Removal of micropollutants from urban wastewater using a UASB reactor coupled to a MBR at different organic loading rates.

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KEYWORDS: UASB; organic pollutants; urban wastewater; organic load; biological wastewater treatment; membrane bioreactor

ABSTRACT.

This study examines the removal of micropollutants (MPs) in a hybrid process that combines anaerobic and aerobic redox conditions under different Organic Loading Rates (OLRs).

A laboratory-scale pilot-plant composed of an Upflow Anaerobic Sludge Blanket reactor (UASB) combined with a membrane bioreactor (MBR) was operated. Six MPs were analyzed: the hormones estrone, 17-α-ethinyl estradiol and 17-β-estradiol, the plasticizer bisphenol A and the pharmaceuticals carbamazepine and diclofenac. In order to study its influence on removal

efficiencies, the system was operated at three different OLRs: high (0.67±0.15 kg COD/m^3 d), medium (0.37±0.06 kg COD/m^3 d) and low (0.11±0.02 kg COD/ m^3 d).

The results demonstrated the synergistic effects due to the double biological treatment, with removal rates above 90% for the hormones and the plasticizer. Pharmaceuticals were the most resistant compounds, being only partially removed of the liquid phase. Removal rates of the MPs were higher at high OLR of the influent.

1. INTRODUCTION

Micropollutants (MPs) are unregulated organic trace compounds with increasing presence in the environment. The consequences of their persistence, bioaccumulation and potential genotoxicity are not entirely known.

Although the development of advanced aerobic biological processes, such as membrane bioreactors (MBR), have been a major advance in the reduction of many of these organic compounds, certain micropollutants are only partially removed (Radjenovic *et al*., 2007, Cartagena *et al*., 2013).

Anaerobic processes have been used for decades in the treatment and disposal of biodegradable organic matter from industrial wastewater with high OLR. Recent studies have shown that some MPs such as the analgesic naproxen, the antibiotics sulfamethoxazole, roxithromycin (Carballa *et al*., 2007), and the estrogens 17α-ethinyl estradiol, 17β-estradiol and estrone (Kreuzinger *et al*., 2004; Carballa *et al*., 2007; Musson *et al*., 2010) are more effectively removed by anaerobic means.

Combined technologies incorporating biological aerobic and anaerobic processes have proven to be more effective in MPs removal since promote synergistic interactions which facilitate the elimination or reduction of the most persistent compounds. Multiple configurations combine the benefits of biological processes. In an extensive review Chan *et al*. (2009) studied 23 different combinations of anaerobic and aerobic processes. In 13 of these combinations the anaerobic process is based on UASB reactors. Regarding the aerobic processes used, the vast majority were CAS processes with attached or suspended biomass. Only one of the combinations used membrane processes, UBF (Up flow Bed Filter) + MBR. A more recent review (Chong, *et al*., 2012) includes several studies in which the effluent from the UASB reactors was also treated with MBR, confirming the good performance of these combined processes on the removal of organic matter and nutrients in influents with high OLR. Furthermore, the UASB + MBR combination has proven effective for the treatment of industrial wastewaters, such as milk residues (Buntner *et al*., 2013), molasses (Yan et al., 2012), high-salinity waters (Shi *et al*., 2014), landfill leachate (Akgul *et al*., 2013) or for the removal of pharmaceuticals antibiotics such as sulfamethoxazole and trimethoprim (Alvarino *et al*., 2016). Consequently, the combined UASB-MBR system is especially promising for approach the degradation of MPs in urban or industrial wastewaters.

The influence of the organic loading rate (OLR) of the influent on the removal of MPs is also an important and scarcely studied issue in the literature. As can be deduced from mentioned articles, UASB reactors have traditionally been used as a single system or in combination with other aerobic systems, for the treatment of industrial influents with high OLR (4.00 to 12.00 kg COD / m^3 d (Kato, 1994; Soto *et al*., 1997). However, the MPs removal of low OLR substrates has been hardly addressed. Alvarino *et al*. (2016) studied their removal of urban wastewater with organic

loading of more than 1 kg COD / m^3 d, and Qiu *et al*. (2013) studied the performance of UASB-MBR ranging from 1.97 to 3.55 4 kg COD / m^3 d.

