

61 (2017) 240–249 January

### Comparison between two MBR pilot plants treating synthetic shipboard slops: the effect of salinity increase on biological performance, biomass activity and fouling tendency

Alida Cosenza, Daniele Di Trapani, Giorgio Mannina\*, Salvatore Nicosia, Michele Torregrossa, Gaspare Viviani

Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali (DICAM), Scuola Politecnica, Università degli Studi di Palermo. Viale delle Scienze ed. 8, 90128 Palermo, Tel. +39 09123896556; Fax: +39 091 238 60810; email: giorgio.mannina@unipa.it

Received 13 April 2015; Accepted 27 November 2016

#### ABSTRACT

The paper reports the main results of an experimental campaign carried out on two bench scale pilot plants for the treatment of synthetic shipboard slops. In particular, two membrane bioreactors (MBRs) with submerged configuration were analyzed. One MBR pilot plant (namely, Line A) was fed with synthetic shipboard slop and was subjected to a gradual increase of salinity. Conversely, the second MBR pilot plant (namely, Line B) was fed with the same synthetic shipboard slop but without salt addition, therefore operating as a "control" unit. Organic carbon, hydrocarbons and ammonium removal, kinetic constants, extracellular polymeric substances (EPSs) production and membranes fouling rates have been assessed. The observed results highlighted a stress effect exerted by salinity on the biological performances, with lower removal efficiencies in the Line A compared to Line B. Significant releases of soluble EPS in Line A promoted an increase of the resistance related to particle deposition into membrane pores (pore fouling tendency), likely due to a worsening of the mixed liquor features. Such a condition enhanced the reduction of the "pre-filter" effect of the cake layer.

Keywords: MBR; Salinity; Hydrocarbons; Slops

#### 1. Introduction

The growing awareness of environmental protection has led to an increasing regulatory pressure by imposing stringent limitations on pollutant concentrations before wastewater discharge into the environment. This aspect is of particular concern when considering specific activities producing saline wastewater that might be characterized by highly recalcitrant, toxic and slowly biodegradable compounds, such as the fish canning, petroleum, petrochemical and tannery industries [1–3]. In this context, a major challenge is represented by wastewater treatment produced during shipboard activities (bilge water or slops), which usually features high oily and saline concentrations [4]. It is worth noting that the direct discharge of wastewater from ships is prohibited by the International Maritime Organization (IMO) regulations [5] specifically referring to the discharge of oily bilge water. IMO regulations mandate that any oil and oil residue discharged in wastewater streams must contain less than 5 ppm hydrocarbons. Therefore, effective treatment of this petroleum-contaminated water is essential prior to its release into the environment. This wastewater can be treated either by physical-chemical or biological methods. Although, physicochemical methods have been successfully applied in the past [6], they impose several issues with regard to chemical consumption, high

\*Corresponding author.

1944-3994 / 1944-3986 © 2017 Desalination Publications. All rights reserved.

*Presented at EuroMed 2015: Desalination for Clean Water and Energy Palermo, Italy, 10–14 May 2015. Organized by the European Desalination Society.* 

energy requirements and secondary pollution. Conversely, the use of biological treatments is becoming increasingly popular in the field of saline wastewater characterized by high organic content and petroleum hydrocarbons [7].

Among the biological processes, in the last years membrane bioreactors (MBRs) have emerged for saline wastewater treatment [8]. MBRs can significantly improve the efficiency of pollutant removal compared to conventional activated sludge (CAS) processes, featuring high-quality effluent, small footprint and low sludge production rates. Therefore, MBRs might be proposed for treatment of saline waters contaminated by "xenobiotic and recalcitrant" compounds, such as petroleum hydrocarbons, deriving from shipboard activities [9]. However, one of the major challenges for MBRs hindering their world-wide application is still represented by the fouling phenomena [10,11]. Specifically, four groups of factors mainly affect membrane fouling: membrane materials, mixed liquor characteristics, feed water characteristics and operating conditions, such as sludge retention time (SRT), hydraulic retention time (HRT) and food-to-microorganism ratio (F/M). This condition might be exacerbated when treating shipboard slops because high levels of salinity and petroleum hydrocarbon content can exert significant stress on the bacterial consortium, providing a worsening of mixed liquor characteristics in terms of viscosity, amount of filamentous bacteria, extracellular polymeric substances (EPSs) and soluble microbial products (SMPs), producing substantial membrane fouling [12–15]. Despite the significant interest towards this topic, to authors' knowledge, the combined effect of salinity (20 g NaCl L<sup>-1</sup>) and hydrocarbons (20 mg TPH L<sup>-1</sup>) during the treatment of shipboard slop with a MBR system has been rarely investigated in the technical literature [16] and needs further investigations. Bearing in mind these considerations, the aim of the present work is to gain insights about the biological treatment of synthetic saline slops, investigating the treatment of a shipboard slop already subjected to physical-chemical pre-treatment with a MBR pilot plant. In particular, the paper presents the comparison between two MBR pilot plants, with the aim to evaluate their behaviour in terms of biological performance, biomass activity and fouling tendency. It is worth noting that, due to the uncertainty to guarantee a sufficient supplying of real shipboard slops of similar characteristics, it was decided to operate the MBR pilot plants with a synthetic influent.

