

MIDES Project: Drinking water production by low-energy microbial desalination powered by wastewater

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Abstract:

Current desalination technologies require high-energy input, being reverse osmosis (RO) the most-widely used technology for seawater desalination with an energy consumption of at least 3 kWhm⁻³. In this context, the MIDES project aims to revolutionize desalination by developing a low-energy sustainable process called Microbial Desalination Cell (MDC) as a pretreatment for RO. The integration of MDC technology with commercial RO allows seawater desalination with an energy consumption below 0.5 kWhm⁻³. MDC treats simultaneously wastewater and performs desalination using the energy contained in the wastewater [1]. In fact, MDC can produce around 1.8 kWh of bioelectricity from energy contained in one cubic meter of wastewater. This energy is directly used to lower salt content in seawater from 35 to 5 gL⁻¹ (brackish water) without external energy input, while further salinity reduction to achieve drinking water quality is performed in the subsequent RO step.

The overall MIDES process includes a pre-treatment of the saline stream by ceramic membranes prior to enter the MDC unit, where it is partially desalinated (70-90%) before the RO post-treatment. The results obtained with lab-scale MDC has led to a significant improvement of water production compared to values reported in literature for a 100-L MDC [2], reaching desalination rates of 0.5-3 Lm⁻²h⁻¹. Industrial wastewater (brewery) has been identified as the optimal feed to enhance the activity of electrogenic bacteria in the MDC. In addition, a ceramic membrane pilot plant operates at Racons brackish water desalination plant (Denia, Spain), with a treatment capacity of 6 m³h⁻¹, to obtain high quality permeate free of suspended solids. This effluent satisfies the quality requirements as saline stream for the MDC.

The MIDES Horizon 2020 project will develop the world's largest demonstrator of the innovative MDC technology in three sites: Spain, Tunisia and Chile. Three pilot plants of 150 Lday⁻¹ will be constructed and operated under real environments in desalination plants operated by Aqualia.

1 INTRODUCTION

Water desalination has become a technologically and economically viable solution to tackle increasing water shortages in many regions of the world [3]. However, its high-energy cost continues to be a major concern, with energy consumption accounting for 75% of the desalination operating cost when excluding capital costs [4]. This energy cost for desalination is about 10 times higher than for conventional water sources, leading to water prices that can easily exceed 0.5 €m^{-3} .

At present, energy consumption for desalination with RO has a technical limit of approximately 3.0 kWhm^{-3} to produce 50 % fresh water from seawater [5]. At this recovery of 50%, the minimum energy to overcome osmotic pressure in a membrane process is 1.09 kWhm^{-3} [6]. Therefore, a new approach is necessary to surpass the barriers in RO desalination and reduce energy consumption. Temperature-driven technologies (multi-stage flash distillation and multi-effect distillation) consume even larger amounts of energy ($5.5\text{-}40 \text{ kWhm}^{-3}$), limiting their use only in countries with low fuel cost. Considerable improvements in efficient system design, high efficiency pumping, and energy recovery devices have been made, and near optimal performance has already been established. Further progress in these categories will only provide marginal reduction in energy consumption [7].

Thus, new approaches are needed to diminish the energy demand associated to current desalination technologies. In this context, Microbial Desalination Cell (MDC) has emerged as an innovative technology, where external energy is not only consumed, but additional energy is produced while providing simultaneous wastewater treatment and desalination [1]. Derived from Microbial Fuel Cells (MFCs), MDC uses the electric potential generated from the microbial metabolism of organic compounds to drive desalination similarly to electro dialysis (ED). The benefit of MDC comes from integrating the degradation of organic wastes and wastewater treatment with desalination. Moreover, MDC operates under neutral pH, pressure and temperature conditions [8].

The MIDES low-energy approach combines MDC technology as pre-desalination step in connection with conventional RO aiming at increasing desalinated water production while maintaining low energy requirements. The MIDES overall process scheme is shown in Figure 1, where the core technologies, named MDC and RO, are integrated with other complementary technologies.

