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Performance of a moving bed-membrane bioreactor treating saline wastewater contaminated by hydrocarbons from washing of oil tankers

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ABSTRACT

This work analyses the performance of a moving bed-membrane bioreactor (MB-MBR) in the treatment of saline wastewater contaminated by hydrocarbons from washing of oil tankers with seawater (slops). In order to allow a biomass acclimation, a gradual increase in salinity and total petroleum hydrocarbons (TPHs) were adopted during six experimental phases. The results showed that acclimation of heterotrophic strains to TPHs occurred during Phase IV (30% by volume of slop). This is confirmed by an evident increase in the biological removal efficiencies of chemical oxygen demand, total organic carbon and TPHs. In particular, the TPHs removal efficiency increased from about 8% up to the range of 35–70%. No inhibition of the ammonia oxidizing bacteria (AOB) was noted except for Phase VI (100% by volume of slop) characterized by a collapse of ammonium removal efficiency from about 95% to about 21–24%. An accumulation of nitrite at the end of Phase IV, suggested an inhibition of nitrite-oxidizing bacteria (NOB), while a simultaneous "salt-in" of bromide indicated the acclimation of the same strains to salinity. Moreover, the hydraulic performance showed a high increase in total resistance to filtration (R_T) during the pseudo-stationary phases (from Phase I to Phase III) and during Phase VI, due to the high salinity and hydrocarbons concentration. The results showed that the MB-MBR system has high potentiality for the treatment of saline oily wastewater.

Keywords: Salinity; Hydrocarbons; MBR; MBBR; TPH

1. Introduction

Sea pollution due to the discharge of the washing waters from oil tankers is an issue of significant impact on a world scale [1]. These kinds of wastewater, also called slops, are usually transported in barges and are constituted by mixtures of residual fuel oils and saline water containing several recalcitrant pollutants (oils, hydrocarbons, surfactants, etc.). Annually million tons of slops are generated and this has resulted in the definition of several laws, such as the

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International Maritime Organization regulations [2], which play a relevant role regulating and preventing marine pollution, specifically referring to the discharge of oily bilge water and slops. These regulations have defined the Mediterranean Sea as "special area", preventing the direct discharge of oils to the sea and forcing harbour authorities to implement wastewater treatments. The most recalcitrant wastewaters, such as the slops, are generally treated by physical and chemical processes including photo–electro–catalytic decontamination, hydrocyclones, coagulation and flocculation [3,4]. However, such treatments involve a considerable use of chemicals and a significant production of chemical sludge to be disposed. Furthermore, an efficient treatment technology should be employed before reuse and/or discharge.

In this context, the use of biological treatments is becoming increasingly popular in the field of saline wastewater characterised by high organic content and petroleum hydrocarbons [1,5], because they are cost competitive and environmental friendly alternative methods to decompose organic compounds in wastewater. However, biological treatments of wastewater that contain high concentration of total petroleum hydrocarbons (TPHs) and salts are particularly challenging due to the inhibition propensity and/or toxicity of these compounds [4]. The salinity of slops can affect the metabolism of micro-organisms in activated sludge systems due to the osmotic stress which would cause an outward flow of intracellular water, resulting in cell dehydration and plasmolysis with subsequent cellular death [6,7]. However, in marine environment with high salt concentration (10–30 g L^{-1} of NaCl), slightly halophilic bacterial strains can be selected [6,8]. Furthermore, as the biological removal of TPHs is uncertain due to a toxic effect towards bacteria [4,9], a biomass acclimation is required before any biological treatment [10]. An increasing interest in the use of membrane bioreactor (MBR) technology has been expressed in the last decades, especially for the treatment of saline wastewaters [6,7,11] and for high salinity wastewater contaminated by hydrocarbons [4,10]. The MBR system has many advantages well known in the literature [12] including, among all, high effluent quality and the possibility to treat slowly biodegradable substances. With the addition of suspended carriers in the mixed liquor of a conventional activated sludge reactor, a hybrid moving bed biofilm reactor (HMBBR) can be obtained with both suspended and attached micro-organisms [13]. This allows to achieve a higher biomass concentration with the possibility to biodegrade the most recalcitrant compounds such those contained in slops. Coupling a MBR system with a HMBBR system or simply MBBR, is possible to create new layouts called moving bed-membrane bioreactor (MB–MBR) and biofilm-membrane bioreactor (BF-MBR) [14,15] which combine the benefits of both the technologies. Like all systems based on membrane technology, the above-mentioned schemes present fouling problems whose minimization represented a great challenge for several years [16,17]. The aim of the present study is to evaluate the effect of simultaneous presence of salinity and hydrocarbons on the performances, in terms of removal efficiencies, of a MB–MBR plant which worked with an ultrafiltration membrane and with mobile carriers made of polyurethane sponges. In particular, the biomass was acclimatized by feeding a mixture of slops and synthetic wastewater with a progressive reduction of the slop dilution factor till the system was fed with a 100% by volume of slop. This last condition was not yet applied in the literature and represents a research highlight.