#### 2. Materials and methods

#### 2.1. Description of the MBR pilot plants

Two MBR pilot plants were built at the Laboratory of Sanitary and Environmental Engineering of Palermo University. In particular, one (named Line A) was fed with synthetic shipboard slop and was subjected to a gradual increase of salinity, whereas the second one (named Line B) was fed with the same synthetic shipboard slop but without salt addition, therefore operating as a "control" unit. A preliminary analysis on a sample of real pre-treated shipboard slop (withdrawn from Augusta harbor) revealed a salinity concentration close to 20 gNaCl L<sup>-1</sup> and a TPH concentration of 20 mg L<sup>-1</sup>. Therefore, the synthetic wastewater was prepared in accordance to the latter values. More in detail, hydrocarbons were dosed as diesel fuel that was composed by a hydrocarbon mixture comprising the semi-volatile fraction ranging from C10 to C30 and including species with even as well as odd number of carbon atoms (typical Diesel range organic (DRO) mix).

A schematic layout of the bench scale MBR is depicted in Fig. 1. Both plants were characterized by equivalent volume tanks (namely, 20 L) and were equipped with an ultrafiltration (UF) hollow fiber membrane module (ZeeWeed<sup>™</sup>01, with specific area equal to 0.093 m<sup>2</sup> and nominal porosity of  $0.04 \,\mu\text{m}$ ). The membrane flux was kept close to  $15 \,\text{Lm}^{-2} \,\text{h}^{-1}$ . Each membrane module was periodically backwashed (every 4 min for a period of 1 min) by pumping a fraction of permeate back through the membrane module. In both pilot plants, filtration was stopped every 15-20 d, or as soon as the transmembrane pressure (TMP) reached 0.6-0.7 bar (value suggested by the membrane manufacturer). The membrane module was then subjected to a physical cleaning, according to the procedure suggested by Mannina and Di Bella [17]. The whole experimental campaign had a duration of more than 200 d and was divided in four phases, depending on the salinity level of Line A (Phase I: 5 g L<sup>-1</sup> NaCl; Phase II: 10 g L<sup>-1</sup> NaCl; Phase III: 15 g L<sup>-1</sup> NaCL; Phase IV: 20 g L<sup>-1</sup> NaCl). It is worth mentioning that starting from the Phase II, in order to sustain the activity of the bacterial consortium, sodium acetate (CH<sub>3</sub>COONa) was also added in the influent wastewater.

Both MBR systems were inoculated with activated sludge collected at Palermo municipal wastewater treatment plant with a mixed liquor suspended solids (MLSS) concentration equal to 4 g TSS  $L^{-1}$ . In Table 1 the mean influent characteristics as well as the plant operational conditions



Fig. 1. Schematic envisage of MBR pilot plant.

Table 1

Average influent characteristic and main operational features of both MBR plants

Parameter	Line A	Line B
COD, mg L <sup>-1</sup>	500	500
TPH, ppm	20	20
$NH_4$ -N, mg L <sup>-1</sup>	20	20
NaCl, mg L <sup>-1</sup>	5-20	_
Conductivity, mS cm <sup>-1</sup>	10–30	_
Membrane flux, L m <sup>-2</sup> h <sup>-1</sup>	15	15
HRT, h	27	27

are summarized. It is worth noting that the synthetic slops were prepared to simulate a real shipboard slops already subjected to a chemical-physical pre-treatment.

#### 2.2. Analytical methods

During experiments, the influent wastewater, the mixed liquor and the membrane permeate have been sampled every 3 d. The following analysis have been carried out: total and volatile suspended solids (TSS and VSS), chemical oxygen demand (COD), 5 d biochemical oxygen demand (BOD<sub>5</sub>), total organic carbon (TOC), total petroleum hydrocarbon (TPH), aromatic hydrocarbon, ammonium nitrogen (NH<sub>4</sub>-N), nitrite nitrogen (NO<sub>2</sub>-N), nitrate nitrogen  $(NO_3-N)$ , total nitrogen  $(N_{TOT})$  and orthophosphate  $(PO_4-P)$ . Referring to the mixed liquor sampling section, excepting TSS and VSS, the analyses have been carried out on the supernatant of mixed liquor filtered at 0.45 µm. Therefore, it was possible to differentiate the "biological" removal efficiency (evaluated upstream the membrane module) from the "total" removal efficiency (downstream the membrane module). All analyses have been carried out according to the Standard Methods [18]. The TPH content in the different sampling sections was evaluated by means of Soxhlet extraction plus gas chromatography. Moreover, throughout the experimental period, both systems were regularly monitored in terms of pH, Temperature (T), and Dissolved Oxygen (DO).