The production of biogas in the methanogenic stage of the anaerobic digestion process is another advantage of UASB-MBR combined systems. The potential of anaerobic systems and their combination with aerobic systems promotes the energy self-sufficient of treatment facilities, since it reduces the energy consumption required for the aeration and, consequently, the costs of operation and maintenance. Moreover, the presence of MPs in the influent could cause the inhibition of the methanogenic activity of the anaerobic sludge (Chernicharo, 2006; Rosa *et al*., 2016)

This research focuses on the study of the removal of the liquid phase of six micropollutants in a hybrid process that combines anaerobic and aerobic redox conditions under different organic loading rates. In addition, the operation of the combined system for the removal of organic matter and nutrients as well as the production of biogas in the UASB reactor has also been studied. For this purpose, a UASB-MBR laboratory-scale pilot plant was operated at three different organic loading stages: high OLR (0.67 ± 0.15 kg COD /m^3d), medium OLR (0.37 ± 0.06 kg COD /m^3d) and low OLR (0.11 ± 0.02 kg COD /m^3d), with average influent concentrations of around 1200, 600 and 170 mg/L COD respectively.

2. MATERIALS AND METHODS.

Description of the laboratory-scale plant.

For the purpose of this study a laboratory-scale system composed of a UASB reactor combined with a MBR was designed, constructed and operated. The design and components are shown in Figure 1.

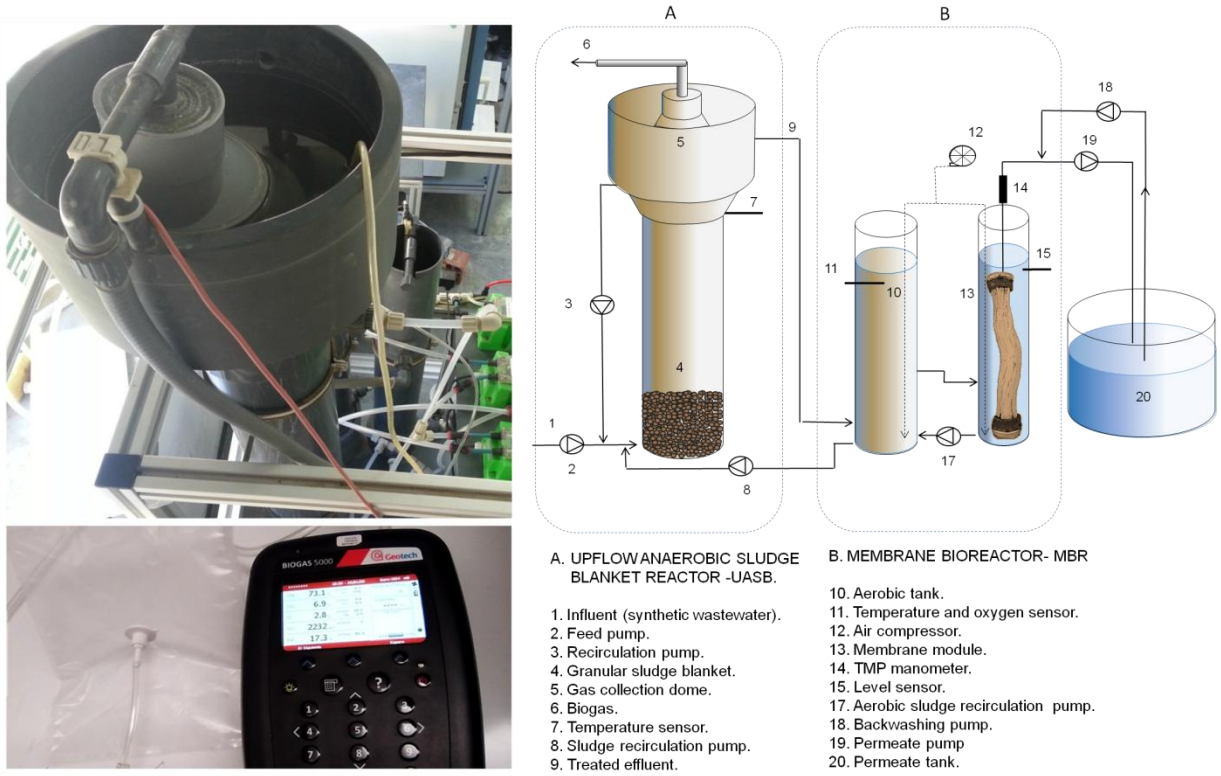


Figure 1. Image of combined UASB-MBR lab-scale plant (top left). Measurement of biogas composition (bottom left). Schematic of combined UASB-MBR system (right).

The anaerobic treatment was carried out by means of a cylindrical UASB reactor of 25 L of available volume seeded with 8 L of fluidized granulated sludge originating from a WWTP of a brewery industry located in Quart de Poblet, Valencia (Spain). The system was equipped with a recirculation peristaltic pump (Dosiper Peristaltic pumps, León, Spain) in order to control and maintain the upflow liquid velocity inside the reactor. The biogas generated during the anaerobic process was collected in a bell-shaped three-phase separation device. Biogas production was measured by a flow meter based on the principle of liquid displacement and a Geotech Biogas-5000 analyzer was used to determine the biogas composition.