2. Materials and methods

2.1. Bench-scale plant description

The bench-scale plant was built at the Laboratory of Sanitary and Environmental Engineering of the University of Enna Kore (Italy), adopting the same configuration of Di Bella et al. [18]. In particular, the plant was progressively adapted to the contaminants and salinity starting with highly diluted slops and progressively reducing the dilution factor (Fig. 1). The system was characterized by a liquid-phase volume of 14 L and by an ultrafiltration (UF) hollow fibre membrane module (Zee-Weed™01, with specific area equal to 0.093 m^2 and nominal porosity of 0.04 μm). The permeate flux was kept in the range of 12–15 L m^{-2} h^{-1}. The membrane was periodically backwashed (every

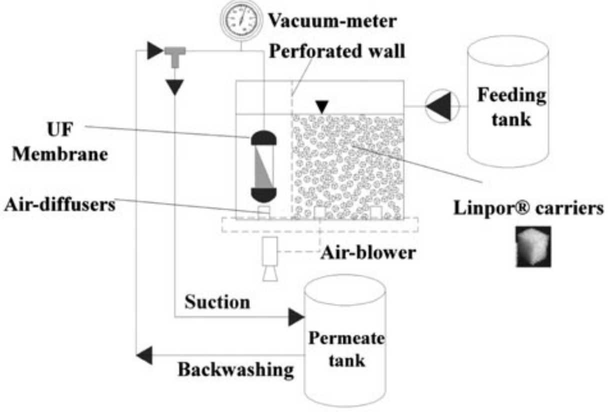

Fig. 1. Layout of MB–MBR bench-scale plant.

5 min for a period of 1 min) by pumping a fraction of permeate back through the membrane module. Furthermore, the transmembrane pressure was measured by means of a vacuum-metre. The membrane was kept in a separated compartment from the rest of the reactor and a perforated wall separated the two compartments in order to avoid collisions of suspended carriers with UF module. Linpor® mobile carriers were utilized, which are polyurethane cubic sponges with a 14 mm side and a 1,000 m^2 m^{-3} specific effective carrier surface area, and the filling ratio was about equal to 31%.

The bench-scale plant has been operated for a period of about 140 d. The experimental campaign was divided in six different phases, each characterized by a decreasing slop dilution factor in order to allow micro-organisms acclimation (Phase I: no slop addition, Phase II: 5% slop volume, Phase III: 10% slop volume, Phase IV: 30% slop volume, Phase V: 50% slop volume, Phase VI: 100% slop volume). Starting from Phase I, the system was fed with a synthetic solution containing sodium acetate, ammonium chloride and potassium diphosphate in proportions to ensure minimum intake of C:N:P for bacterial metabolism with the ratio of 100:5:1. From Phase II and till the end of Phase V, the slop was mixed with the synthetic solution in order to maintain a chemical oxygen demand (COD) next to values of 1,000 1,500 mg L^{-1}. Lastly, in Phase VI, the system was fed with slops only and the COD resulted about equal to 1,100 mg L^{-1}.

Slops were sampled from barges of a coastal oil refinery in the Augusta harbour (Sicily, Italy) and subjected to preliminary treatments of de-oiling and gravity separation prior to biological treatment in order to remove a large amount of non-biodegradable oils and greases. In Tables 1 and 2, the average main slop characteristics and the average operational parameters are summarized.

2.2. Methods

Throughout the whole experimental duration, the influent wastewater, the mixed liquor and the effluent permeate have been sampled twice per week and analysed according to the Standard Methods [19]. In particular, the following parameters were measured: total and volatile suspended solids (MLTSS and MLVSS), COD, ammonia nitrogen (NH_4-N), anions (nitrite (NO_2^-), nitrate (NO_3^-), chloride (Cl^-), bromide (Br^-), sulphate (SO_4^{2-})) and TPHs concentration. The mixed liquor samples were firstly filtered through a 0.45-μm filter. During all the experimentation, COD was measured by means of chemical titration.