#### 2.3. Respirometric batch tests

Respirometric batch experiments were conducted using a "flowing gas/ static-liquid" type as batch respirometer [19]. The suspended biomass samples were taken from the bioreactor of both plants and in case diluted with permeate in order to obtain a mixed liquor concentration in the range of 2.0-3.0 g VSS L<sup>-1</sup>. Before running the respirometric test, each sample was aerated until endogenous conditions were reached. For further details on the adopted procedure, the reader is referred to literature [8]. In the batch tests aimed to evaluate the heterotrophic biokinetic parameters, the nitrifying biomass was inhibited by adding 10-15 mg L<sup>-1</sup> of Allylthiourea (ATU), while the exogenous oxygen uptake rate (OUR) was enhanced by the addition of a readily biodegradable organic substrate (sodium acetate in the present study). The substrate biodegradation rate was assumed proportional to the exogenous OUR, according to the following expression:

$$\Delta \text{COD} = \frac{\Delta O_2}{1 - f_{cv} \cdot Y_H} \tag{1}$$

where  $f_{cv}$  is the conversion coefficient from COD to VSS, assumed equal to 1.42 mgCOD mg<sup>-1</sup>VSS, while  $Y_H$  is the yield coefficient [mgVSS mg<sup>-1</sup>COD]. The yield coefficient  $Y_H$  has been derived from the integral of the exogenous OUR chart, according to the methodology suggested by Vanrolleghem et al. [20]. The maximum heterotrophic growth rate  $\mu_{H,max}$  (d<sup>-1</sup>) and the half saturation coefficient  $K_S$  (mgCOD L<sup>-1</sup>) were evaluated by solving the Monod-type

kinetic expression with the finite difference procedure, by fitting the following equation:

$$\frac{\Delta \text{COD}}{\Delta t} = \frac{\mu_{H,\text{max}}}{Y_H} \cdot \frac{\text{COD}}{(K_s + \text{COD})} \cdot X_H \tag{2}$$

where COD is the carbonaceous substrate concentration at time *t* (mg L<sup>-1</sup>),  $X_H$  is the biomass active fraction (mgVSS L<sup>-1</sup>), while  $\mu_{H,\text{max}}$  and  $K_S$  have been previously defined. The estimation of the endogenous decay coefficient  $b_H$  and  $X_H$  were carried out according to the "single batch test" procedure (among others, [8,21]).

The kinetic parameters of autotrophic species were estimated with the same procedure. Nevertheless, in this case no inhibiting substance like ATU was added and ammonium chloride (NH<sub>4</sub>Cl) was directly spiked to evaluate the biokinetic parameters. The conversion factor between oxygen and ammonium (NOD: nitrogen oxygen demand) is equal to:

$$\Delta NH_4 - N = \frac{\Delta O_2}{4.57} \tag{3}$$

## 2.4. Extracellular polymeric substances extraction and measurement

The EPSs were measured during the whole duration of experiments, in order to evaluate their role in membrane fouling mechanisms. The soluble EPSs also referred to as SMPs were obtained by centrifugation at 5,000 rpm for 5 min, while the bound EPS (EPS<sub>Bound</sub>) content was extracted by means of the thermal extraction method (among others [22,23]). The extracted EPS<sub>Bound</sub> and the SMP were analysed for proteins by using the Folin method with bovine serum albumin as the standard [24], whilst the carbohydrates according to DuBois et al. [25], which yields results as glucose equivalent. Moreover, the sum of proteins and carbohydrates content was considered as the total EPSs (EPS<sub>T</sub>), according to the following equation:

$$EPS_{T} = \underbrace{EPS_{P} + EPS_{C}}_{EPS_{Bound}} + \underbrace{SMP_{P} + SMP_{C}}_{SMP}$$
(4)

where the subscripts "P" and "C" indicate the content of proteins and carbohydrates, that typically constitute the main fractions of  $\text{EPS}_{Bound}$  and SMP [26].