The UASB reactor effluent (supernatant) was led to the aerobic biological stage. The membrane bioreactor consisted of two chambers: a 12 L aerobic chamber seeded with 6 L of mixed liquor from a municipal WWTP (Rincon de León, in Alicante, Spain) and an 8 L filtration chamber where a PDVF hollow-fiber membrane module Micronet R, with a pore size of 0.4 μm and 0.2 m2 of filtration surface was placed on.

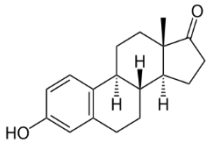
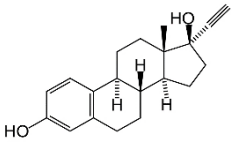
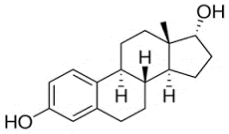
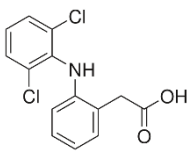
The system was provided with a temperature probe and level sensors in both the anaerobic and aerobic reactors. The MBR was equipped with a dissolved oxygen meter (Oxymax COS61 Endress + Hauser) and a pressure transmitter (TPR-14 from DESIN Instruments) for transmembrane pressure data control. Dosiper C1 R Peristaltic pumps (León, Spain) were used to feed the plant and drive the different sludge recirculations. The permeate was extracted from the membrane chamber by a Watson-Marlow 323 U/D peristaltic pump with a maximum flow rate of 2000 mL/min (Watson-Marlow Ltd., Falmouth, UK). The critical flow of the membrane was 12.5 L/m^2 h, and was determined based on the flux-step method developed by Van der Marel *et al*. (2009). Finally, software developed by the research group was used for the continuous monitoring and control of the main operating parameters of the combined system.

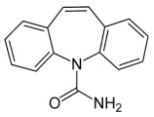
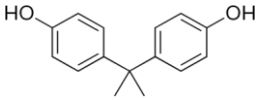
The synthetic wastewater was prepared in order to simulate three different rates of organic load of an urban wastewater. The composition for a COD reference of 1200 mg O_2/L included: peptone (634.7 mg/L) and beef extract (434.5 mg/L) as major sources of carbon and nitrogen, minerals in trace concentrations (7.9 mg/L of $MgSO_4 \cdot 7\ H_2O$, 15.7 mg/L of $CaCl_2 \cdot 2\ H_2O$ and 27.6 mg/L of NaCl), as well as sodium carbonate (20 mg/L) and bicarbonate (40 mg/L) to maintain the bicarbonate alkalinity and buffer capacity of the system.

Selection of micropollutants.

The selection of MPs comprised six organic micropollutants of different nature (three hormones, one plasticizer and two pharmaceutical compounds). In order to avoid the possible inhibition of the methanogenic activity and the loss of biomass (Buntner, 2013; Sanchez, 2016), the use of methanol as a solvent was ruled out. According to Cartagena *et al*. (2013) the contaminants were introduced into the synthetic feed dissolved in dichloromethane (DCM) (12.5 mL of DCM per 50 L of synthetic feed). The selected MPs were introduced in the influent at concentrations of 10 μg/L of each compound. MPs standards, with purity greater than 90%, were supplied by Sigma-Aldrich (Steinheim, Germany). The list of the studied compounds together with their molecular formula and CAS number is included in Table 1.

Table 1. List of compounds in the study.

Compound	CAS No.	Formula	Structure	Usage
Hormones				
Estrone	53-16-7	$C_{18}H_{22}O_2$		Estrogenic hormone
17-α-ethinyl estradiol	57-63-6	$C_{20}H_{24}O_2$		Estrogenic estradiol derivative
17-β-estradiol	50-28-2	$C_{18}H_{24}O_2$		Steroid hormone
Pharmaceuticals				
Diclofenac	15307-86-5	$C_{14}H_{11}C_{l2}NO_2$		Anti-inflammatory agent
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$		Analgesic,

				antiepileptic
Plasticizer				
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$		Plasticizer

Analytical Methods and Techniques.

Samples were taken daily basis at different points in the combined system: influent, effluent from the UASB reactor (supernatant), liquor-mix from the MBR aerobic tank, plant permeate and, less frequently, anaerobic granular sludge. Daily pH controls (pH-meter model Basic 20+ Crison) and electrical conductivity (Conductometer CM 35 Crison) were carried out. The quantification of the total suspended solids (TSS) present in both the granular and the aerobic sludge was based on gravimetric Standard Methods (APHA *et al*., 1992). Chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), nitrogen-nitrate (NO_3-N), nitrogen-nitrite (NO_2-N) and ammonium (NH_4) analyses were performed based on colorimetric methods (APHA *et al*., 1992) (tube-test and spectrophotometer NANOCOLOR® Machery-Nagel GMBh & Co., Düren).

