M. & Ekama, G. 1992 *Simple Titration Procedures to Determine H_2CO_3 Alkalinity and Short-chain Fatty Acids in Aqueous Solutions Containing Known Concentrations of Ammonium, Phosphate and Sulphide Weak Acid/Bases*. Water. Res. Commission, Report, No. TT 57/92.

Morales, N., Boehler, M. A., Buettner, S., Liebi, C. & Siegrist, H. 2013 Recovery of N and P from urine by struvite precipitation followed by combined stripping with digester sludge liquid at full scale. *Water* **5**, 1262–1278.

Norddahl, B., Horn, V. G., Larsson, M., du Preez, J. H. & Christensen, K. 2006 A membrane contactor for ammonia stripping, pilot scale experience and modeling. *Desalination* **199** (1–3), 172–174.

Pretel, R., Durán, F., Robles, A., Ruano, M. V., Ribes, J., Serralta, J. & Ferrer, J. 2015 Designing an AnMBR-based WWTP for energy recovery from urban wastewater: the role of primary settling and anaerobic digestion. *Separation and Purification Technology* **156**, 132–139.

Pretel, R., Robles, A., Ruano, M. V., Seco, A. & Ferrer, J. 2016 Economic and environmental sustainability of submerged anaerobic MBR-based (AnMBR-based) technology as compared to aerobic-based technologies for moderate-/high-loaded urban wastewater treatment. *Journal of Environmental Management* **166**, 45–54.

Puyol, D., Batstone, D. J., Hülsen, T., Astals, S., Peces, M. & Krömer, J. O. 2017 Resource recovery from wastewater by biological technologies: opportunities, challenges, and prospects. *Frontiers in Microbiology* **7** (2106), 1–23.

Sharma, B., Sarkar, A., Singh, P. & Singh, R. P. 2017 Agricultural utilisation of biosolids: a review on potential effects on soil and plant grown. *Waste Management* **64**, 117–132.

Sialve, B., Bernet, N. & Bernard, O. 2009 Anaerobic digestion of microalgae as a necessary step to make microalgal biodiesel sustainable. *Biotechnology Advances* **27** (4), 409–416.

Sid, S., Volant, A., Lesage, G. & Heran, M. 2017 Cost minimization in a full-scale conventional wastewater treatment plant: associated costs of biological energy consumption versus sludge production. *Water Science and Technology* **76** (9), 2473–2481.

Viruela, A., Murgui, M., Gómez-Gil, T., Durán, F., Robles, Á., Ruano, M. V., Ferrer, J. & Seco, A. 2016 Water resource recovery by means of microalgae cultivation in outdoor photobioreactors using the effluent from an anaerobic membrane bioreactor fed with pre-treated sewage. *Bioresource Technology* **218**, 447–454.

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