#### 2.5. Analysis of membrane fouling

The total resistance to filtration  $(R_T)$  was described by the general form of the Darcy's law:

$$R_T = \frac{\text{TMP}}{J\mu} \tag{5}$$

where  $R_T$  is the total fouling resistance (10<sup>12</sup> m<sup>-1</sup>) calculated by the general form of Darcy's Law, TMP is the

transmembrane pressure (Pa),  $\mu$  the permeate viscosity (Pa•s), and *J* the permeation flux (m s<sup>-1</sup>). Furthermore, a resistance-in-series (RIS) model based on cake layer removal with "extraordinary physical cleaning" was employed to investigate the specific deposition mechanisms (among others, [8,27–30]. In details, according to this approach the fouling mechanisms can be evaluated by means of ordinary cleaning actions (e.g., backwashing) or extraordinary physical cleaning actions (e.g., hydraulic washing and mechanical scrubbing). The superficial cake deposition (irreversible or reversible) is determined by the calculation of permeate flux and TMP measurement before and after cake layer removal from the membrane surface (see for instance [17]). On the basis of this on this approach, the total resistance to filtration can be decomposed as follows:

$$R_T = R_m \underbrace{+R_{PB} + R_C}_{R_F}$$
(6)

where  $R_m$  is the intrinsic resistance of membrane and was estimated by measuring the water flux of ultrapure water;  $R_{PB}$  is the fouling resistance related to the clogging of membrane pores, that can be partially removed by chemical cleaning only;  $R_c$  is the fouling resistance related to superficial cake deposition that can be removed by extraordinary physical cleanings (hydraulic/water washing). The sum of  $R_{PB}$  and  $R_c$  yields the overall resistance to filtration related to fouling mechanism.

#### 2.6. *Microscopic observations*

Microscopic observations were carried out for filamentous bacteria identification as well as to observe the potential effects caused by salinity on the suspended biomass features. A microscope phase contrast ( $100 \times$  and  $1,000 \times$ magnifications) was used for the observations. The filamentous microorganisms were morphologically identified using the Eikelboom classification system. Filamentous microorganism abundance and dominance were estimated using the criteria suggested by Jenkins et al. [31].

#### 3. Results and discussion

#### 3.1. Organic carbon removal

In Fig. 2 the COD concentrations (Figs. 2(a) and (b)) as well as the "total" and "biological" COD removal efficiencies (Figs. 2(c) and (d)) are reported.

Both plants showed good removal efficiencies with average values equal to 81% and 87% for Line A and B, respectively. These values are lower compared to conventional treatments of municipal wastewater; however, due to the specific features of the wastewater (i.e., synthetic shipboard slop water) used in the present study, the removal efficiencies can be considered satisfactory. Therefore, the observed results confirmed the high robustness of MBRs for the treatment of wastewater containing toxic or recalcitrant compounds. In terms of biological removal



Fig. 2. COD concentrations for Line A (a) and Line B (b), respectively; COD removal efficiency for Line A (c) and Line B (d), respectively.

(evaluated upstream the membrane modules) the average removal efficiencies were equal to 46% and 71% for Line A and B, respectively. This result was likely due to the effect of salinity that could hinder the biomass activity in Line A; however, the good acclimation of heterotrophic biomass was confirmed by the respirometric batch tests, as better outlined in the next paragraph. Previous studies also highlighted the potential acclimation of the bacterial community to a saline environment [32].

Referring to hydrocarbon removal, Fig. 3 shows the aromatic hydrocarbon removal efficiency for Line A and Line B, throughout the duration of experiments. It is worth noting that Line A was affected by the salinity level with a reduced removal efficiency. Indeed, the removal efficiencies (as average) were equal to 60% and 76% for Line A and Line B, respectively. This result could be likely due to a stress effect of salinity on the heterotrophic biomass activity. Nevertheless, the removal efficiencies showed slight fluctuations also in Line B and this result could be related to the fact that the bacterial consortium (not specialized) was not fully acclimated to the hydrocarbon content.



Fig. 3. Aromatic hydrocarbons removal efficiency for both plants during experiments.

#### 3.2. *Nitrification efficiency*

Fig. 4 reports the removal efficiency of ammonium nitrogen concentrations (Fig. 4(a)) and the nitrate nitrogen concentrations in the effluent of both plants Fig. 4(b).

The NH<sub>4</sub>-N removal showed significant fluctuations, with average values close to 70% for both plants. A clear influence of salinity was not noticed on ammonium removal, differently from previous studies (among others, [8,12,33]). However, by analyzing the graph reported in Fig. 4(b), it is worth noting that the nitrate production in Line A was significantly lower compared to Line B. This fact could likely have promoted a shortened nitrification with nitrite accumulation as final product. Indeed, nitrite oxidizing bacteria (NOB) species are very sensitive to the salinity level [34]. These considerations were also confirmed by the respirogram charts that enabled to monitor the biokinetic behavior of the bacterial species in both plants.