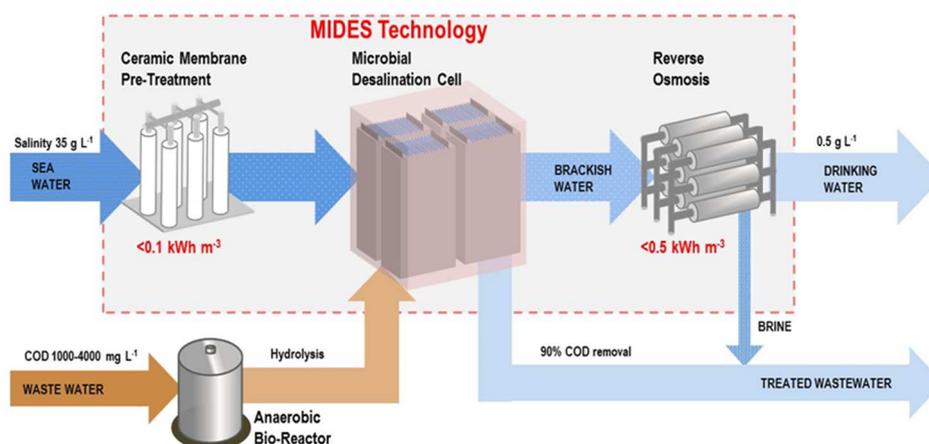


Figure 1. MIDES overall process.

The overall process includes the pre-treatment of two different streams, the wastewater stream and salted water stream. The initial treatment of municipal wastewater in a conventional anaerobic reactor to produce an acetate-rich effluent as a fuel for the MDC. In the case of salted water, in conventional RO desalination, seawater or brackish water undergoes several pretreatment steps (chemical coagulation, sedimentation and filtration) to protect the membranes from pollutants. In MIDES, polymeric submerged

membranes substitute this whole pre-treatment, leading to a reduction in chemicals usage and footprint, as well as lowering by 80% the energy demand.

After pre-treatment, pre-digested wastewater and pre-treated seawater enters the MDC, which employs the energy contained in wastewater to lower the salt content of seawater from 35 to 5 g L^{-1} , and returns a treated wastewater with a 90% reduction of the initial COD. Further salinity reduction to achieve drinking water quality is performed by the subsequent RO step. Since the RO process efficiency and energy requirement largely depends on feed water salinity, pre-treatment of the feed water with MDC will lower the energy demand for downstream RO.

The construction of three pilot plants in different locations within the scope of MIDES project is envisaged. By then, the implementation, deployment and versatility of this technology will be validated by the treatment of saline streams of diverse composition under more complex conditions.

1.1 Objectives

In the framework of MIDES project, the present study summarizes the research conducted so far on: i) wastewater pre-treatment, ii) MDC performance at lab-scale and iii) brackish water pre-treatment. More precisely, this work presents the preliminary results about:

- i. The potential use of different wastewater sources as fuels for the MDC.
- ii. The feasibility of MDC technology as pre-treatment step for RO at laboratory-scale.
- iii. The performance of polymeric submerged membranes brackish river water from the Racons river (Denia, Spain).

2 Materials and methods

2.1 Waste water pre-treatment

Acetogenic fermentation was used for wastewater pre-conditioning with the aim of producing an enriched acetate effluent to be fed into the MDC. The biofilm growing in the anode degrades the acetate and transfers the electrons to the anode, generating an electric current. Four pre-pilot up-flow anaerobic sludge blanket reactors (UASB) have been operated for more than a year in different locations, treating wastewater of different sources. These reactors (5.2 and 11 L) run at different hydraulic retention time (HRT) to maximize the concentration of volatile fatty acids (VFA) and acetate in the effluent stream. Reactors 1 to 3 were located at the wastewater treatment plant El Torno (Chiclana de la Frontera, Cádiz, Spain), and reactor 4 was located at IMDEA Water (Alcalá de Henares, Madrid, Spain).