Samples were also collected at each stage of the research to determine the composition of the biogas generated in the anaerobic process. Tedlar® PVDF sampling bags equipped with a push / pull lock valve were used. These were fitted to the Geotech Biogas-5000 analyzer from Geotechnical Instruments Ltd, UK, which can determine the concentration of the five main gases that compose biogas (methane, oxygen, carbon dioxide, hydrogen and hydrogen sulphide).

Related to the analysis of the micropollutant concentrations remaining in the treated effluent in both the individual systems and in the combined UASB-MBR system, the analysis procedure

began with the sampling of each of the currents described above. The volume of each sample of the synthetic feed was 200 mL, while the volume of the effluents samples (supernatant) of the UASB reactor and the permeate of the combined lab-scale plant was 500 mL in both cases. Samples were preconditioned by filtration (glass fiber 1.2 mm, Millipore^{TM}) and diluted in ultrapure water (1:2) (Sigma-Aldrich). The extraction of analytes from the samples was carried out by Solid Phase Extraction-SPE method (Thermo ScientificTM DionexTM AutoTraceTM 280 extractor). It was carried out in an acidic medium (pH <4) (sulfuric acid, 96%, p/p) to favor the retention of the compounds with lower octanol-water coefficient (log k_{ow}). Oasis HLB cartridges 6 cc / 200 mg Waters were used. The solvents used in the activation / conditioning of the cartridges were: ethyl acetate (5mL, 4 mL / min), methanol (5 mL, 4 mL / min) and ultrapure water (5 mL, 4 mL / min.) (Sigma-Aldrich). For elution, ethyl acetate (4 mL, 4 mL / min) and ethyl acetate: methanol (1: 1 v / v) 4 mL, 4 mL / min) were used. The estimated extraction time for each batch of 6 samples was 110 minutes for 200 mL volume samples and 140 minutes for 500 mL samples. Evaporation was carried out by adding 100 µl of internal standard solution (500 µg/L of triphenyl phosphate and carbamazepine-d10 in methanol) to the extracts collected in each tube, which were dried by N_2 gas flow. Samples were reconstituted by adding 50 µL of BSTFA: TMCS (N, O-bis- (trimethylsilyl) trifluoroacetamide; trimethylchlorosilane)) (99: 1 v/v) and 50 µL of pyridine (Sigma-Aldrich (Steinheim, Germany). According to Gómez *et al*. (2007), Radjenovic *et al*., (2009), Hai *et al*. (2011) and Azzouz *et al*., (2014), each vial was capped and incubated in a thermoblock at 60 ° C for 30 minutes. Samples were stored at 4 ° C until analysis by gas chromatography coupled to mass spectrometry (GC / MS). All analyses were performed using an Agilent 7890A gas chromatograph coupled to a quadrupole mass spectrometer Agilent 5975C quadrupole mass spectrometer, equipped with capillary column (30 m × 250 µm × 0.25

μm film thickness) (Agilent Technologies, Inc., Santa Clara, USA). The mobile phase used was helium (1.3 mL • min-1). The initial temperature of the oven was 105 °C and the temperature ramps were from 105 to 200 °C at 17 °C · min^{-1}. 1 min at 200 °C, from 200 to 220 °C at 2 °C min^{-1}.2 min at 220 °C, and from 220 to 290 °C at 5 °C · min^{-1}·1 min at 290 °C. A volume of 1 μL was injected in splitless mode (injection without division of the sample). The ionization mode used was electron impact ionization at 70 eV. The equipment was operated in SIM mode. The mass range used for the SCAN was 40-500, with a delay time of 3 minutes. Regarding linearity, limits of detection and quantification, and repeatability of the method, a calibration line was made for each of the selected compounds by standards at different concentrations (0.0125, 0.025, 0.025, 0.050, 0.100, 0.250; 0.500, 1,000, 2,000, 5,000 and 10,000 ppm) analyzed according to the same sequence as that used for the samples under study. The specific recovery percentages of each compound were calculated experimentally by preparing 6 replicates of a standard solution (concentration: 10 μg/L) of the micropollutants studied in a volume of 200 mL of ultrapure water, which were extracted, evaporated and reconstituted according to the described procedure. The percentages of recovery and standard deviations, limits of quantification (LOQ) and detection (LOD) determined for each of the compounds under study, are included in Supporting Material.