#### 3.3. Suspended biomass growth

As aforementioned, both plants were started-up with sludge inoculum, at a MLSS concentration of 4gTSS L<sup>-1</sup>. The suspended biomass trend as well as the VSS/TSS ratio are reported in Fig. 5, referring to Line A (Fig. 5(a)) and Line B (Fig. 5(b)), respectively.

It is worth noting that until the experimental day 54, a decrease of suspended biomass was observed. Such a result could likely be related to the stress effect exerted by the hydrocarbons on the biomass that was not acclimated to such a substrate (not easily biodegradable). Moreover, the salinity concentration in Line A (equal to 5gNaCl L<sup>-1</sup> at the start up) reinforced this behavior, highlighting a higher MLSS decrease. Therefore, in order to sustain the biomass activity toward a recalcitrant organic substrate, from experimental day 54 it was decided to spike sodium acetate in both plants. Thereafter, a sensible increase of MLSS concentration was observed in both plants, referring in particular to Line B.

However, from Fig. 5, a different behavior between the two biomasses can be observed. Indeed, while the MLSS of Line A reached a quite stable value, close to 5 gTSS  $L^{-1}$ , at



Fig. 4. Ammonium nitrogen removal efficiency (a) and nitrate production (b), in both systems.

the end of experiments, the suspended biomass of Line B constantly increased up to 7 gTSSL<sup>-1</sup>, suggesting a higher biomass activity compared to Line A. Moreover, the VSS/TSS ratio of Line A decreased progressively in Phase III and Phase IV, mainly due to salinity, suggesting biomass ageing and mineralization. On the contrary, the VSS/TSS ratio of Line B reached a stable value at the end of experiments, equal to 0.8, thus underlining a good condition of the suspended biomass in Line B.

#### 3.4. Biomass respiratory activity and biokinetic parameters

Respirometric batch tests were carried out for measuring the biomass activity during the experimental campaign by evaluating the main kinetic and stoichiometric parameters of both heterotrophic and autotrophic species. The obtained respirogram charts featured the typical exogenous and endogenous behavior as a consequence of the readily biodegradable substrates addition, sodium acetate for heterotrophs and ammonium chloride for autotroph, respectively. Referring to heterotrophic species, no significant differences were noticed between Line A and Line B, respectively. This result could suggest that the salinity level did not exert a significant stress effect on the heterotrophic biomass and that the low respiration rated could be related to the presence of hydrocarbons. This result is in good agreement with the study of Mannina et al. [35], where a sort of adaptation of heterotrophic species to a saline environment was found. Furthermore, the heterotrophic biomass showed a "storage" phenomenon, typical of systems subjected to dynamic conditions. This situation likely enhanced the growth of bacterial groups able to rapidly convert the organic substrate into storage products. The storage yield coefficient  $Y_{\rm STO}$  was evaluated according to the procedure proposed by Karahan–Gül et al. [36]. Fig. 6 reports the trend of specific respiration rate (SOUR) values (Fig. 6(a)) and maximum growth rate  $\mu_{\rm max,H}$  (Fig. 6(b)) for both plants.

Referring to autotrophic activity, the respirometric batch tests highlighted lower nitrification rates and biomass respiratory activity in the samples collected from Line A, in good agreement with what previously discussed. Nevertheless, at the end of experiments it was observed a significant increase of autotrophic respiration rates, suggesting a potential acclimation of biomass to the saline conditions. Figs. 7(a) and (b) shows the OUR values and the nitrification rated throughout the experimental campaign.



Fig. 5. Suspended biomass trend and VSS/TSS ratio during the experiments, respectively for Line A (a) and Line B (b).



Fig. 6. SOUR values (a) and maximum growth rates (b) for Line A and Line B during experiments.

# 3.5. Extracellular polymeric substances production and composition

Fig. 8 reports the  $\text{EPS}_{Bound}$  (Figs. 8(a) and (b)) and the SMP (Figs. 8(c) and (d)) concentrations during the overall experimental campaign.

Referring to EPS<sub>Bound</sub>; it was noticed a slight decrease in both systems until experimental day 54. This result could

be related to the inhibitory stress exerted by hydrocarbons, with a reduced metabolic activity, thus preventing the production of polymeric substances. Indeed, after sodium acetate was added in the influent as rapidly biodegradable substrate, a significant increase of EPS<sub>Bound</sub> concentrations was observed in both plants. Such a behavior was more evident in the Line B, since the salinity increase in the Line A hindered the metabolic production of EPS<sub>Bound</sub>. However, at



Fig. 7. OUR values (a) and nitrification rates (b) for Line A and Line B during experiments.