Reactor 1 (R1) consisted of an UASB reactor inoculated with flocculated biomass and fed with raw municipal wastewater doped with molasses (1% v/v). Reactor 2 (R2) consisted of an UASB reactor inoculated with granular biomass and fed with raw municipal wastewater doped with molasses (1% v/v). The rationale of the addition of molasses lied in the increase of organic matter available to be degraded. Reactor 3 (R3) was similar to reactors 1 and 2, being fed with raw municipal wastewater, and Reactor 4 consisted of an expanded granular sludge bed (EGSB) reactor inoculated with granular biomass and fed with industrial wastewater (brewery industry).

The performance of these anaerobic reactors was assessed by the total volatile fatty acids concentration (TVFA) and the ratio of conversion of soluble COD in the influent to VFA and acetate in the effluent (ratio mass acetate COD (effluent) per mass soluble COD (influent)).

2.2 Saline stream pre-treatment

The pre-treatment of the saline stream within MIDES project was carried out at the brackish water desalination plant (BWDP) Racons, in Denia, eastern coast of Spain. In the city of Denia drinking water is produced from brackish water collected from the Racons river. The composition of the river water suffers even hourly fluctuations, which difficult the steady-state operation of the BWDP. An ultrafiltration (UF) membrane pilot plant was operated continuously treating this brackish river water. This pilot plant was fully automatized and recorded all the data process. The membrane installed in this pilot plant was a submerged UF membrane made of polyvinylidene fluoride (PVDF), with a nominal pore size of 0.03 μm , with out-in filtration operating in dead-end mode. Feed and permeate streams were characterized according to standard methods for total organic carbon (TOC), chemical oxygen demand (COD), Suspended solids (SS), pH, alkalinity, conductivity, turbidity, sulphate, silica, hardness and total coliforms. The quality of the RO feed water, this is the water after pre-treatment, was assessed by means of the silt density index (SDI), whose value should be lower than 5 and preferably below 3.

2.3 Laboratory MDC performance on real waste waters

The MDC laboratory-prototype had a three-compartment stack design consisting of a desalination chamber (70 cm^3) separating the anodic and cathodic chambers (70 cm^3 each once) by an anionic exchange membrane (AMX Neosepta) and a cation exchange membrane (CMX Neosepta), respectively. Anode and cathode consisted of carbon felts and graphite plates as electric collectors. The flow rate of anolyte, catholyte and saline streams was 95 mL min^{-1} . The whole system was kept under anaerobic conditions by flushing a mixture of N_2/CO_2 into the tanks in a temperature-controlled bath at 30 $^\circ\text{C}$. The anolyte consisted of 2 L of the effluents of reactors 1, 2 and 3, and the raw brewery waste water (influent of reactor 4). These solutions were previously vacuum-filtered to prevent membrane fouling. The saline stream was NaCl at 10 g/L and the catholyte was 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$. The three solutions were recirculated over their feed tanks until the conductivity in the saline stream reached values of conductivity below 1 mS/cm . The same experiment was previously carried out using synthetic wastewater as anolyte for comparative purposes. The MDC laboratory-scale was previously inoculated with *Geobacter sulfurreducens*. The MDC performance was assessed by the nominal desalination rate (NDR), expressed as volume of desalted water per area of membrane and time unit ($\text{Lm}^{-2}\text{h}^{-1}$), NaCl removal (%) and current utilization (ηc) as previously described [9].

3 Results and discussion

3.1 Wastewater pre-treatment by anaerobic digestion

Three UASB reactors have been operated at the municipal wastewater treatment plant (WWTP) "El Torno" in Chiclana de la Frontera, Cadiz (Spain). Two reactors were fed with municipal wastewater with a 1% v/v of molasses (R1 y R2) and another one (R3) with wastewater without molasses. One expanded granular sludge bed (ESGB) reactor has been operated at IMDEA Water (Alcalá de Henares, Spain) treating brewery wastewater. HRT of the reactors fed with wastewater plus molasses 1% (v/v) ranged from 48 to 24 h, while for the reactor fed with wastewater ranged from 5 to 3 h. The HRT of the ESGB reactor ranged from 8 to 2 h.