3. RESULTS AND DISCUSSION.

Performance of combined UASB-MBR system.

During the first days of operation of the lab-scale pilot plant, the equipment was verified. The measuring instrumentation was calibrated and the pumps were tested and calibrated. The experimental period comprised four distinct stages. Stage 1 (start-up of the system) began on day 20 with the seed of fluidized granular sludge and mixed liquor in the UASB reactor and the

MBR respectively. At this stage, the values of the main operating parameters of both the individual and combined systems were established (Table 2).

Table 2 Operation conditions of the combined UASB-MBR plant.

Stage	**1**	**2**	**3**	**4**
Period of time (d)	20-55	56-87	88-125	126-172
OLR (kg COD/mg/L)	0.66±0.31	0.67±0.15	0.37±0.06	0.11±0.02
T (ºC)				
UASB	26±3	29±1	31±1	30±1
MBR	23±2	27±2	29±1	26±2
HRT (h)				
UASB	37	37	37	37
MBR	26	30	30	30

Stage 2 of the experimentation began with the introduction of the mixture of MPs in the synthetic substrate. The removal / degradation at high organic load (0.67 ± 0.31 kg COD /m^3 d) was studied. After an intermediate stabilization period, Stage 3 of the operation was carried out at medium organic load (0.37 ± 0.06 kg COD /m^3 d). The last stage of the experimental period, Stage 4, studied the removal of the compounds at low organic load (0.11 ± 0.2 kg COD /m^3 d).

The UASB reactor was operated at high sludge retention time (SRT), performing periodic purges to maintain the age of the sludge in 90 days. With this strategy of operation, the solids retention time inside the UASB reactor was maximized, thus optimizing the effectiveness of the anaerobic treatment (Lettinga, *et al*., 1983; Rizvi *et al*., 2015). In order to avoid biomass losses in the anaerobic reactor, both the upflow liquid velocity and the recirculation flow between the MBR reactor and the UASB reactor were maintained at values of 0.1 m/h and 0.01 L/h respectively.

UASB reactor was operated during the first 40 days at room temperature and subsequently at a controlled temperature close to 30 ° C to guarantee the stability of methanogenic activity in the system since the best growing conditions for methanogenic microorganisms are between 30-35 °C (Souto *et al*., 2010). The MBR was maintained at room temperature throughout the experimental period and with a SRT of 90 days to stimulate the development of slow-growing prokaryotic communities as well as the presence of macroflocs in the aerobic sludge, optimizing the reduction of nitrogen compounds in the system (Le-Clech, 2003 and Judd, 2011). The permeate flux of the membrane was 5.3 $L/m^2/h$ and filtration/backwashing cycles of 10 / 0.5 minutes were used.

Removal of Organic Matter.

Because of the satisfactory performance of the previous anaerobic treatment, the influent of the MBR had a low OLR during the experimentation, with maximum values of 0.89 kg COD/kg MLSS/d in the high OLR stage and a minimum of 0.07 kg COD/kg MLSS/d at low OLR.

Figure 2 shows the degradation rates of organic matter achieved by individual biological reactors as well as by the combined UASB-MBR system.

