Brewery wastewater treatment using MBR coupled with nanofiltration or electrodialysis: biomass acclimation and treatment efficiency

B. Sawadogo, Y. Konaté, G. Lesage, F. Zaviska, M. Monnot, M. Heran and H. Karambiri

ABSTRACT

Breweries release significant amounts of wastewater loaded with various organic and mineral materials. Prior studies of membrane bioreactor (MBR) wastewater treatment have been conducted with very little interest granted to the conditions of biomass acclimation. This study displays biomass behavior during brewery wastewater treatment by an aerobic MBR. In addition, nanofiltration and electrodialysis have been studied as potential post-treatment to decrease mineral concentrations and permit further water reuse for agriculture. An anoxic/aerobic laboratory MBR, associated with a flat sulfonated polyether membrane was used for synthetic brewery wastewater treatment. Biomass acclimation was performed using a feeding substrate. Organic concentrations in the MBR influent varied from 700 mg COD/L to 10,600 mg COD/L (COD: chemical oxygen demand) for 110 days. The results indicate a good acclimation to effluent with high salts and organic matter loads. Steady evolution of biomass concentration and activities was achieved after 90 days of operation. A reduction of COD of around 95% was obtained with MBR and up to 99% with nanofiltration post-treatment for the reconstructed brewery effluent with an organic loading rate of 7 g COD/L·d and a solid and hydraulic retention time of 30 days and 36 hours. A good reduction of the salt content was also recorded primarily with the nanofiltration and electrodialysis processes.

Key words | brewery wastewater, electrodialysis, membrane bioreactor, nanofiltration

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INTRODUCTION

Food industries are a major source of pollution due to the large volumes of wastewater generated and pollutants that it contains. In most cases, discharges across different steps of the production process vary in quality. Effluents are mainly produced in the washing, cleaning and rinsing activities commonly practiced in these industries and are characterized by high concentration of organic matter, nutrients and solids (Simate 2015; Valta *et al.* 2015; Jaiyeola & Bwapwa 2016; López-Avilés *et al.* 2018).

In the food industry, the brewing sector is an important economic link in several countries (Fillaudeau *et al.* 2007). In fact, it has been reported that beer is one of the most consumed beverages in the world (Fillaudeau *et al.* 2006). Brewing generates large volumes of effluents containing various pollutants and byproducts (Xiangwen *et al.* 2008). Processes that contribute to the wastewater load during production include bottle washing, tank and machine cleaning, cooling system rinsing, and hygienic operations (Braeken *et al.* 2004; Parawira *et al.* 2005; Rao *et al.* 2007).

It is common for brewery wastewater to discharge to an outfall which may be a sewage system, a waterway or the industry treatment unit (Huige 2006; Goldammer 2008; Xiangwen *et al.* 2008). Compliance with standards and regulatory requirements for wastewater discharges requires the use of treatment or pre-treatment techniques adapted to raw sewage and environmental conditions. The installed treatment plants use physical, chemical or biological techniques or a combination of these methods (Simate *et al.* 2011).

The scarcity of water resources, increasing water prices, strict regulations and high volumes of discharged wastewater justify the practice of wastewater reuse and recycling in industries, particularly in breweries (Götz *et al.* 2014).

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Among existing systems for industrial wastewater treatment, membrane technologies paired with conventional treatment components are believed to be one of the most widely used techniques in this field (Holt *et al.* 2006; Peng *et al.* 2009; Judd 2010). Membrane biological reactors (MBRs) combine two proven technologies, enhanced biological treatment using activated sludge and membrane filtration. It is a technique with the main advantage of potentially operating with mixed liquor highly loaded with suspended solids (SS), and with a higher solid retention time (SRT). Additionally, the membrane filtration system provides a complete retention of the biomass (Andrade *et al.* 2013). In addition, the MBR presents better removal efficiency for micropollutants, persistent organic pollutants and slowly biodegradable pollutants (Bernhard *et al.* 2006; Judd 2016). Studies on its use for the treatment of brewery wastewater have been conducted but few data are available on the conditions of biomass acclimation (Song *et al.* 2008; Dai *et al.* 2010). In this research, biomass acclimation during MBR operation and post-treatment of MBR effluent by nanofiltration and electrodialysis laboratory-scale units are investigated.