Raw municipal wastewater doped with molasses (1% v/v) was the affluent with higher COD, up to 6500 mg/L , while raw municipal wastewater showed the lowest values, around 500 mg/L . The highest acetate concentration was found in wastewater doped with molasses, around 1500 mg/L , which represented approximately the 60% of the total measured organic VFA, as depicted in Figure 2A y B. In addition, brewery wastewater had a high concentration in VFA (1200 mg/L) and acetate represented approximately the 50% of the total VFA.

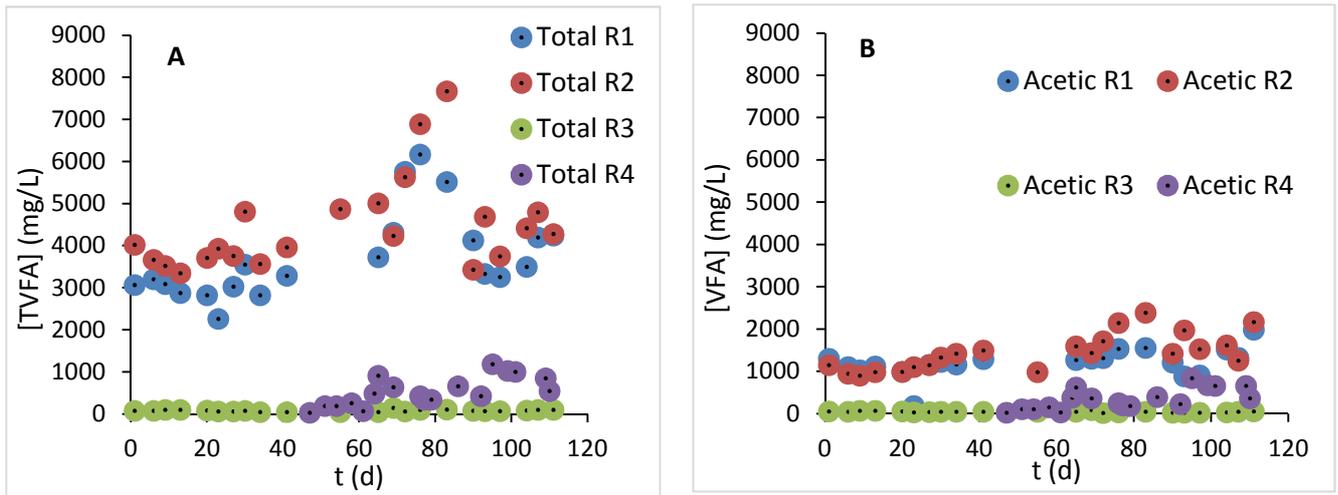


Figure 2. A) Total volatile fatty acids concentration and B) acetate concentration in effluents of anaerobic reactors 1-4.

The ratio of conversion of soluble COD in the influent to COD corresponding to VFAs in the effluent was 50% for reactor 1 and 60% for reactor 2. The ratio of COD conversion to acetate accounted for 16 and 19%, respectively. This means that reactor 2 performed better in terms of VFA production due to the microbiology present in the granular biomass. The effluent of the reactor 3 showed a noticeable lower concentration of VFA compared to that of reactors 1 and 2, due to its lower COD content in the influent. The ratio of conversion of soluble COD in the influent to COD corresponding to VFA in the effluent of reactor 3 was found to be 27%, representing approximately the half of the reported value for reactors 1 and 2. The ratio of COD conversion to acetate was 14%, lower than those found in reactors 1 and 2. In reactor 4, complete organic matter mineralization to CO₂ occurred due to the adaptation of the inoculum to this kind of wastewater and no increase in the VFA concentration in the effluent of the reactor was detected. This was in agreement with the value of the ratio of conversion of soluble COD in the influent to COD corresponding to VFA in the effluent, which exceeded 100%. Same results have been found for COD conversion to acetate.

In the case of reactor 4, by decreasing the hydraulic retention time (HRT) from 8 to 2 h, the formation of VFA was favored and methanogenesis was limited, as depicted in Figure 3. As the HRT was minimized, less organic matter was consumed by microorganisms (around 60% from the influent), this reducing the gas production and increasing above 28% the VFA generation in the inlet stream.

