The effect of hydrocarbon on a pilot plant membrane bioreactor system

A. Cosenza[1], D. Di Trapani[1], M. Torregrossa[1], G. Viviani[1], G. Mannina[1]

[1] Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy
alida.cosenza@unipa.it, daniele.ditrapani@unipa.it, michele.torregrossa@unipa.it, gaspare.viviani@unipa.it, giorgio.mannina@unipa.it

Slops; Total petroleum hydrocarbon; membrane fouling

Abstract

The paper reports the main results from an experimental gathering campaign carried out on a bench scale plant for the evaluation of hydrocarbon effect on the system performance. In particular, a membrane bioreactor (MBR) under submerged configuration was analysed. The MBR plant was fed with synthetic wastewater containing hydrocarbons. Organic carbon, hydrocarbons and ammonium removal, kinetic constants, extracellular polymeric substances (EPSs) production and membranes fouling rates have been assessed. The observed results highlighted good system performance in terms of both COD removal and nitrification, thus showing a sort of biomass adaptation to hydrocarbon. Such a result has been also confirmed by the biomass respirometric tests. Moreover, membrane fouling analysis showed an increase of the total resistance in the last period of the experiments. Such a result was most likely due to the hydrocarbon which caused an irreversible fouling due to oil deposition onto the membrane surface.

Introduction

Nowadays, the growing awareness on environmental protection has led to increasing regulatory pressure on wastewater treatment, imposing severe limitations on pollutant concentrations before discharge into the environment. In this context, one of the major challenges is represented by the treatment of wastewater produced during shipboard activities (bilge water or slops), which are characterized by high oil and saline concentrations (Sun et al., 2010). Therefore, in order to prevent hydrocarbon discharge into the sea from ships, the International Maritime Organization (IMO) enacted the MARPOL 73/78 convention. According to the latter, any oil and oil residue discharged in wastewater streams must contain less than 5-ppm hydrocarbons. Consequently, effective treatment of this petroleum-contaminated water is essential prior to its discharge into the environment, in order to prevent or minimize pollution problem of marine ecosystems as well as for human health. The use of biological treatments is becoming increasingly popular in the field of saline wastewater characterised by high organic content and petroleum hydrocarbons (Reid et al., 2006), even if the presence of high concentrations of a separate oily phase usually requires proper pre-treatment. In recent years, membrane bioreactors (MBRs) have been applied for saline wastewater treatment (among others, Abdollahzadeh Sharghi et al., 2014; Di Trapani et al., 2014), since they feature high-quality effluent, small footprint and low sludge production rates (Judd, 2011). Therefore, MBRs can be suitably applied for the treatment of wastewater deriving from shipboard activities and contaminated by hydrocarbons. Indeed, membrane technology has been recently introduced as an efficient technique to separate oil/water mixture due to its ability to effectively remove the oil droplets when compared to the current conventional technologies (Singh et al., 2011; Padaki et al., 2015). Nevertheless, in presence of "recalcitrant or xenobiotic" compounds and low aqueous solubility of hydrocarbon, a modification of biomass biokinetic activity as well as sludge characteristics may arise (Padaki et al., 2015). Indeed, hydrocarbons are characterized by high molecular weight, thus making sludge highly hydrophobic. The high hydrophobic value strongly influences flocculation, sedimentation, dewatering and filterability in activated sludge during wastewater treatment (Jin et al., 2004). This condition is of importance, since microbial community characteristics can play an important role in membrane fouling, which still represents one of the major challenges for MBRs, hindering its extended application world-wide (Meng et al., 2009; Guo et al., 2012; Gao et al., 2013). Several studies have been recently performed in order to evaluate how the presence of oil (or hydrocarbon) influences the MBR performance especially in terms of membrane fouling (Zhu et al., 2014; Padaki et al., 2015). However, these studies are mainly focused on membrane material (such as hydrophobic surfaces versus hydrophilic, etc…). As far as authors are aware no studies have still been performed to evaluate the modification of the biologic consortium induced by the oil presence and the relative consequence on the MBR system (in terms of both membrane fouling and biological performance).

Therefore, bearing in mind these considerations the main aim of the present work is the investigation of a MBR system treating wastewater contaminated by petroleum hydrocarbons, in terms of removal efficiency, biomass respiratory activity and membrane fouling.