MATERIAL AND METHODS

MBR experimental set-up

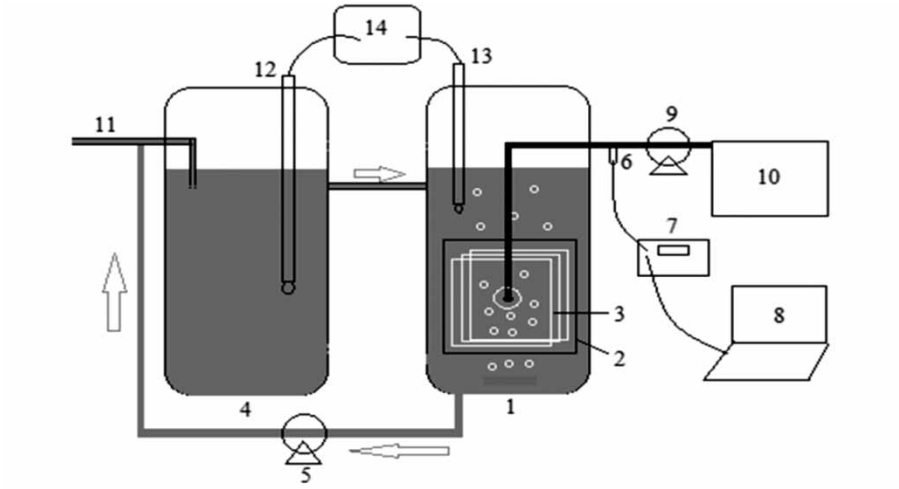
The laboratory-scale MBR used in this work consisted of two 30 L tanks. The first tank was aerated (oxic conditions) while the second was under anoxic conditions. The substrate to be treated was introduced into the system at a constant flow rate (40 L/d). The recirculation of the mixed liquor between the aerated and anoxic tanks occurred at a rate of 400% and was provided by a peristaltic pump. A stirrer was used to provide biomass and substrate mixing in each tanks. A flat polyethersulfone membrane with pore size of 0.04 μm and a total filtration surface area of 0.34 m^2 was immersed in a filtration module connected to the aeration tank (Table 1). The permeate was extracted at a constant flux by a peristaltic pump and pressure sensors were used to assess transmembrane pressure (TMP). Level sensor and valve systems were installed to control the water feeding at working volume of 60 L in the reactor. A dosing system was adopted for an automatic pH regulation with diluted hydrochloric or sulfuric acid solutions. A programmable logic controller system was used for the MBR operation control and data collection. Figure 1 displays a schematic of the experimental set-up.

Acclimation substrate and brewery wastewater

The reactor was fed with synthetic solutions consisting of sodium acetate, ammonium chloride, potassium hydrogenophosphate and potassium dihydrogenophosphate for biomass acclimation. The solutions were prepared by considering a C/N/P ratio of 100/5/1. The tests were conducted increasing progressively the organic loading rate (OLR) by gradually raising the influent concentration (from 0.7 to 3.5 g COD/L; COD: chemical oxygen demand). A variation in feeding periods was imposed to determine the biomass withstanding ability. Then the synthetic brewery wastewater prepared from a slightly modified recipe used by Chen *et al.* (2016) was introduced in the reactor for the assessment of biomass strength and treatment efficiency. Synthetic wastewater was constructed to match characterization data of Brakina's wastewater. Brakina is an industrial unit producing beverages in

Table 1 | MBR, electrodialysis (ED) and nanofiltration (NF) membrane properties

Parameters	MBR	NF	ED
Type	flat sheet	flat sheet	cation/anion exchange
Material	polyethersulfone	polyamide on polyether	–
Pore diameters (μm)	0.04	0.00017	–
Membrane thickness (mm)	2	0.159	0.14–0.17
Filtering surface (m^2)	0.34	0.0028	0.2
Hydraulic resistance (10^{12} m^{-1})	1.51	26	–
Electric resistance (Ω/cm^2)	–	–	2.4–3.0
Contact angle (°)	63.2	50 +/−10	–
Zeta potential	–	negative (−30 mV)	–
Model/Manufacturer	Microdyn Nadir	NF90/Dow Filmtec	Neoseta AMX/CMX/Tokuyama Corporation



1. aerated reactor	8. supervision computer
2. filtration module	9. filtration pump
3. membrane	10. permeate tank
4. anoxic reactor	11. substrate feeding
5. recycling pump	12. oxidation reduction potential meter
6. pressure sensor	13. pH meter
7. pressure display screen	14. Varion®Plus 700 IQ probe

Figure 1 | Schematic of laboratory-scale MBR system used in the study.

Ouagadougou, Burkina Faso. For simplicity (preparation, storage and stabilization), the influent was the result of a mix of concentrate stream (2 L/d) with tap water (38 L/d) for a total daily supply of 40 L. Table 2 displays the MBR feeding conditions.

MBR operating conditions

The reactor was initially inoculated with sludge from a municipal wastewater activated sludge treatment unit. Sixty litres of a mixing sludge from membrane and aerobic zone was taken from the treatment units to feed the reactor. The initial concentrations of SS and volatile suspended solids (VSS) were 1.8 g/L and 1.6 g/L respectively. The MBR started with an OLR of 0.47 g COD/L·d and the OLR was increased step-by-step to reach 7.07 g COD/L·d. The MBR was operated for an aggregate period of 110 days, with six increasing substrate compositions and reconstituted influent. The phases lasted between 10 and 24 days. During the first 50 days, there was no sludge wasting to accelerate biomass acclimation and growth. After this date, the mixed liquor suspended solids (MLSS) concentration had reached 10 g/L and the SRT was set to 30 days by a daily wasting of about 2 L of sludge. The hydraulic retention time (HRT) was set to 36 hours. The pH of the reactor was adjusted at 7.0 ± 0.3 using a diluted sulfuric