Fig. 8. EPS<sub>Bound</sub> values for Line A (a) and Line B (b); SMP values in Line A (c) and Line B (d) during experiments.

the end of experiments, the EPS<sub>Bound</sub> reached a stable value in Line A, suggesting a biomass adaptation to the saline environment. The SMP production and release in the bulk liquid was almost negligible in Line B, throughout experiments. Conversely, the SMP release was higher in Line A, due to the saline environment that caused a significant stress on the biomass. The observed predominance of proteins was likely due to the excretion of intracellular polymers or cell lysis, deriving from the osmotic stress exerted by the saline environment on the non-acclimated biomass. This result had a significant influence on membrane fouling, promoting irreversible mechanisms of deposition, as better outlined in the following.

#### 3.6. Microscopic observations

Qualitative microscopic observations were carried out on mixed liquor samples. They revealed a significant deflocculation of activated sludge flocs in Line A, mainly due to the stress effect exerted by the saline environment (Fig. 9(a)). Moreover, the significant presence of flagellate bacteria suggested that the bacterial consortium was not acclimated to the environment conditions (Fig. 9(b)). Conversely, a good floc structure (Fig. 9(c)) and a relative high number of higher life forms, such as sessile ciliated (Fig. 9(d)) colonial protozoa, amoebas, was observed in Line B. This result is liked due to a good acclimation level of biomass toward the environmental conditions.

#### 3.7. Effect of salinity on membrane fouling

Fig. 10 shows the trend of the specific membrane resistances in both plants, evaluated at each membrane physical cleaning through the application of the RIS model, as previously discussed. As reported in Fig. 10(a), it was observed a significant increase of total resistance  $R_{\tau}$  in the Line A since the beginning of the experimental campaign, in agreement with previous findings [37], likely due to a worsening of mixed liquor viscosity. Conversely, excepting experimental day 34, the membrane resistances of Line B were almost negligible up to day 134, highlighting a good performance of the filtering system. In both plants, the main fouling mechanism were represented by the cake deposition; nevertheless, in Line A it was noticed a significant increase of the membrane fouling due to pore blocking mechanism ( $R_{pR}$ ). Indeed, the  $R_{pR}$  increased from 0.69  $10^{12}$  m<sup>-1</sup> at experimental day 11 up to 14  $10^{12}$  m<sup>-1</sup> at experimental day 208. This behavior was likely related to the salinity, that promoted SMP release (mainly as protein fraction) into the mixed liquor, as a consequence of cell lysis due to the osmotic pressure on bacteria. This fact enabled a gradual transfer of foulants to the membrane pores, producing an almost irreversible membrane fouling (partially removable by means of "aggressive" chemical cleaning actions), that might likely affect the membrane "life-span".



Fig. 9. Qualitative images of mixed liquor of Line A (a and b) and Line B (c and d), respectively.



Fig. 10. Specific fouling resistances for Line A (a) and Line B (b), respectively.

#### 3.8. General discussion

The experimental results showed in this paper provided useful information to upgrade knowledge on the potential application of MBRs for the treatment of wastewater characterized by the presence of salt and hydrocarbons (shipboard slops). In terms of carbon removal the MBR has provided quite high removal efficiency, despite the biological activity was partially compromised by the salt presence. Relating to the nitrification process, it was noticed a partial inhibition of AOB and NOB species, with NO<sub>2</sub> accumulation. Interesting results were noticed in terms of membrane fouling. Indeed, the presence of salt in the Line A promoted a significant development of pore blocking. Indeed, by comparing the  $R_{PR}$  value between the two lines the highest value was obtained for the Line A. Such a result was mainly related to the significant amount of SMP produced in the Line A which indicates the biomass stress conditions mainly ascribed to the salt. This means that treating saline wastewater the energetic demand due to the permeate extraction (for a fixed TMP value) of the MBR increases; furthermore, the operational costs may also increase due to the increased requirement of chemicals for membrane cleaning operations.

#### 4. Conclusions

The main aim of the present study was the analysis of the effect of salinity increase on the biological performance of a non-specialized biomass for the treatment of synthetic shipboard slop. The results showed that the saline environment exerted a slight effect on the removal performance of organic matter removal, with higher efficiencies observed in the MBR plant without salinity. The respirometric batch tests highlighted that the heterotrophic biomass was not significantly influenced by the saline environment, whereas a higher stress was observed on autotrophic species. It was noticed a significant release of SMP in the Line A as a consequence of the osmotic stress on the biomass. This effect had a strong influence on the membrane fouling, with deposition mechanisms mainly irreversible. This aspect is of great concern, since it directly influences the membrane service life. As final remarks, when treating saline wastewater, the use of halophilic consortium is suggested for the achievement of high performances. Otherwise, if adopting non-halophilic species, moderate salt increase are required to enhance the acclimation of the biomass to a saline environment. Moreover, the possibility of chemical addition in order to enhance membrane filtration might be explored. Nevertheless, the use of chemicals could entail a notable increase of operation costs. Therefore, MBR option as a possible solution for treating shipboard slops should be carefully assessed by a cost-benefit analysis.