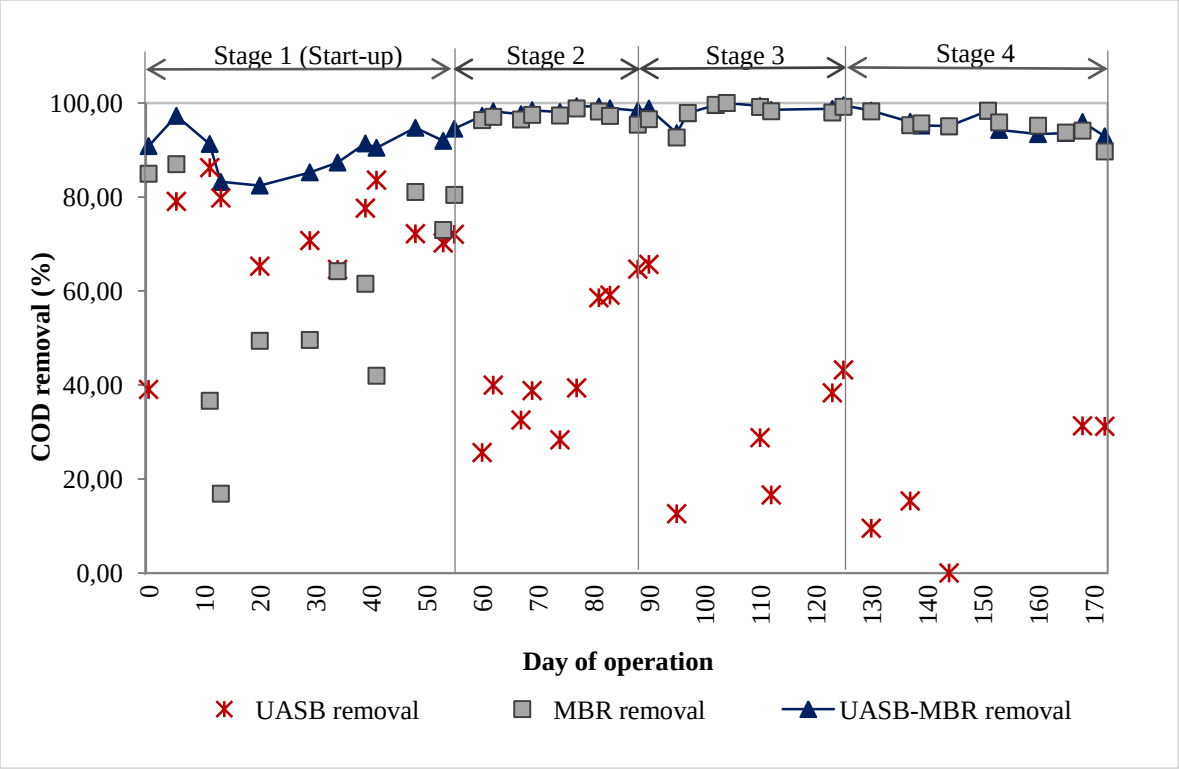


Figure 2 COD removal efficiencies of the MBR, UASB and combined UASB-MBR reactors at different OLRs.

During Stage 1, the UASB reactor achieved efficiencies in organic matter removal of around 86% with a specific biogas production rate of 0.29 m^3/kg COD. The MBR reached an organic matter removal rate of 87%. The maximum performance efficiency of the combined UASB-MBR system was 97%.

The introduction of MPs into the synthetic influent at high OLR (Stage 2) produced an immediate decrease in the production of biogas, although in later stages the production increased again due to the conditioning of the anaerobic biomass to the introduced contaminants. The UASB reactor reduced its efficiency by 34% after introducing the MPs, which confirms a certain inhibition of the system caused by these compounds (Buntner, 2013). This resulted in a higher organic load in the MBR influent, which improved its COD elimination rates and restored the efficiency of the global system.

The synergies established between the aerobic and anaerobic biological systems resulted in average yields of the combined UASB-MBR system of 97% during Stages 2, 3, and 4 (high, medium and low OLR respectively), achieving maximums of 99%, which are coincident with those obtained by Buntner *et al*. (2013).

The results confirm the high efficiency of the combined system in the degradation of organic matter for all the OLRs ranges analyzed. At high OLR (0.67 ± 0.15 kg COD /m^3 d) the anaerobic reactor plays a fundamental role in the degradation of organic matter, while at medium and low OLRs (<0.4 kg COD /m^3 d) the MBR system is main responsible for COD removal.

Removal of nutrients.

A maximum reduction of total nitrogen in the UASB reactor (around 20%) was achieved, which basically consisted of its transformation to the ammoniacal form by hydrolysis of the proteins and, to a lesser extent, to its gaseous form as a component of the biogas generated in the process of anaerobic digestion. This confirms the results of previous studies (Buntner, 2013; Qiu *et al*., 2013). The regular dosing of Na_2CO_3 and $NaHCO_3$ in order to maintain the bicarbonate alkalinity of the system also benefited denitrification in the anaerobic reactor (Ahn *et al*., 2007).

The MBR was the main responsible for the nutrient reduction of the combined lab-scale pilot plant. The operation strategy of the MBR improved the effectiveness of the combined system. Operating at high SRT and with a high recirculation ratio between the aerobic chamber and the membrane chamber, the specialization of the bacterial communities were enhanced, achieving significant nitrification-denitrification rates. The MBR system was not affected by the presence of the MPs and maintained average TN and TP removal rates close to 40% throughout the experimentation, with maximum values of 42% and 54% respectively at low OLR (Stage 4).

MPs removal.

Figure 3 shows the MPs removal efficiencies in the UASB reactor (left) and in the combined UASB-MBR system (right) for the different stages of OLR studied, as well as the hydrophobicity coefficient (log Kow) of the compounds tested.