Table 2 | MBR phases description

Phase	Substrate	Operation periods	Organic loading rate (kg COD/m^3·d)	SRT (days)	HRT (hours)
Phase 1	acclimation solution	days 1 to 20	0.47	∞	36
Phase 2	acclimation solution	days 21 to 40	0.93	∞	36
Phase 3	acclimation solution	days 41 to 50	1.40	∞	36
Phase 4	acclimation solution	days 51 to 64	1.87	30	36
Phase 5	acclimation solution	days 65 to 90	2.33	30	36
Phase 6	synthetic brewery wastewater	days 91 to 110	7.07	30	36

acid solution with an online dosing system. The reactor was operated at room temperature with extreme values ranging between 18 and 26 °C for the entire study period. An air inlet in the reactor provided the aeration of the aerobic tank and the membrane scouring. At day 81, a membrane fouling due to inadequate membrane scouring was noted and the membrane was replaced to keep the permeate extraction flow.

Nanofiltration experimental set-up

Nanofiltrations (NFs) were performed in a laboratory-scale cross-flow filtration unit (Koch Membrane Systems Lab-cell-F-1). The experimental set-up is illustrated in Figure 2. The MBR permeate, placed in the feed tank (1) of a maximum capacity of 500 mL, circulated in cross-flow mode thanks to a centrifugal pump (3) that enabled a velocity of 1.6 m/s. It is possible to regulate the temperature of the feed tank thanks to its double envelope (5). The membrane was mounted on the membrane module (2). TMP was generated by the compressed N_2 system (4), monitored by a manometer, which implied a constant TMP operating mode. The permeate flow rate (6) was obtained from measurements of permeate mass by an electronic balance (7).

A flat-sheet NF membrane from Dow Filmtec (NF90) with an effective membrane area of 28 cm^2 and made of polysulfone on a polyamide support layer was tested. The characteristics of the membranes are shown in Table 1. Experiments were performed by filtrating 300 mL of MBR permeate at two constant TMPs, 12 or 16 bar, until a volumetric concentration factor of 3 (being a conversion rate of 67%). After deconditioning the new membrane coupons

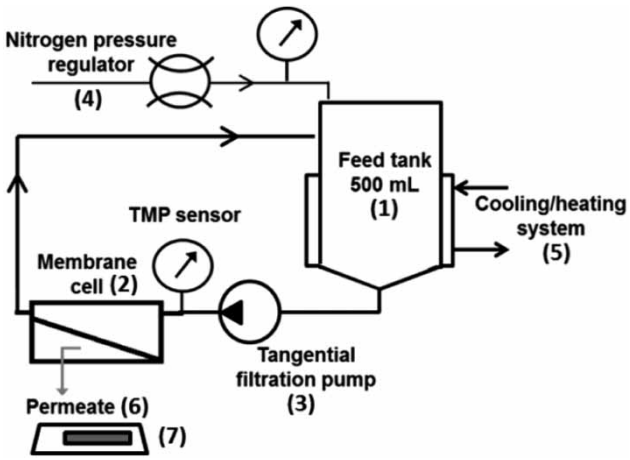


Figure 2 | Illustration of the filtration experimental set-up.

and in order to evaluate membrane fouling, membrane permeability corrected at 20 °C was measured with Milli-Q water twice for each experiment: before filtration and after filtration plus water rinsing (Carretier *et al.* 2015; Monnot *et al.* 2017).

Electrodialysis pilot

The electrodialysis (ED) experiments were performed with an ED stack (EUR2B-10) from Eurodia, France. It is composed of 10 cells of anion/cation-exchange membrane (Neosepta AMX/CMX, Tokuyama Corp, Japan). The effective membrane surface is 0.02 m^2 per cell, i.e. the total effective membrane surface is 0.2 m^2. The characteristics of the membranes are shown in Table 1. The ED experiments were operated in batch mode. The pilot set-up consisted of three separated circuits for diluate, concentrate and electrolyte solution, with three 2 L associated vessels. The feed flow rates were set at constant values of 300 L/h for all three solutions. The electrolyte compartment was fed with 2 L of Na_2SO_4 solution at a concentration of 0.5 mol/L. The intensity was fixed to 2 A. Experiments were stopped when the diluate conductivity reached 1 mS/S in order not to overpass the limiting current intensity.