#### Acknowledgements

This research was funded by the National Operational Programme for Research and Competitiveness 2,007–2,013. Project STI-TAM (Sviluppo di Tecnologie Innovative per il trattamento di rifiuti liquidi della navigazione finalizzate alla Tutela dell'Ambiente Marino) – PON 02\_00153\_2849085 – CUP B61C12000840005; Italian Ministry of Education, University and Research and Ministry of Economic Development. Part of this research has been also financially supported by the Italian Ministry of Education, University and Research with the Research project of national interest PRIN 2010–2011 (D.M. 1152/ric 27/12/2011, prot. 2010 WLNFYZ) entitled 'Emerging contaminants in air, soil, and water: from source to the marine environment'.

#### References

- G. Munz, R. Gori, L. Cammilli, C. Lubello, Characterization of tannery wastewater and biomass in a membrane bioreactor using respirometric analysis, Bioresour. Technol., 99 (2008) 8612–8618.
- [2] A.R. Pendashteh, C.A. Luqman, A. Fakhru'l-Razia, S.S. Madaeni, Z.A. Zainal, A.B.R. DayangRadiah, Evaluation of membrane bioreactor for hypersaline oily wastewater treatment, Process Saf. Environ. Prot., 90 (2012) 45–55.

- [3] L. De Temmerman, T. Maere, H. Temmink, A. Zwijnenburg, I. Nopens, Salt stress in a membrane bioreactor: dynamics of sludge properties, membrane fouling and remediation through powdered activated carbon dosing, Water Res., 63 (2014) 112–124.
- [4] C. Sun, T. Leiknes, J. Weitzenbock, B. Thorstensen, Development of a biofilm-MBR for shipboard wastewater treatment: the effect of process configuration, Desalination, 250 (2010) 745–750.
- [5] MARPOL 73/78 International Maritime Organization's regulation Prevention of Air Pollution from Ships, IMO MARPOL 73/76, London, United Kingdom, 1997.
- [6] G. Li, S.H. Guo, F.M. Li, Treatment of oilfield produced water by anaerobic process coupled with micro-electrolysis, J. Environ. Sci., 22 (2010) 1875–1882.
- [7] O. Lefebvre, R. Moletta, Treatment of organic pollution in industrial saline wastewater: a literature review, Water Res., 40 (2006) 3671–3682.
- [8] D. Di Trapani, G. Di Bella, G. Mannina, M. Torregrossa, G. Viviani, Comparison between moving bed-membrane bioreactor (MB-MBR) and membrane bioreactor (MBR) systems: influence of wastewater salinity variation, Bioresour. Technol., 162 (2014) 60–69.
- [9] S. Soltani, D. Mowla, M. Vossoughi, M. Hesampour, Experimental investigation of oily water treatment by membrane bioreactor, Desalination, 250 (2010) 598–600.
- [10] W. Guo, H.H. Ngo, J. Li, A mini-review on membrane fouling, Bioresour. Technol., 122 (2012) 27–34.
- [11] W.J. Gao, M.N. Han, X. Qu, C. Xu, B.Q. Liao, Characteristics of wastewater and mixed liquor and their role in membrane fouling, Bioresour. Technol., 128 (2013) 207–214.
- [12] D. Jang, Y. Hwang, H. Shin, W. Lee, Effects of salinity on the characteristics of biomass and membrane fouling in membrane bioreactors, Bioresour. Technol., 141 (2013) 50–56.
- [13] W.C.L. Lay, Y. Liu, A.G. Fane, Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: a review, Water Res., 44 (2010) 21–40.
- [14] G. Di Bella, N. Di Prima, D. Di Trapani, G. Freni, M.G. Giustra, M. Torregrossa, G. Viviani, Performance of membrane bioreactor (MBR) systems for the treatment of shipboard slops: assessment of hydrocarbon biodegradation and biomass activity under salinity variation, J. Hazard. Mater., 300 (2015) 765–778.
- [15] E. Reid, X. Liu, S.J. Judd, Effect of high salinity on activated sludge characteristics and membrane permeability in an immersed membrane bioreactor, J. Membr. Sci., 283 (2006) 164–171.
- [16] G. Mannina, A. Cosenza, D. Di Trapani, M. Capodici, G. Viviani, Membrane bioreactors for treatment of saline wastewater contaminated by hydrocarbons (diesel fuel): an experimental pilot plant case study, Chem. Eng. J., 291 (2016) 269–278.
- [17] G. Mannina, G. Di Bella, Comparing two start-up strategies for MBRs: experimental study and mathematical modeling, Biochem. Eng. J., 68 (2012) 91–103.
- [18] APHA, Standard Methods for the Examination of Water and Wastewater, APHA, AWWA and WPCF, Washington, DC, USA, 2005.
- [19] H. Spanjers, P.A. Vanrolleghem, G. Olsson, P. Dold, Respirometry in control of the activated sludge process, Water Sci. Technol., (1996) 34 117–126.
- [20] P.A. Vanrolleghem, H. Spanjers, B. Petersen, P. Ginestet, I. Takacs, Estimating (combination of) activated sludge model