Materials and methods

An MBR bench scale system was realized at the Laboratory of Sanitary and Environmental Engineering of Palermo University. The MBR plant was fed with synthetic oily wastewater and equipped with an ultrafiltration (UF) hollow fibre membrane module (ZeeWeed™01, with specific area equal to 0.093 m^2 and nominal porosity of 0.04 μm) in a submerged configuration. The membrane flux was kept near 15 L m^{-2} h^{-1}. The membrane was periodically backwashed (every 4 min for a period of 1 min) by pumping a fraction of permeate back through the membrane module. Filtration was stopped almost every 15-20 days, 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 (2012). A schematic layout of the MBR plant is reported in Figure 2.1.

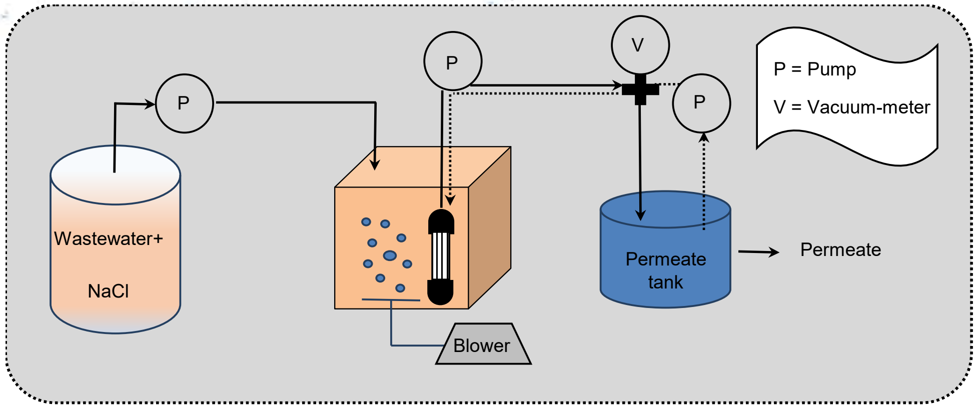

Figure 2.1 Pilot plant schematic layout

The whole experimental campaign had a duration of more than 200 days and MBR was operated under aerobic conditions throughout experiments. The pilot plant was started up with sludge inoculum, withdrawn from Palermo Municipal wastewater treatment plant (WWTP), to obtain an initial Mixed Liquor Suspended Solids (MLSS) concentration of 4 g L^{-1}. During plant operation the influent wastewater, the mixed liquor and the membrane permeate have been sampled every 3 days and analysed for total and volatile suspended solid (TSS and VSS) concentrations, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), aromatic hydrocarbons and total petroleum hydrocarbons (TPH), ammonium nitrogen (NH_4-N), nitrite nitrogen (NO_2-N), nitrate nitrogen (NO_3-N) and total nitrogen (TN). It is worth noting that samples collected from the mixed liquor, excepting TSS and VSS, have been analyzed on the supernatant of mixed liquor filtered at 0.45 μm. In this way it was possible to differentiate the "biological" removal efficiency (evaluated upstream the membrane module) from the "total" removal efficiency (downstream the membrane module), referring in particular to COD and ammonium nitrogen. The main synthetic oily wastewater characteristics as well as the main operational conditions are reported in Table 2.1.

Parameter	Units	Value
COD	[mg L^{-1}]	500
TPH	[ppm]	20
NH_4-N	[mg L^{-1}]	20
Conductivity	[mS cm^{-1}]	1.6
Permeate Flux	[L m^{-2} h^{-1}]	13
Flow rate	[L h^{-1}]	0.8
HRT	[h]	27

Table 2.1 Main characteristics of the feeding wastewater (on average) and operational conditions.

The synthetic oily wastewater was prepared with the aim to simulate a shipboard slops pre-treated by means of a de-oiling and coagulation/flocculation processes. Therefore, it contained residual metals (in the form of: P_bSO_4, C_uSO_4, M_nSO_4, Z_nSO_4, M_gCl_2), diesel fuel, surfactant (as sodium dodecylbenzenesulfonate), organic substrate (acetate) and nutrients (as NH_4Cl, KH_2PO_4). In order to prevent hydrocarbon volatilization, the synthetic oily wastewater was stored inside a mixed and covered feeding tank. Respirometric batch tests were carried out by means of a "flowing gas/static-liquid" type batch respirometer for the evaluation of biomass biokinetic parameters. The biomass samples were taken from the bioreactor of MBR plant and diluted with permeate in order to obtain a MLSS concentration in the range of 2 – 3 g TSS L^{-1}. Before running the respirometric test, each sample was aerated until endogenous conditions were reached, on the basis of the observed oxygen uptake rate (OUR) values. The samples were maintained at a constant temperature of 20 ± 1 °C with a thermostatic cryostat. The aeration intervals were set from 3 to 5 mgO_2 L^{-1}. For further details on the adopted procedure and experimental apparatus, the reader is referred to literature (Di Trapani et al., 2014, 2015).