Table 1
Characteristics of the slop after gravity separation

Parameter	Value
Chemical oxygen demand (COD), mg L^{-1}	1,566 ± 251
Total carbon (TC), mg L^{-1}	428 ± 62
Inorganic carbon (IC), mg L^{-1}	38 ± 5
Total organic carbon (TOC), mg L^{-1}	390 ± 3
Ammonium NH_4^+, mg L^{-1}	≈0
Phosphates PO_4^{3-}, mg L^{-1}	≈0
Chlorides, Cl^-, mg L^{-1}	23,455 ± 121
Fluorides F^-, mg L^{-1}	5 ± 1
Bromides Br^-, mg L^{-1}	411 ± 23
Sulphides SO_4^-, mg L^{-1}	3,541 ± 52
Total petroleum hydrocarbons (TPH), mg L^{-1}	30 ± 3
Suspended solids (SS), mg L^{-1}	352 ± 84
pH	7.78 ± 0.62

Moreover, in high salinity conditions COD was measured by means of chemical titration with the addition of mercury sulphate in order to eliminate chloride interference. The measures of ammonium and of all anions were carried out by means of ionic chromatography by ICS Dionex 1100. The total organic carbon (TOC) was measured by means of thermos-catalytic oxidation with a high-temperature TOC-V_{CSH} analyser that also provides the total carbon (TC) and the inorganic carbon (IC).

In the case of the evaluation of performance in terms of COD and TOC, the concentrations of the biological system (C_{BIO}) were analysed. They are fractions of soluble COD and TOC measured in the supernatant of mixed liquor samples. In particular, they were obtained after centrifugation at 5,000 rpm for 10 min and a filtration through a 0.45 μm filter paper. In this way, it was possible to define two different performances of the system: the first took into account only the biological effect of the biomass in the bioreactor (1), the second expressed a total bio-physical removal due to both biomass and membrane filtration (2):

$$\eta_{BIO} = \frac{C_{IN} - C_{BIO}}{C_{IN}} \quad (1)$$

$$\eta_{TOT} = \frac{C_{IN} - C_{OUT}}{C_{IN}} \quad (2)$$

The TPHs concentrations were measured at the end of each phase using a gas chromatograph equipped with a flame ionization detector (GC-FID, Agilent 6890N), after extraction of TPHs from samples with hexane. Periodically, samples of suspended carriers were taken

Table 2
Operational parameters (average values)

Parameter	Phase I (18 d)	Phase II (14 d)	Phase III (24 d)	Phase IV (49 d)	Phase V (15 d)	Phase VI (20 d)
COD, mg L^{-1}	1,095 ± 346	1,329 ± 200	1,303 ± 205	1,070 ± 444	1,487 ± 186	1,092 ± 52
TC, mg L^{-1}	459 ± 84	521 ± 41	533 ± 29	496 ± 86	554 ± 106	299 ± 17
IC, mg L^{-1}	79 ± 31	113 ± 32	174 ± 56	133 ± 94	59 ± 20	43 ± 8
TOC, mg L^{-1}	380 ± 54	408 ± 73	359 ± 84	362 ± 169	495 ± 123	256 ± 25
N-NH_4, mg L^{-1}	115 ± 37	167 ± 66	155 ± 75	102 ± 56	144 ± 27	149 ± 38
Phosphates, mg L^{-1}	15 ± 1	13 ± 4	16 ± 2	15 ± 3	18 ± 2	14 ± 4
Chlorides, mg L^{-1}	216 ± 5	1,446 ± 121	2,393 ± 260	7,361 ± 668	12,059 ± 514	23,919 ± 482
Bromides, mg L^{-1}	≈ 0	21 ± 5	41 ± 8	143 ± 46	253 ± 12	579 ± 80
Sulphides, mg L^{-1}	≈ 0	143 ± 17	263 ± 48	812 ± 64	1,384 ± 20	3,628 ± 140
TPH, mg L^{-1}	≈ 0	1.50 ± 0.20	3.10 ± 0.50	9.20 ± 1.00	15.50 ± 1.00	31.40 ± 2.00
pH	7.78 ± 0.60	7.70 ± 0.60	7.72 ± 0.60	7.68 ± 0.60	7.65 ± 0.50	7.71 ± 0.50

and analysed for total solids in order to evaluate the growth of the attached biomass on mobile carriers. For the details on the adopted procedure, the reader is referred to the literature [13].

Furthermore, throughout all the experimental period, the membrane fouling was analysed in terms of total resistance to filtration, expressed by means of the Darcy's law (3):

$$R_T = \mathrm{TMP}/(J\mu) \quad (3)$$

where TMP is the transmembrane pressure (Pa), μ the permeate viscosity (Pa s) and J the permeate flux ($m^3\ m^{-2}\ s^{-1}$). Periodically, physical cleanings were assessed in order to limit excessive load losses through the membrane. So, it was necessary to extract the membrane from the reactor and to wash it with ultrapure water according to the "manual water rinsing" [20].

3. Results and discussion

3.1. Solid concentrations

The MB–MBR system was inoculated with a mixed liquor total suspended solids (MLTSS) concentration almost equal to 3.3 g L^{-1}. Fig. 2 shows the MLTSS and the mixed liquor volatile suspended solids (MLVSS) (a), as well as the attached biomass (b).