No.1 parameters and component by respirometry, Water Sci. Technol., 39 (1999) 195–214.

- [21] A. Ramdani, P. Dold, S. Déléris, D. Lamarre, A. Gadbois, Y. Comeau, Biodegradation of the endogenous residue of activated sludge, Water Res., 44 (2010) 2179–2188.
- [22] X.Q. Zhang, P.L. Bishop, B.K. Kinkle, Comparison of extraction methods for quantifying extracellular polymers in biofilms, Water Sci. Technol., 39 (1999) 211–218.
- [23] A. Cosenza, G. Di Bella, G. Mannina, M. Torregrossa, The role of EPS in fouling and foaming phenomena for a membrane bioreactor, Bioresour. Technol., 147 (2013) 184–192.
- [24] O.H. Lowry, N.J. Rosebrough, A.L. Farr, R.J. Randall, Protein measurement with the Folin phenol reagent, J. Biol. Chem., 193 (1951) 265–275.
- [25] M. DuBois, K.A. Gilles, J.K. Hamilton, P.A. Rebers, F. Smith, Colorimetric method for determination of sugars and related substances, Anal. Chem., 28 (1956) 350–356.
- [26] A. Drews, J. Mante, V. Iversen, M. Vocks, B. Lesjean, M. Kraume, Impact of ambient conditions on SMP elimination and rejection in MBRs, Water Res., 41 (2007) 3850–3858.
- [27] I.-S. Chang, S.-O. Bag, C.-H. Lee, Effects of membrane fouling on solute rejection during membrane filtration of activated sludge, Process. Biochem., 36 (2001) 855–860.
- [28] F. Meng, H.M. Zhang, Y.S. Li, X.W. Zhang, F.L. Yang, J.N. Xiao, Cake layer morphology in microfiltration of activated sludge wastewater based on fractal analysis, Sep. Purif. Technol., 44 (2005) 250–257.
- [29] F. Meng, F. Yang, Fouling mechanisms of deflocculated sludge, normal sludge, and bulking sludge in membrane bioreactor, J. Membr. Sci., 305 (2007) 48–56.
- [30] W. Zhiwei, W. Zhichao, T. Shujuan, Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor, Water Res., 43 (2009) 2504–2512.
- [31] D. Jenkins, M.G. Richard, G.T. Daigger, Manual on the Causes and Control of Activated Sludge Bulking, Foaming and Other Solids Separation Problems, IWA Publishing, London, 2003.
- [32] W. Luo, H.V. Phan, F.I. Hai, W.E. Price, W. Guo, H.H. Ngo, L.D. Nghiem, Effects of salinity build-up on the performance and bacterial community structure of a membrane bioreactor, Bioresour. Technol., 200 (2016) 305–310.
- [33] M.A.H. Johir, S. Vigneswaran, J. Kandasamy, R. BenAim, A. Grasmick, Effect of salt concentration on membrane bioreactor (MBR) performances: detailed organic characterization, Desalination, 322 (2013) 13–20.
- [34] K.N. Yogalakshmi, K. Joseph, Effect of transient sodium chloride shock loads on the performance of submerged membrane bioreactor, Bioresour. Technol., 101 (2010) 7054–7061.
- [35] G. Mannina, M. Capodici, A. Cosenza, D. Di Trapani, G. Viviani, Sequential batch membrane bio-reactor for wastewater treatment: the effect of increased salinity, Bioresour. Technol., 209 (2016) 205–212.
- [36] Ö. Karahan-Gül, N. Artan, D. Orhon, M. Henze, M.C.M van Loosdrecht, Respirometric assessment of storage yield for different substrates, Water Sci. Technol., 46 (2002) 345–352.
- [37] W. Luo, F.I. Hai, J. Kang, W.E. Price, W. Guo, H.H. Ngo, L.D. Nghiem, Effects of salinity build-up on biomass characteristics and trace organic chemical removal: Implications on the development of high retention membrane bioreactors, Bioresour. Technol., 177 (2015) 274–281.