Sampling and analytical methods

TMP, electric conductivity, pH and temperature were continuously recorded during operation time of the MBR. Samples were taken three times per week from the anoxic and aerobic tanks and the membrane effluent for analysis. Aliquots of the sludge were collected for SS and VSS quantification. The soluble parameters were obtained after sample filtration through a 0.45 μm glass fiber membrane. Nitrate, nitrite, ammonium, orthophosphate, chloride, sulfate, calcium, magnesium and sodium were analyzed by ionic chromatography (Dionex ICS-1000 with IonPac AS19 column for anions and Dionex ICS-900 with IonPac CS12A column for cations). Hach kits were used for COD determination, and dissolved organic carbon (DOC) was determined with a total organic carbon (TOC) analyzer (TOC-Vcsh/csn, Shimadzu). All of these analyses were performed in accordance with the recommendations of *Standard Methods for the Examination of Water and Wastewater* (APHA 2005). MLSS and mixed liquor volatile suspended solids (MLVSS) concentrations were measured using standard methods AFNOR NFT 90-105 and 90-029. COD was measured using standard method AFNOR NFT 90-101 (AFNOR 2012).

Three-dimensional excitation–emission matrix

Fluorescence spectra were obtained using a Perkin-Elmer LS-55 spectrometer (USA) after sample dilution with pure water (Milli-Q, Millipore Co. Ltd) to avoid inner filter effect (UV254 absorbance lower than 0.1 m^{-1}). Dilution ratio was determined using the successive dilutions method to limit overlapping signals (Carstea *et al.* 2016). Scan ranges were set at 200–500 nm and 280–600 nm in excitation (Ex) and emission (Em), respectively (Chen *et al.* 2003). Scan speed was fixed to 1,000 nm/min and the increment to 2 nm, while slit width was fixed at 10 nm in excitation and emission. To allow spectra comparison, they have been normalized by Raman area (Goletz *et al.* 2011) and Milli-Q water spectrum (Peiris *et al.* 2010). Spectra are divided into four areas defined by Chen *et al.* (2003), corresponding to the different group of fluorophores. Region I + II associated with aromatic protein-like type I + II fluorophores (tyrosine type) is in the range Ex = 200–250 nm/Em = 280–380 nm; Region II corresponds to fulvic acid-like fluorophores (Ex = 200–250 nm/Em = 380–600 nm); Regions III and IV are associated with soluble microbial product-like fluorophores (Ex = 250–350 nm/Em = 280–380 nm; tryptophane type) and humic acid-like fluorophores (Ex = 380–600 nm/Em = 250–500 nm), respectively.

To estimate the fluorescent dissolved organic matter (DOM) retained by the membrane, a simple mathematical subtraction was performed between the spectra obtained from bulk supernatant MBR samples (activated sludge) and permeate MBR samples. Hence, a new spectrum corresponding to DOM retained by the membrane was obtained. This method allows a quick visual estimation of the DOM which is preferentially retained by the membrane and could therefore be implied in fouling mechanisms.

Integration was carried out over the four listed regions. This method permits the whole fluorescence information within each region to be taken into account and semi-quantification to be performed (Jacquin *et al.* 2017). Volumes of fluorescence (Φ) were calculated from the corrected matrix, following the integration method according to Chen *et al.* (2003) within each region (i), applying Equation (1):

$$\Phi(i) = MF(i) \sum_{ex} \sum_{em} I(\lambda ex \lambda em) \Delta\lambda ex \Delta\lambda em \quad (1)$$

in which $MF(i)$ is a multiplication factor, $\Delta\lambda ex$ is the excitation wavelength interval (taken as 2 nm), $\Delta\lambda em$ is the emission wavelength interval (taken as 0.5 nm) and $I(\lambda ex \lambda em)$ is the fluorescence intensity at each excitation–emission pair (Raman units).

In a previous study, calibration curves were established between the volume of fluorescence in Region III + V and Region IV with liquid chromatography–organic carbon detection measurements of proteins from biopolymers and humic substances. From this calibration it was possible to calculate directly the concentration in TOC of proteins from biopolymers and humic substances from fluorescence data (Jacquin *et al.* 2017).

Active biomass concentration measurements

After sampling, the activated sludge was placed under aeration for 24 hours to ensure endogenous state. Then respirometric measurements with an oximeter were performed to estimate heterotrophic bacteria, ammonia oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB) concentrations in the activated sludge following the protocol described by Lahdhiri *et al.* (2015) and Benaliouche *et al.* (2017). Then different kinds of biomass concentrations were calculated using the following equations:

$$X_H = \frac{OUR_{endo+ATU} + OUR_{endo+ClO3} - OUR_{\text{endo}}}{(1 - f_{Xi}) b_H} \quad (2)$$

$$X_{AOB} = \frac{OUR_{endo} - OUR_{endo+ATU}}{(1 - f_{Xi}) b_{AOB}} \quad (3)$$

$$X_{NOB} = \frac{OUR_{endo} - OUR_{endo+ClO3}}{(1 - f_{Xi}) b_{NOB}} \quad (4)$$

where:

OUR_{endo} = endogenous oxygen uptake rate (OUR) (mg O_2/L·h)
$OUR_{endo+ATU}$ = OUR obtained after adding ATU (mg O_2/L·h)
$OUR_{endo+ClO3}$ = OUR obtained after adding ClO_3 (mg O_2/L·h)
f_{xi} = inert DOC fraction generated by biomass lysis (=0.2)
b_H = decay coefficient of heterotrophic bacteria (=0.20 1/d)
b_{AOB} = decay coefficient of AOB (=0.15 1/d)
b_{NOB} = decay coefficient of NOB (=0.15 1/d)
X_H = concentration of heterotrophic bacteria (g/L)
X_{AOB} = concentration of AOB (g/L)
X_{NOB} = concentration of NOB (g/L).