In Phase I, it was observed an immediate decreasing of MLTSS, from about 3.3 g L^{-1} down to about 2.1 g L^{-1} on day 3, due to an initial entrapment of the biomass into the porosity of unspoiled spongy carriers. Subsequently, the growth rate of MLTSS was relatively constant from the inoculum value up to about 8 g L^{-1} at the beginning of Phase III.

The system was operated with a complete sludge retention time (SRT) during the whole experimental period. However, in order to maintain the concentration of total suspended solids within the system almost constant between 7 and 8 g L^{-1}, sludge withdrawals were carried out from the system occasionally during Phase III and Phase IV, resulting in a SRT in the range of 22–28 d.

In Phase VI, the decrease in total and volatile suspended solids was likely due to both a partial decay of the biomass and to a considerable entrapment of suspended biomass within the pores of the spongy carriers.

Observing the trend of MLVSS/MLTSS ratio, it increased from an initial value almost equal to 75% to a value next to 87% at the end of Phase III. On the contrary, starting from Phase IV till the end of Phase VI, the MLVSS/MLTSS ratio was slowly decreasing from about 87% to about 60%, denoting a great mineralization and biomass ageing with a decrease of its organic fraction. This might be attributed to the decrease in influent biodegradability and to accumulation of inorganic compounds inside the microbial flocs.

Regarding to the attached biomass, it was observed an increase in the attached solids until about 13.2 g L^{-1} in 91 d of operation. Subsequently, a reduction of the attached biomass down to about 5.1 g L^{-1} occurred, due to a withdrawal of attached biomass. Indeed, an extraordinary squeezing of the spongy carriers was performed in order to preserve their porosity and to enhance the oxygen diffusion within the inner layers. Afterwards, the concentration of the attached solids is resumed up to about 17.1 g L^{-1} at the 140th day of operation.

3.2. Bench-scale plant performance

The performances in terms of organic matter, TPHs and ammonium removal were evaluated by analysing

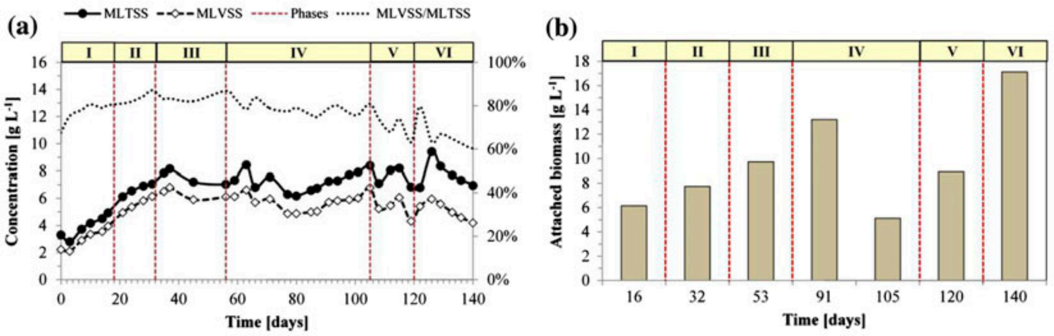

Fig. 2. Trends of MLTSS, MLVSS suspended solids (a) and attached biomass (b).

the concentrations of the analytes in the influent, the mixed liquor supernatant and the permeate. Table 3 shows the average removal efficiencies for the bench-scale plant.

3.2.1. Organic matter (COD, TOC) removal

The variation of the organic matter, expressed as COD and TOC concentration in the influent and effluent, is shown in Fig. 3(a) and (c). The measurement of TOC as a direct measurement of the carbon source is more accurate than the COD, although legislation mandates the measurement of the latter parameter before discharge. Therefore, the TOC was used as control parameter. It is apparent that despite the variations in the influent, the permeate quality after a biological–physical treatment is quite stable approximately below about 300 and 40 mg L^{-1} for COD and TOC, respectively, during all the experimentation periods. Moreover, the membrane acted as an additional purification phase to reject the remaining particulate matter and to produce a permeate of better quality.

Reasoning in terms of removal efficiencies (Fig. 3(b) and (d)), the total (biological–physical) removal efficiency of COD and TOC reached high values on average around 90% during the whole study, highlighting the filtering effect exercised by the membrane towards the dissolved organic compounds. On the other hand, the biological removal efficiencies were always lower than the biological–physical removal efficiencies. Starting from the end of Phase III and until the day 73 in Phase IV characterized by a slop volume of 30%, the biological removal efficiencies decreased to a minimum value equal to 15 and 30% for COD and TOC, respectively. Subsequently, there was an increase up to values of 85 and 90% for COD and TOC at the end of Phase IV.