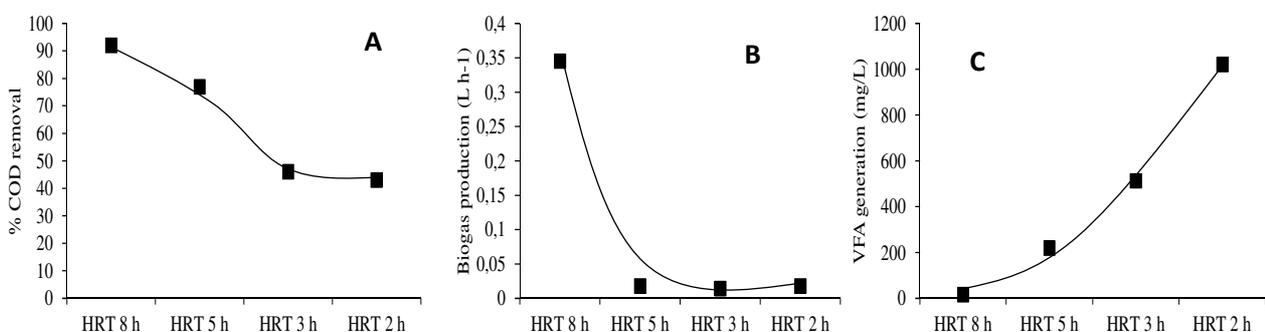


Figure 3. A) COD removal, B) biogas production and C) VFAs concentration in raw brewery wastewater at selected HRTs.

Among the three types of wastewater treated by anaerobic digestion, municipal wastewater doped with molasses showed the best performance in terms of acetate production. However, its low pH (around 4) prevented its use as MDC feed due to inhibitory effects on the anode bacterial biofilm activity [10]. Raw brewery waste water, despite its lower organic matter content compared to molasses-doped municipal waste water, presented two main advantages as a fuel for the MDC: i) high buffer capacity, which prevented potential bacterial inhibition, and ii) the anaerobic digestion can be avoided as the acetate concentration in the raw water was enough to feed the bioanode of the MDC.

3.2 Screening of pre-treated wastewater as fuel for MDC

The effluents of the anaerobic reactors treating municipal (reactor 3) and molasses-doped wastewater (reactor 2) and the influent of the anaerobic reactor treating brewery wastewater (reactor 4) were evaluated as feed for the MDC at lab-scale. The objective of these tests was to assess the feasibility of using wastewater as organic matter source for MDC operation and compare the MDC performance on real wastewater with synthetic wastewater. Table 1 summarizes the main parameters defining MDC performance.

Table 1. Main parameters of lab-MDC performance on real and synthetic wastewater.

	Synthetic waste water	Effluent reactor 2 (municipal ww + molasses)	Effluent reactor 3 (municipal ww)	Influent reactor 4 (raw brewery ww)
COD _i (mgL ⁻¹)	2538	6550	500	1232
Acetate (mgL ⁻¹)	1140	1432	36	662
pH _i (-)	7.78	4.12	7.55	7.68
NDR (Lm ⁻² h ⁻¹)	2.56	0.3	0.2	0.54
η _c (%)	81.4	94.2	88.7	94.6
NaCl removal (%)	99.3	94.9	91.3	91.2

The performance of the MDC was mainly a function of substrate availability. In all cases, the NaCl removal exceeded 90% and current utilization above 80% was achieved. The desalination rates using real wastewater as feed for the bioanode of the MDC were from 10 to 5-fold lower than those achieved with synthetic media at the same initial saline concentration 10 gL⁻¹. Taking into account the MDC performance on synthetic media as a reference, raw brewery wastewater showed the best performance in terms of desalination rate. In contrast, the lowest desalination rate (NDR) was obtained when using municipal wastewater as anolyte, owing to its low acetate concentration. Despite the high concentration of acetate in the pre-digested wastewater doped with molasses, bacterial activity may be limited because of the acidic pH and low buffering capacity, two factors that played a crucial role in the desalination process [10]. In light of these results, raw brewery wastewater was chosen as a feed for the MDC for further research.