Finally, the total active biomass concentration (X_{tot}) was calculated using the following equation:

$$X_{tot} = X_H + X_{AOB} + X_{NOB} \quad (5)$$

RESULTS AND DISCUSSION

Biomass growth and conversion yield

Characterization of effluent from the brewery revealed sodium content ranging between 237 and 1,137 mg/L, with fluctuations in pH (5.4–12.7). The performance of biological reactors is linked to the biomass activity, including its ability to oxidize organic matter in the presence of various and varied pollutants. Acclimation is emerging as a key step in the investigative process of MBR as a treatment option for brewery effluent. Sludge used for reactor inoculation was characterized by MLSS and MLVSS values of 1.8 g/L and 1.5 g/L respectively. Figure 3 shows that MLSS and MLVSS increase regularly over time. The difference of slope of the MLSS and MLVSS concentration evolution curve with the reactor operation time displays changes depending on the load of the substrate. The use of sodium acetate as a carbon source in the substrate makes the environment rich in salts and submits biomass to an increasing of sodium loads. In fact, the sodium concentration due to the use of sodium acetate as synthetic pollutant increases from 0.25 g/L (phase 1) to 1.26 g/L (phase 5). The results show that the evolution of MLSS and MLVSS is not disturbed by salts increasing at the frequencies proposed by the study.

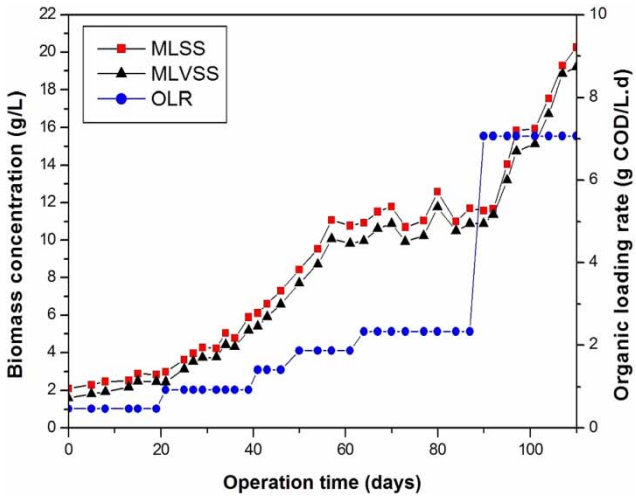


Figure 3 | Biomass concentration and OLR variation with operation time.

The operating conditions proved favorable for a continuous growth of the biomass throughout the period of study. Separate phases characterize the evolution of biomass in this study. The first phase that takes place during the first 3 weeks (days 1–21) is characterized by a plateau. This could be associated with a phase of recognition of the medium by microorganisms. Moving from one frame to another, due to the new environmental conditions, it is assumed that a latency period can be manifested in the evolution of the load until the stabilization of the system (Alvarado-Lassman *et al.* 2008). It is followed by a second phase (days 21–41) during which a strong growth of the biomass was highlighted. Therefore, it appears that the analytical conditions imposed on the reactor have been favorable to good growth of the microorganisms. This also indicates that changes in loads during this period did not affect the evolution of biomass. From day 50, the quantity of MLVSS was maintained at around 10 g/L by a daily racking of sludge. The impact of sludge extraction does not occur instantly. But from day 55 to day 90, the graph is characterized by a slow evolution of MLVSS where the sludge production is close to the sludge extraction. The extraction of the sludge was started once the total suspended solids concentration was close to 10 g/L. In fact, according to the observed conversion yield (Table 3), the MLVSS is supposed to reach a constant value when the sludge production (Y_{Obs} Q (feed flow) S_{Si} (soluble substrate (COD) in the influent)) is equal to the sludge extraction (MLVSS Q_{Waste} (sludge extraction flow)) (Equation (6)).

$$\text{MLVSS} = Y_{\text{Obs}} C_F S_{Si} \quad (6)$$

where CF = concentration factor = SRT/HRT.