In general, there is no difficulty in achieving biological carbon removal in elevated salt environment. Within the large and diverse group of halophilic and halotolerant micro-organisms, there are a great number of aerobic heterotrophs that are able to biodegrade the organic carbon matter present in wastewater [21].

So, the particular removal trend observed is attributable to an initial inhibition and a subsequent acclimation of the heterotrophic strains to slops.

In confirmation of the biomass acclimation in Phase V, characterized by a slop volume of 50%, the

Table 3
Bench-scale plant performances (average values)

Parameter		Units	Phase I	Phase II	Phase III	Phase IV	Phase V	Phase VI
COD	η_{BIO}	%	74 ± 8	72 ± 3	77 ± 5	54 ± 37	87 ± 2	84 ± 4
	η_{TOT}	%	84 ± 12	89 ± 7	95 ± 4	84 ± 14	90 ± 5	87 ± 2
TOC	η_{BIO}	%	91 ± 5	89 ± 4	77 ± 2	66 ± 30	86 ± 1	86 ± 1
	η_{TOT}	%	98 ± 2	95 ± 1	94 ± 2	93 ± 3	95 ± 2	87 ± 1
NH_4-N	η_{BIO}	%	97 ± 1	98 ± 1	96 ± 3	96 ± 4	98 ± 1	22 ± 5
	η_{TOT}	%	97 ± 1	98 ± 1	96 ± 3	98 ± 2	99 ± 1	28 ± 5
TPH	η_{TOT}	%	–	<1	8 ± 2	35 ± 2	50 ± 3	70 ± 2

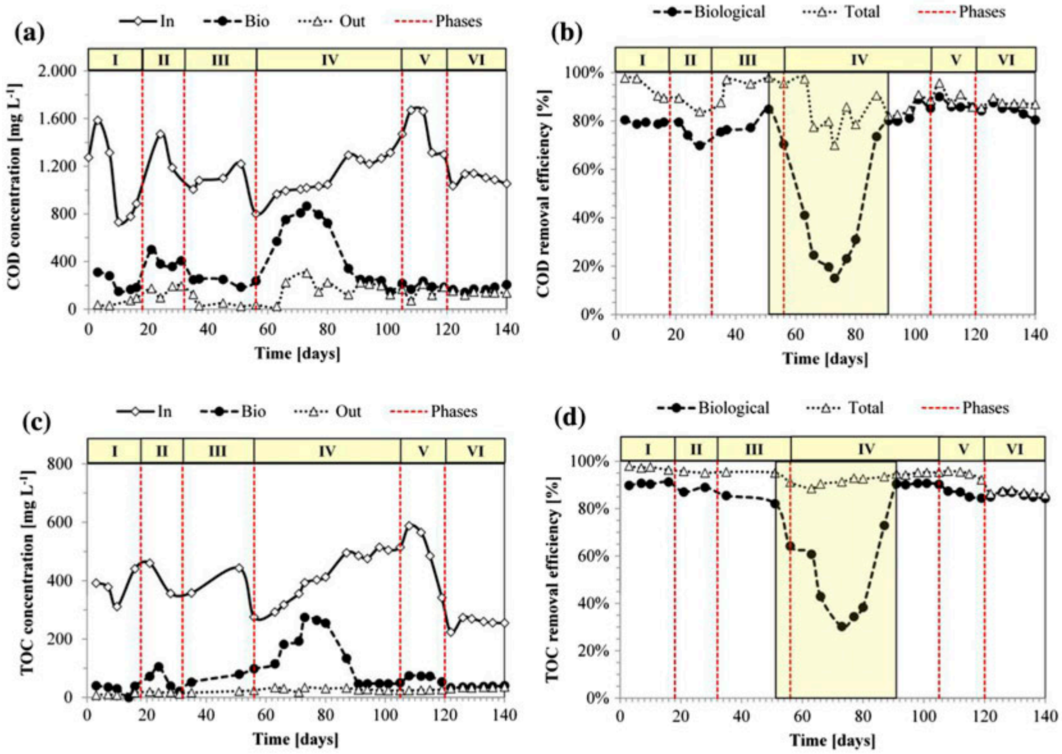

Fig. 3. Variation and removal efficiency of COD (a and b) and TOC (c and d).

biological removal increased reaching efficiencies on average equal to 86% for both the COD and the TOC. Finally, in Phase VI, in which the system has been fed exclusively with slop, the biological removal efficiencies of COD and TOC were on average next to 84 and 85%, respectively. These last results are very good, confirming that the acclimatization of micro-organisms occurred in presence of a saline and recalcitrant substrate.