3.3 Pre-treatment of real brackish water by polymeric submerged membranes

The UF pilot plant was operated during six months, treating the brackish water collected from Racons river. Different fluxes and filtration periods were tested to evaluate their influence on the plant performance, cleaning requirements and permeate quality to be subsequently directed to a RO desalination process.

3.3.1 Permeate quality of brackish water pre-treatment

Table 2 shows the average values obtained in the feed and permeate characteristics, as well as the membrane removal performance. Almost complete solids and turbidity removal efficiencies (>99%) were achieved despite the aforementioned fluctuations.

Table 2. Average feed and permeate composition during long-term UF experimentation.

	SS (mg/L)	Turbidity (NTU)	pH	Conductiv. (mS/cm)	TOC mg/L	COD mg/L	Alkalin. (mg/L)	Hardness (mg/L)	Sulphate (mg/L)	Silica (mg/L)	Total coliforms ufc/100mL	SDI
Feed	11.13	13.98	7.49	6.47	6.91	28.85	258.69	905.13	264.05	8.38	67043.67	
Permeate	0.07	0.14	7.46	6.44	5.38	20.39	261.67	879.56	256.81	8.32	2.00	2.44
Removal (%)	99.4	99.0			22.2	29.3			2.7		100.0	

Figure 4 shows the time-evolution of turbidity levels measured in feed and permeate streams. No differences in permeate turbidity during all the experimental procedures were observed, obtaining a high quality permeate despite the influent characteristics. Natural organic matter (NOM) was identified as the main foulant in raw water and the membranes suffered organic and biological fouling.

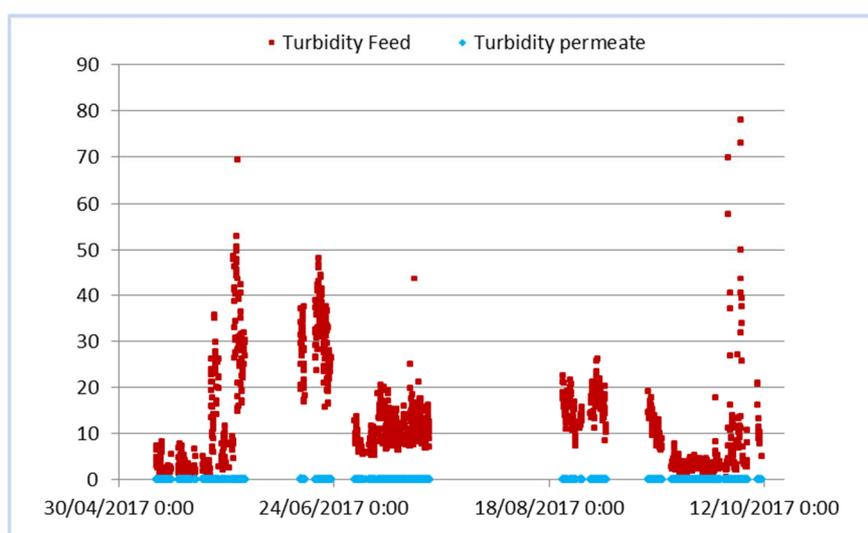


Figure 4. Time-course of feed and permeate turbidity in the experimental period.

3.3.2 Submerged polymeric membrane performance

The membrane permeability evolved along the experimental procedure according to the variations in the feed composition. Figure 5 shows the membrane permeability values, which greatly depend on turbidity changes along the experimental period. After membrane adaption to the process conditions, a slight pressure decrease was observed. Then, a sudden increase of turbidity in the feed occurred caused by a high-suspended solids concentration, which led to a substantial reduction of permeability.