When no sludge was extracted, the observed conversion yield increases with the OLR. But this value is stabilizing with the sludge extraction. On the other hand, after day 91 (i.e. the last phase: day 91–110), a strong evolution of the

Table 3 | Sludge conversion yield

	Phase				
	1	2	3	4	5
Organic loading rate (kg COD/m^3·d)	0.47	0.93	1.4	1.87	2.33
Observed conversion yield, Y_{Obs} (kg VSS/kg COD)	0.096	0.151	0.182	0.165	0.166

biomass is highlighted on the curve of Figure 3. During this phase the reactor was fed with a synthetic solution of brewery wastewater with a very high loading rate (three times higher than the phase 5). Thus, this abrupt change in slope, when switching from one feed solution to another, is attributed to variations in feed load. The quantity of microorganisms present in a biological reactor conditions the purifying activity, but the characteristics of the effluent to be treated thus appear to be a preponderant element for the evaluation of the purification performance of the device. On the other hand, these results clearly show that the biomass is able, after acclimatation, to treat synthetic brewery wastewater. A biomass acclimation pathway has thus been demonstrated for the purification of brewery wastewater which is particularly loaded with sodium. The time of cultivation before wastewater feeding was 3 months. It is longer than that reported by Shao *et al.* (2008), which operated for 2 months, and shorter than that shown by Sung & Dague (1995) with a 10 month operating duration.

Chemical oxygen demand removal

The first goal of this study was to find a good biomass acclimation method for brewery wastewater treatment. After biomass growth, a treatment test with synthetic wastewater was conducted for 31 days from the 90th day of operation of the pilot. During the various stages of the pilot feeding the COD removal rate was evaluated and the results are shown in Figure 4.

Low COD removal rates (80%) were obtained during the early days of this study. This low level reflects insufficient conditioning of the microorganisms due to the change of environment during the pilot start-up period. Low purification efficiencies during the start-up phase of the cultivation of biomass have also been demonstrated in previous work on industrial wastewater treatment by biological reactors (Alvarado-Lassman *et al.* 2008; Chen *et al.* 2016; Sheldon & Erdogan 2016). Despite the increase in the influent OLR, the COD removal rates increased and stabilized at values higher than 96%. The highest COD removal efficiency was obtained when using the synthetic brewery wastewater solution. This COD removal rate is higher than those reported in previous studies on brewery or soft drink wastewater (Öktem & Tüfekçi 2006; Dong *et al.* 2015; Chen *et al.* 2016; Sheldon & Erdogan 2016). This evolution of the removal performance can also be explained by the biological activity of the biomass in the reactor. Indeed, in Figure 5 which shows the evolution of

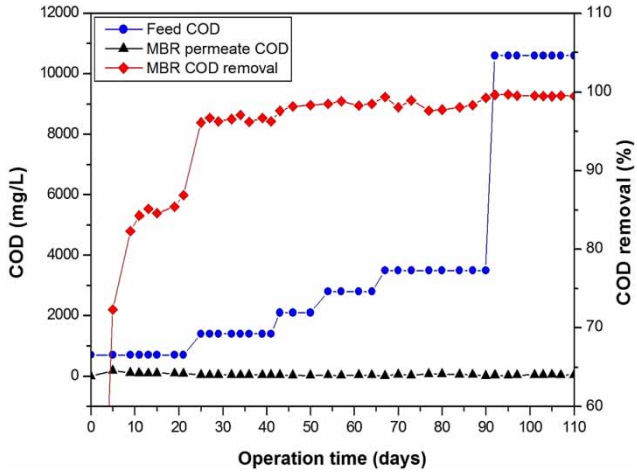


Figure 4 | Influent and effluent COD and COD removal efficiency through the wastewater treatment phases.

oxygen up-take rate at the beginning of the experience and during pilot running (days 60 and 80), there is a significant increase in microbial activity over time. Biomass activity increased linearly with the OLR despite changes in operating (salt) conditions.

Nitrogen treatment within the MBR

During the acclimation period, the reactor was fed with a substrate containing ammonium with concentrations ranging between 35 and 175 mg/L. It corresponds to the nitrogen demand for heterotrophic growth; in fact the

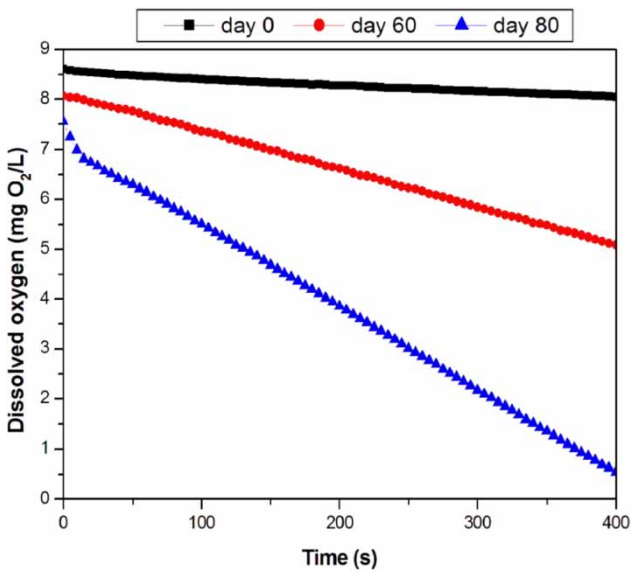


Figure 5 | Biomass activity assessment with aerated tank's dissolved oxygen evolution.