3.2.2. TPHs removal

Fig. 4 shows the average removal efficiencies of TPHs in each phase. Until Phase III the removal efficiency was negligible, on average next to about 8%. This low value is due to an initial physical entrapment of hydrocarbons within the pores of the spongy carriers. With the decrease in slop dilution factor from Phase I to Phase VI, the readily biodegradable carbon source provided by sodium acetate decreased against the slowly biodegradable carbon source provided by TPHs. This led to an inhibition of micro-organisms which reached its peak during Phase IV as discussed in the previous paragraph. Furthermore, in the same phase there has been a significant increase in the TPHs removal efficiency up to about 35% probably due to an acclimation of bacteria to the hydrocarbons. In particular, the observed trend is attributable to an initial inhibition and a subsequent acclimation of the heterotrophic strains to TPHs contained in slops. In the previous phases and up to Phase III with 10% by volume of slop, the low concentrations of TPHs were not inhibitory and toxic enough for biomass.

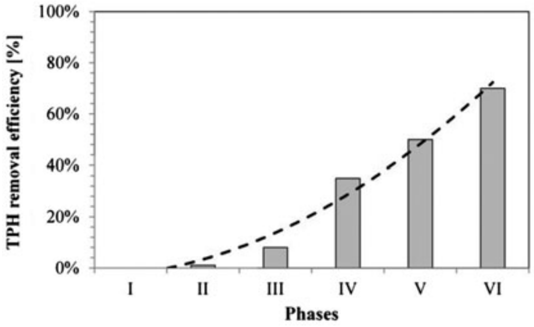

Fig. 4. TPHs average removal efficiencies.

This is in agreement with the biological removals of COD and TOC aforementioned (Fig. 3(b) and (d)), while the micro-organisms' acclimation is more confirmed by the increase of TPHs removal efficiency up to about 50%, during Phase V and about 70% in Phase

VI in which only real slops were fed to the system. Therefore, both the suspended and the attached biomass on the surface of the mobile carriers, has gradually acclimatized to the growing fraction of organic carbon contained in the hydrocarbon chains.

The biodegradation of hydrocarbons was conducted by both the attached and suspended biomass. Probably the recalcitrant substrate was firstly adsorbed within the pores of the spongy carriers and subsequently hydrolysed and biodegraded by the attached biomass.

Moreover, the MBR system allowed to operate with a high sludge retention time (SRT) and ensured a high contact time between the suspended biomass and the recalcitrant substrate improving the micro-organisms' acclimation.

3.2.3. Nitrification

As regards ammonium removal, in Fig. 5(a) and (b) the trends of NH_4-N concentrations and removal efficiencies are shown. No worsening in biological and total removal efficiencies of ammonium occurred and values on average above 95% were achieved. However, during Phase VI, characterized by no slop dilution factor, both the biological and total removal efficiencies of NH_4-N decreased down to about 21 and 28%, respectively. Since it is well known that the autotrophic strains are severely influenced by the saline content of the bulk solution [6,11], the collapse of the ammonium removal efficiency was likely due to an inhibitory effect mainly exerted by the high salinity (23.4 g L^{-1} of chlorides) and also by the hydrocarbons of slops towards the ammonia-oxidizing bacteria (AOB).

At the end of Phase IV, in the period between the day 91 and the day 105, an inhibition of the nitrite-oxidizing bacteria (NOB) was noted. As shown in Fig. 5(c), an accumulation of nitrite and a decrease of nitrate, suggested that the ammonium oxidation stopped at the nitrite formation and did not proceed until to nitrate production. This is mainly due to an inhibitory effect of salinity, although in the present study this aspect was observed at a low salinity (about 7.4 g L^{-1} of chlorides) then other works [22].

Furthermore, as confirmed in the literature [6], in the course of acclimation the effect of an increasing saline environment on the nitrifiers is more pronounced at the lower salt concentrations up to around 10 g L^{-1}, like in Phase IV. In this concentration range, it was reported that the loss of nitrification activity was larger [23].

Subsequently, starting from Phase V and till the end of Phase VI, nitrate and nitrite resumed their original trend. This suggested that acclimation of NOB to saline environment was achieved.

The obtained results are confirmed by the dualism of two opposing views in the literature as to which group of nitrifiers is more susceptible to increasing salt level. The first view holds that the nitrite oxidisers are more susceptible than the ammonia oxidisers to salt effects, based on the accumulation of nitrite [24]. The second view is that the nitrite oxidisers are less affected by salt stress than the ammonia oxidisers, at least at the lower salt levels [25].

From this work experiments both effects were observed. Indeed, at the end of Phase IV the NOB were much more susceptible to osmotic stress than the AOB, which is in agreement with some former observations [26]. Subsequently, for the whole Phase VI, the high salinity affected only the AOB, limiting the ammonium oxidation.