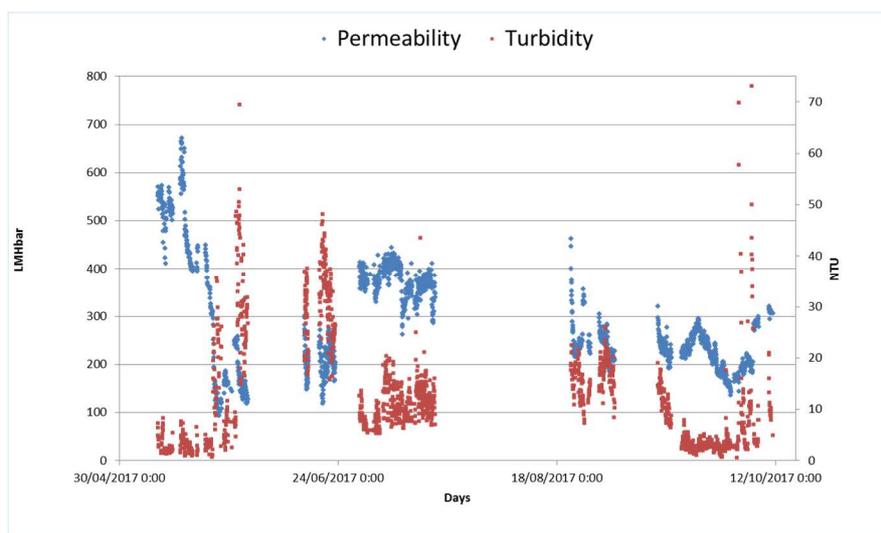


Figure 5. Time-course of permeability and turbidity of the feed.

Permeate fluxes ranging from 30 to 70 $\text{Lm}^{-2}\text{h}^{-1}$ (LMH) were tested to evaluate the influence of the flux over the membrane fouling kinetics and membrane recovery capacity using mechanical procedures. High-suspended solids concentration hindered the UF plant operation, especially under dead-end mode. Thus, membrane systems without air scouring during filtration periods and working in dead-end strategy led to high fouling rate and improper plant operation at suspended solids concentration higher than 100 mgL^{-1} in the membrane tank.

3.3.3 Membrane cleaning procedures

Removal of foulants adhered to the membrane surface was accomplished by developing cleaning strategies. Conventional cleaning strategies are based on mechanical and chemical cleanings, depending if chemical reagents are involved or not.

The mechanical cleanings used in the present study comprised an initial air scouring, backwash with permeate at 1.3 times the filtration flow and partial drainage of the membrane tank. This mechanical process was able to remove most of the foulants during normal operation, being effective enough to maintain acceptable permeability values with the help of chemical cleanings.

Chemical cleanings followed two strategies: a less aggressive chemical cleaning performed regularly for maintenance, and a more aggressive chemical cleaning to restore the permeability. In both the UF permeate was used to prepare the chemical solutions. The former aggressive chemical cleaning was a chemical enhanced backwash (CEB), performed with 100 mgL^{-1} of sodium hypochlorite during 30 minutes. A CEB every two days was necessary to maintain a sustainable plant performance. Otherwise, permeability started to decline notably.

The oxidant chemical cleaning was performed when the organic matter fraction was predominant [11]. Oxidation degraded the NOM functional groups to carboxyl, ketonic and aldehyde groups, which made them more susceptible to hydrolysis and increased hydrophilicity of their parent compounds. Therefore, oxidation reduced the adhesion of fouling materials to membranes [12]. In this study, two oxidant chemical reagents were used: sodium hypochlorite and hydrogen peroxide. Both were effective in foulant removal, but hydrogen peroxide was more effective when there were not available softened water to prepare the cleaning solutions.

4 Conclusions

The pre-treatment of real wastewater of different sources was performed towards the production of an acetate-enriched effluent to be fed to the MDC bioanode. Three UASB reactors and one ESGB reactor treated municipal wastewater, municipal water doped with molasses and brewery wastewater to enhance VFA generation in the effluent. Brewery wastewater stated as the optimal fuel for the MDC given its high buffering capacity and COD content. This fact was further corroborated by MDC tests using the pre-digested wastewater (municipal and molasses-doped) and the raw brewery wastewater as anolyte for the lab-MDC.

The pre-treatment of brackish water from Racons river at the BWDP Racons in Denia was conducted in a ultrafiltration pilot plant based on submerged membranes technology. The operation of the UF plant even with high fluctuations in the feed turbidity was feasible, assuring the quality of the permeate by developing new alternative operation procedures.

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6 References

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