Table 4 | MBR permeate water quality and removal rates of ED, NF at 12 bar and NF at 16 bar

Parameters	MBR permeate	ED removal rate	NF removal rate 12 bar	NF removal rate 16 bar
COD (mg/L)	56 ± 28	42.9%	81.2%	94.8%
DOC (mg/L)	12.3 ± 0.7	31.9%	92.7%	95.1%
Conductivity (mS/cm)	9.3 ± 0.3	94.7%	86.9%	90.4%
NH_4^+(mg/L)	0.0	–	–	–
NO_3^- (mg/L)	16 ± 6	67.1%	0.0%	0.0%
NO_2^- (mg/L)	0.0	–	–	–
PO_4^{3-} (mg/L)	66 ± 15	94.0%	98.0%	99.4%
SO_4^{2-} (mg/L)	6,290 ± 453	97.4%	98.1%	98.9%
Cl^- (mg/L)	221.5 ± 0.3	88.5%	0.0%	0.0%
Na^+ (mg/L)	2,676 ± 172	96.6%	88.7%	91.2%
Ca^{2+} (mg/L)	128 ± 13	97.6%	97.8%	98.6%
K^+ (mg/L)	92 ± 1	99.1%	89.7%	92.2%
Mg^{2+} (mg/L)	26 ± 2	97.8%	94.3%	97.3%

C/N/P ratio was adjusted at 100/5/1, which means that all ammonium is used by microorganisms for cell growth (Yang *et al.* 2014). Disturbances of the nitrogen uptake at the beginning of each feeding phase was demonstrated with an increase in the concentration of the ammonium in the permeate, which is not the case for organic compounds. This proves the ability of heterotrophic bacteria to store organic substrat as storage product, but they were not able to store nitrogen compounds. Table 4 shows the concentrations of ammonium, nitrate and nitrite obtained after 84 days. The results obtained reflect nitrogen removal efficiency close to 100% after the 84th day of the reactor operation which runs in steady-state condition. Additionally, the synthetic brewery wastewater solution has a lower concentration of nitrogen than the acclimation substrate used for the reactor feeding.

Dissolved organic matter analysis

The fluorescence spectra obtained with the sludge extract reveal four distinct zones representing each of the characteristic groups of dissolved organic compounds. They are shown in Figure 6. The comparison with the permeate and concentrate spectra shows an important retention of proteins and soluble microbial products (SMP). On the other hand, the membrane seems to have no effect on the humic and fluvic acids removal. These observations are confirmed by the related calculated retention yields. Indeed, proteins and SMP are retained at 52% and 35% respectively. It is therefore clear that the size of the compounds is an important element in the membrane's retention capacity relative to the soluble organic compounds (Jacquin *et al.* 2017).

NF and ED post-treatments of synthetic brewery effluent

Table 4 presents the MBR permeate water quality and the ED and NF removal rates. Concerning the COD and DOC, it can be observed that ED could only remove less than 45% due to the ED principle itself. Indeed, DOM may not be as electrically charged as ions and may not have the same size of ions, which would make the transfer through the ion exchange membrane very difficult. In contrast, as NF is a physical barrier, COD and DOC were retained by more than 80% at 12 bar and by about 95% at 16 bar. Concerning ion removal, the overall conductivity was reduced by approximately 95%, and 87% or 90% thanks to ED and NF respectively. ED removed all ions by more than 88.5% except for NO_3^- in really low initial concentration. NF at 12 bar removed all ions by more than 88.5% except for NO_3^- and Cl^- which were not retained at all. At 16 bar, the same trend was observed for NO_3^- and Cl^- but all the rejection rates of other ions were higher. Indeed, derived from basic transfer equations, an increase of the effective pressure increases the salt rejection rate in NF. As also expected, NF rejection was a bit higher for divalent ions than for monovalent ions due to steric effects. Then, a high rejection of SO_4^{2-}, present in relatively high quantity in comparison to divalent cations, may impose a