3.2.4. Salinity acclimation

Bearing in mind the previous considerations, the acclimation to a high salinity is confirmed by the bromide "salt-in" phenomenon that most probably occurred during the same period between the day 91 and the day 105, as shown in Fig. 6(a).

As known, the osmotic stress would cause an outward flow of intracellular water, resulting in cell dehydration and, eventually, plasmolysis and loss of activity of the cells for these micro-organisms [27]. The ability to cope with osmotic stress by maintaining osmotic balance between the intracellular environment of the cytoplasm and the elevated salt environment, is therefore an essential attribute of the halophilic and halotolerant micro-organisms. One strategy, known as the "salt-in" strategy, typically involves the accumulation of potassium (K^+) and chloride (Cl^-) ions within the cytoplasm for osmotic balance [28].

In this study, no chloride accumulation within the cytoplasm was noted (Fig. 6(b)), while a bromide "salt-in" likely occurred. In particular, during the whole experimentation, a quantity of bromide equal to about 50% moved inside the cell wall. Only from 91st to 105th day of operation, it was noted about the 100% of bromide "salt-in". Since no advanced microbiological analysis were assessed in this study, during these 15 days it was supposed that the bromide constituted the main intracellular anion, balancing the high potassium and sodium concentrations in the cells of selected slightly halophilic bacteria. This was in agreement with how expected by other authors in the past [29].

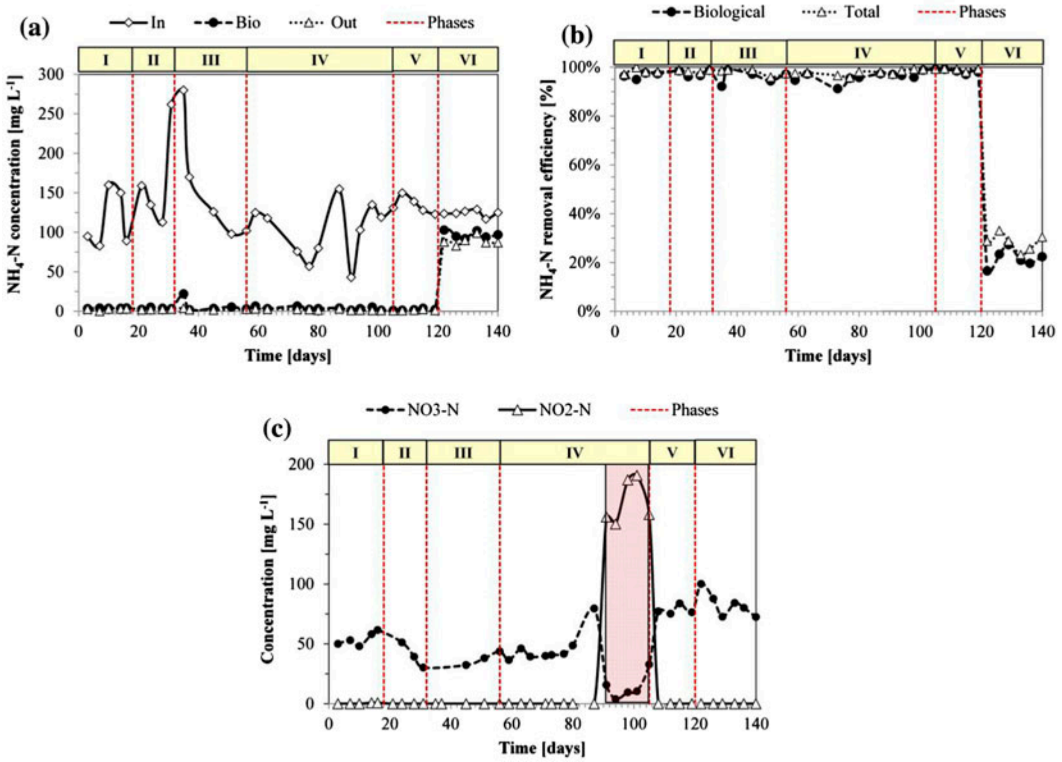

Fig. 5. Variation (a) and removal efficiency (b) of NH_4-N; variation of NO_3-N and NO_2-N (c).