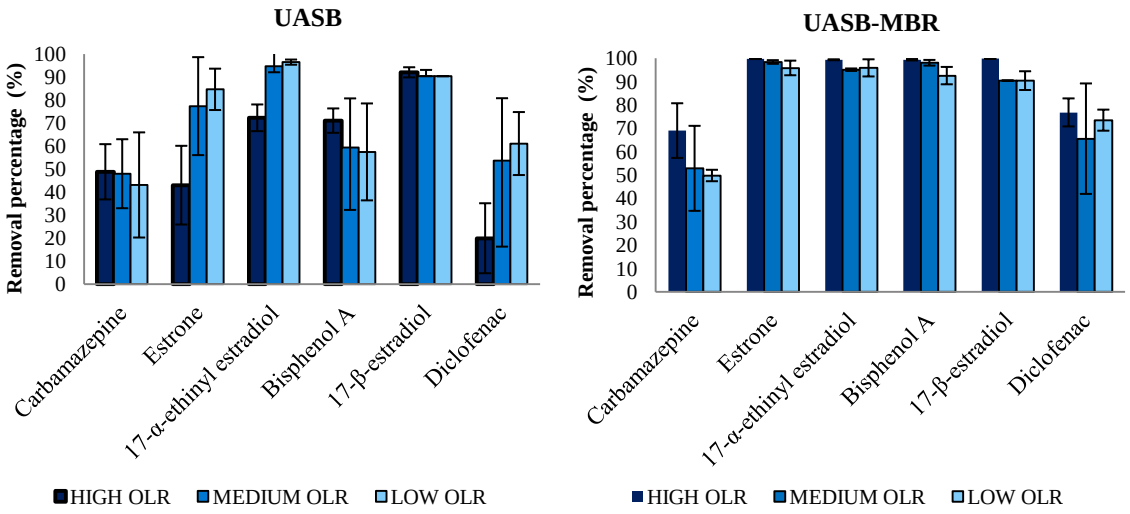


Figure 3 Overall removals of MPs in the UASB reactor (left) and combined UASB-MBR pilot plant (right) at high, medium and low Organic Loading Rates (stages 2 to 4).

Regarding the MPs removal efficiencies in the MBR (Figure 4), these were very irregular, depending mainly on the efficiency of the UASB reactor, whose effluent fed the MBR.

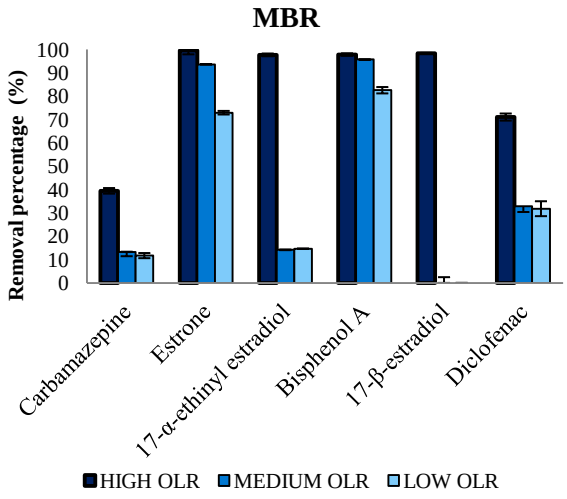


Figure 4 Overall removals of MPs in the MBR at high, medium and low Organic Loading Rates (stages 2 to 4).

The UASB reactor effluent was treated aerobically by the MBR. The best removed compounds were those that remained in higher concentration after the anaerobic treatment, such as the hormone estrone and the plasticizer bisphenol A, in all the organic loading stages, and the hormones 17-α-ethinyl estradiol and 17-β-estradiol, and the pharmaceutical diclofenac, in high OLR.

- **MPs removal rates in the UASB system.**

The compounds which were most effectively eliminated in the UASB reactor were the hormones 17-α-ethinyl estradiol and 17-β-estradiol. The compounds that were partially removed of the liquid phase by the anaerobic route were the plasticizer bisphenol A and the hormone estrone, with removal rates around 57-59% and 43-84% respectively. These results are similar to those reported by Carballa *et al*., 2007. The most recalcitrant compounds to anaerobic treatment were the pharmaceutical active compounds carbamazepine and diclofenac, with removal rates above 43% for carbamazepine, higher than those obtained in previous investigations (Heberer, T. (2002), Clara *et al*. (2005), Joss *et al*. (2006)), and ranging from 20% to 61% for diclofenac.

As for the effect of the OLR of the influent, higher removal rates were observed at low OLRs in the case of the hormones. However, this tendency could not be corroborated in the case of the pharmaceutical compounds because although carbamazepine was better removed at high OLR by contrast the removal of diclofenac was improved at low OLR. Regarding plasticizer bisphenol A, its anaerobic treatment was more efficient at high OLR.