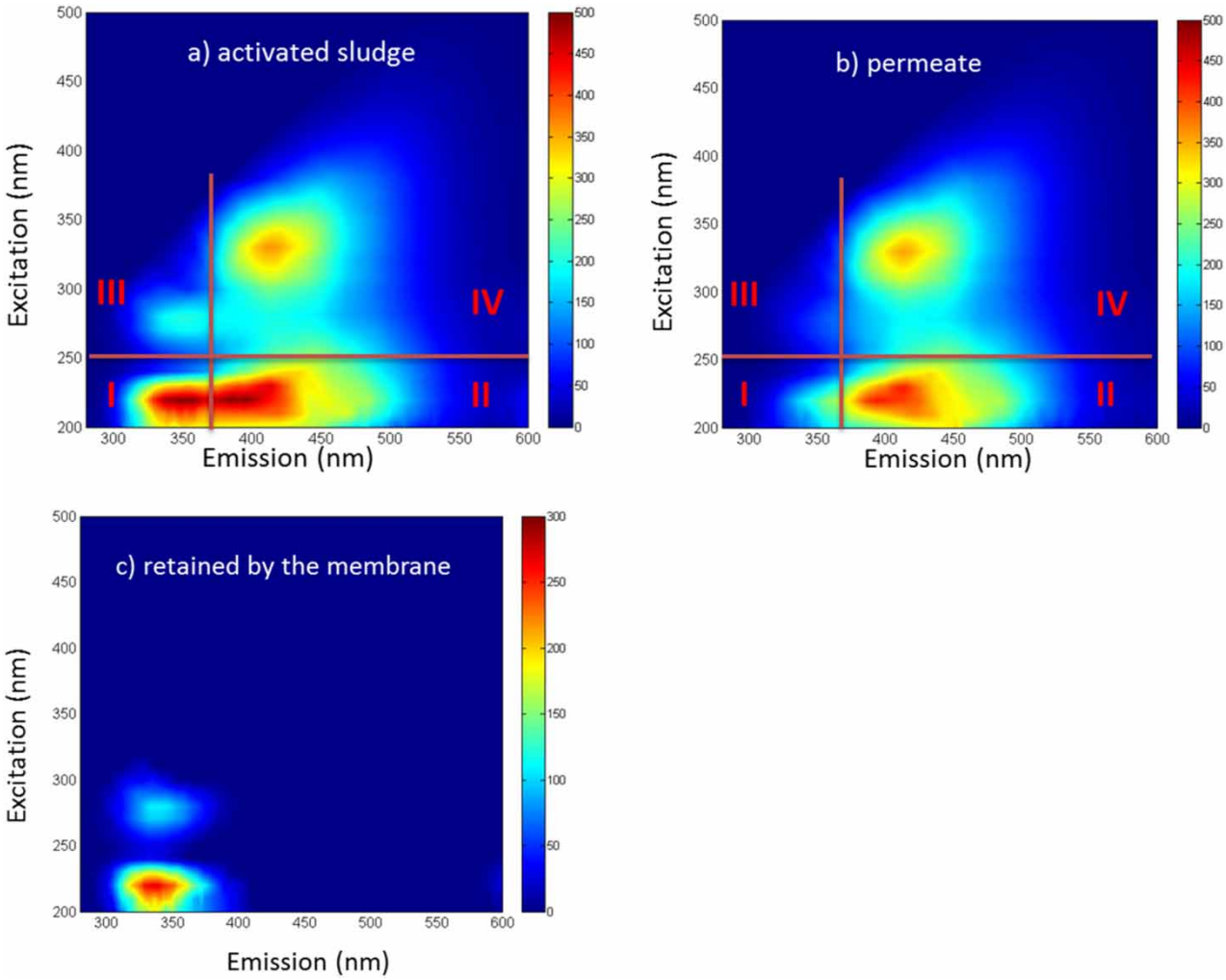


Figure 6 | MBR thee-dimensional excitation–emission matrix spectra.

lower rejection of other anions to insure permeate electroneutrality (Nicolini *et al.* 2016) also known as Donnan effect. Between the monovalent anions, NO_3^- and Cl^- are those with the lowest hydration energy (Paugam *et al.* 2004), which might explain why they could pass more easily through the pores of the NF membrane inducing a lower rejection rate. Additionally, the presence of salts at high concentration reduces the zeta potential (the membrane may become less negatively charged here), which may induce a possible shielding effect which could reduce the electrical repulsion between the negatively charged membrane and the anions.

The concentrations of SO_4^{2-} and Na^+ were particulary high in the MBR permeate, which would make it unsafe for a release in the environment or water reuse. The use of ED or NF could drastically reduce these concentrations. According to the desired concentration levels, ED would be efficient to remove all ions but no DOM whereas NF could remove most of the effluent DOM and most ions except for chlorides and residual nitrates. Moreover, an increase of the effective pressure in NF could slightly enhance the removal rates but this also increases the energy need and the scaling potential.

CONCLUSION

This paper presents interesting and noteworthy information about biomass cultivation and brewery wastewater treatment efficiency by using an anoxic/aerobic MBR coupled with NF or ED. This cultivated biomass was very little disturbed by variations in load and proved particularly

effective for the purification of brewery wastewater. Operating with sludge from a municipal wastewater treatment plant, cultivation by increasing OLR phases provided a good biomass activity after 90 operating days. With operating conditions characterized by an SRT of 30 days and an HRT of 36 hours, the COD removal efficiencies reached 99% with an average of around 95%. With NF or ED post-treatment, there was a significant reduction in the concentration of the main ions analyzed even though chloride concentrations remained relatively high with NF. In conclusion, the two-stage aerobic/anoxic MBR has allowed a good elimination of organic and nitrogen pollution in brewery wastewater, and post-treatment by NF or ED was useful for elimination of the high contents of salts with efficiencies higher than 99.97% for sodium.

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