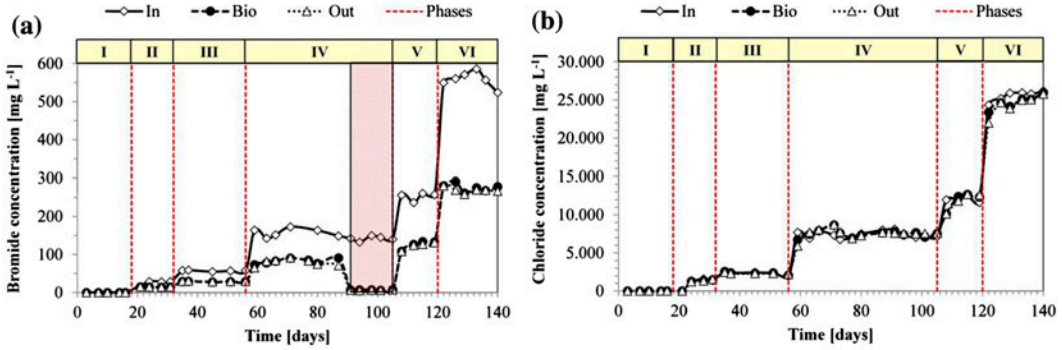

Fig. 6. Bromides (a) and chlorides (b) concentrations.

3.3. *Membrane filtration performance*

Throughout all the experimental period, the TMP was measured in order to calculate the resistance to filtration for the analysis of the hydraulic performance of the membrane. In Fig. 7, the total resistance to filtration is shown and the physical cleanings are also indicated with red dotted lines. The physical cleanings were performed at each change of phase and whenever the permeate flow decreased significantly.

During the first 49 d the total resistance to filtration (R_T) grew almost linearly. From Phase I to Phase III R_T grew ever more rapidly due to both the growth of MLSS in non-stationary phase and to the influence of salinity and hydrocarbons towards micro-organisms. This likely implied a production of extracellular polymeric substances which played a key role in the deposition of irreversible fouling on membrane surface. From the day 50th and until the 91st day R_T increased more slowly due to both the achievement of pseudo-stationary biological condition and to the inhibition of micro-organisms as expressed previously in Fig. 3. The first implied an almost constant concentration of

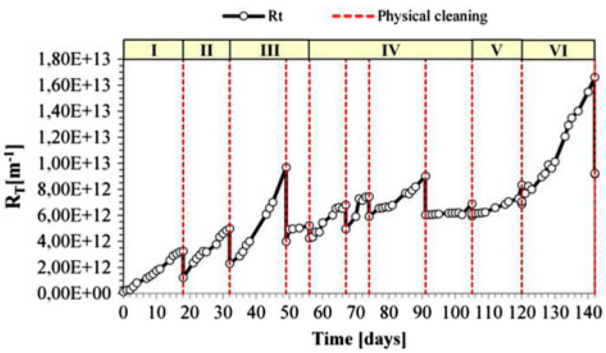

Fig. 7. Total resistance to filtration.

MLSS, the second resulted in a less biological activity which contributed to a less production of foulants.

Starting from the day 91 the perforated wall, which separated the two compartments, was removed from the reactor in order to observe the effect of the collision of the spongy carriers towards fouling. As expected, this involved a significant slowdown of membrane fouling, attributable to the abrasive action of the spongy carriers which clashed against the membrane fibres.

In Phase V it was noticed a gradual increase of R_T, while in Phase VI a sudden rise of resistance was registered in response to the high salinity and hydrocarbons concentration of slop which implied a great fouling production.

4. Conclusions

A MB–MBR bench-scale system treating saline wastewater contaminated by hydrocarbons from washing of oil tankers was investigated. The attached biomass on mobile carriers, as well as the membrane filtration, contributed to increase the overall biological–physical performances confirming the robustness of the system in the treatment of recalcitrant substrates. During Phase IV a decrease and a subsequent sudden increase in the biological removal efficiencies of COD and TOC to a minimum value, suggested an initial inhibition and a following acclimation of heterotrophic strains to slops. Moreover, a significant increase in the TPHs removal efficiency from about 8% of Phase III up to about 35% in Phase IV and till 70% in Phase VI, highlighted the acclimation of bacteria to the hydrocarbons, since in Phase VI only real slops were fed to the system. As regards nitrification, both biological and total ammonium removal efficiencies were on average above 95%, till the Phase V. A sudden collapse of removal efficiencies down to 21–28% in Phase VI was noted, highlighting a severe inhibition of AOB at high salinity (about 23.4 g L^{-1} of chlorides). An accumulation of nitrite at the end of Phase IV (about 7.4 g L^{-1} of chlorides) suggested an inhibition of NOB, while a probable simultaneous "salt-in" of bromide indicated a contextual acclimation of the same strains to salinity, also confirmed by an increase of nitratation for the remaining phases.

Regarding to the hydraulic performance, the highest increase in total resistance to filtration was registered during the pseudo-stationary phases (from Phase I to Phase III) and during Phase VI, due to the high salinity and hydrocarbons concentration. However, from the end of Phase III, till the end of Phase V it was observed a slow increase of resistance to filtration due to both inhibition of micro-organism, which reduced the biological production of foulants, and to the removal of perforated wall from the day 91, which favoured the abrasion of the cake on membrane surface.

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