- **MPs removal rates in the combined UASB-MBR system.**

The combined UASB-MBR lab-scale plant achieved high removal rates for the three hormones, estrone (95-99%), 17-α-ethinyl estradiol (95-99%) and 17-β-estradiol (90-99%) and also for the plasticizer bisphenol A (92-99%) with all the OLRs tested. These results were consistent with those obtained by Wijekoon *et al*. (2013). The partially removed compounds were carbamazepine and diclofenac, with maximum removal percentages of 69% and 76% respectively at high OLR, confirming its high persistence to biological treatments (Clara *et al*., 2005; Carballa *et al*., 2007; Alvarino *et al*., 2014).

This research focuses on the elimination of MPS from the aqueous phase. Specific studies are required on other mechanisms of elimination (adsorption onto sludge, volatilization) as well as on the possible metabolites of the studied MPs.

Biogas.

During the experimentation, the UASB reactor achieved a specific biogas production rate of 0.29 m^3/kg COD, reaching this maximum in Stage 1. After the introduction of MPs (Stage 2) in the synthetic feed the production of biogas declined considerably. Although it increased again after the adaptation of the anaerobic biomass to the presence of MPs, the production of biogas became irregular and decreased in later stages (medium and low OLR). Regarding biogas composition, the results of the analyzer tests confirmed the high quality of the biogas generated in the UASB reactor, with an average methane content of 73.2% which was above the values indicated by Surendra et al. (2014). The minor components present in biogas were carbon dioxide (6.2%), hydrogen sulphide (<0.3%), oxygen (3.5%) and nitrogen and other gases (16.8%), all of them trace-gases typical of the composition of biogas produced by the anaerobic degradation of organic matter (EBA, 2013). Regarding the oxygen concentration, it was mainly due to the

oxygen introduced into the UASB reactor through the synthetic feed pipe as well as the recirculation pipe from the MBR to the UASB reactor.

According to Converti *et al*. (1993) and Rizzi *et al*., (2006), high OLRs but not exceeding the maximum operational value of this parameter results in a higher rate of methane production.

4. CONCLUSIONS

The double biological treatment carried out by the UASB-MBR system improved the removal rates of the six analyzed compounds compared to those achieved by the individual biological treatments. The hormones estrone and 17-α-ethinyl estradiol were best eliminated by the UASB reactor when the system was performed at OLR (84.68 % and 77.39 %). The UASB-MBR combined system reached removal rates of 99.76 %, 99.34% and 99.86% for the hormones estrone, 17-α-ethinyl estradiol and 17-β-estradiol. The pharmaceuticals were the most resistant compounds, being only partially removed of the liquid phase. The removal rate of Carbamazepine in the UASB reactor was 48.88 % while the UASB-MBR combined system reached a maximum removal of 69.03 %, both when the influent was at high OLR. Diclofenac was poorly removed by the UASB reactor, achieving the best removal rate (above 61.14 %) at low OLR. Regarding the plasticizer bisphenol A, at medium and low OLR was partially removed by the UASB reactor. Nevertheless, the combined treatment improved the removal efficiencies reaching a 99.86 at high OLR.

Average yields of nitrogen and phosphorous removal were around 40%, which was almost entirely eliminated in the MBR system. Nitrogen after anaerobic treatment was mainly found in ammoniacal form while after filtration in the membrane bioreactor was found mainly in the form of nitrates, confirming the results of research such as Qiu et al. (2013).

The processes that take place in the anaerobic treatment serve as conditioning of these compounds favoring their subsequent elimination of the fraction remaining in the effluent by means of the membrane bioreactor (MBR).

The maximum flow rate of biogas obtained was 5 L/d, with a percentage of methane around 73% and low percentages of CO_2 and H_2S. However, production decreased following the introduction of the MPs and at medium and low OLR.

Regarding the influence of the OLR of the influent, the maximum removal rates of the six micropollutants by the combined UASB-MBR lab-scale pilot plant occurred when the OLR was in the range of 0.67 ± 0.15 kg COD / m^3 d, with average concentrations of about 1200 mg/L COD.

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6. ACKNOWLEDGMENT

This study was partially funded by the Spanish Ministry of Economy and Competitiveness through the project "Combined treatments for the degradation and/or elimination of emerging pollutants in water" (CTM2013-46669-R) and was developed at the University Institute of Water and Environmental Sciences. University of Alicante.

ASSOCIATED CONTENT

Supporting Information.

Table S1. Limits of quantification, hydrophobicity coefficient and recoveries.

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This manuscript was written through contributions of all authors named and all of them have given their approval to the final version of the manuscript.

Funding Sources

Spanish Ministry of Economy and Competitiveness through the project "Combined treatments for the degradation and/or elimination of emerging pollutants in water" (CTM2013-46669-R) and University of Alicante.