The fouling analysis was carried out by measuring the total resistance to filtration (R_T) according to the following expression 1:

$$R_T = \frac{TMP}{\mu \cdot J} \quad [1]$$

where R_T is the total fouling resistance (10^{12} m^{-1}) calculated by the general form of Darcy's Law, TMP is the transmembrane pressure (Pa), μ the permeate viscosity (Pa s), and J the permeation flux (m s^{-1}).

With the aim to investigate the specific deposition mechanisms, it was employed the resistance-in-series (RIS) model based on cake layer removal with the "extraordinary physical cleaning" strategy (*among others* Meng et al., 2005; Meng and Yang, 2007; Zhiwei et al., 2009). Specifically, the RIS model allowed the total resistance to filtration (R_T) decomposition according to the following expression 2:

$$R_T = R_m + R_{Pb} + R_{C,irr} + R_{PC,rev} \quad [2]$$

where: R_m represents the intrinsic membrane resistance; R_{PB} is the irreversible resistance due to particles deposition into the membrane pore; $R_{C,irr}$ is the fouling resistance related to irreversible superficial cake deposition (removable with extraordinary physical cleaning); $R_{C,rev}$ is the fouling resistance related to superficial cake deposition that can be removed by ordinary backwashing.

The Extracellular Polymeric Substances (EPSs) were also measure during the whole experimental campaign; the microbial products (SMPs) were obtained by centrifugation at 5000 rpm for 5 min, whereas the bound EPS (EPS_{Bound}) content was extracted by means of the thermal extraction method (among others Zhang et al., 1999; Cosenza et al., 2013). The EPS_{Bound} and the SMP were analysed for proteins by using the Folin method with bovine serum albumin as the standard (Lowry et al., 1951), whilst the carbohydrates according to DuBois et al. (1956), which yields results as glucose equivalent.

Results

3.1 Suspended biomass growth

As aforementioned, the MBR plant was started-up with sludge inoculum, at a MLSS concentration of 4 g TSS L^{-1}. The suspended biomass trend as well as the VSS/TSS ratio are reported in Figure 3.1. From the observation of Figure 3.1, it is worth noting that until experimental day 54 a decrease of suspended biomass was observed. Such a result could be likely related to the stress effect exerted by the hydrocarbons on the biomass that was not fully acclimated to this substrate (not easily biodegradable). Therefore, in order to sustain the biomass activity toward a recalcitrant organic substrate, from experimental day 54 it was decided to add a small amount of sodium acetate in the influent wastewater.

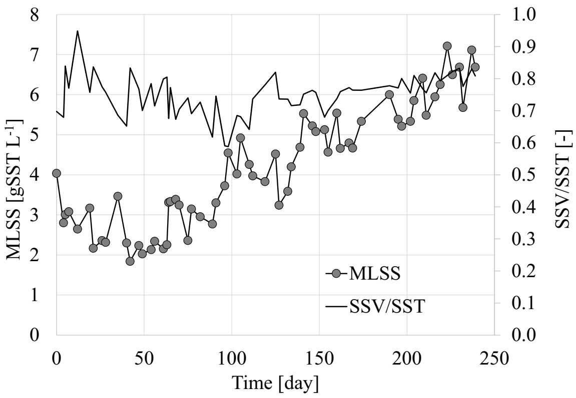

Figure 3.1 Suspended biomass trend and VSS/TSS ratio during the experiments

The suspended biomass of the MBR plant constantly increased up to 7 gTSS L^{-1}, thus suggesting a good acclimation level and development of biomass activity. Indeed, the VSS/TSS ratio reached a stable value at the end of experiments, almost equal to 0.8, thus underlining a good condition of the suspended biomass.

3.2 Organic carbon and hydrocarbons removal

In Figure 3.2 the "total" and "biological" performance, together with the membrane contribution are reported. The experimental results highlighted that the MBR system provided good COD removal efficiencies throughout experiments, especially in the last experimental days. Indeed, the total COD removal (average value) was close to 88%, confirming the robustness of MBR systems for the treatment of recalcitrant wastewater. Moreover, the biological contribution was also high, with an average value close to 70%, highlighting a good development of biomass activity, even in presence of hydrocarbons. Therefore, the membrane contribution was not decisive for the achievement of such high removal efficiencies, but represented a decisive protection in case of failures of the biological process, as experimental day 97.

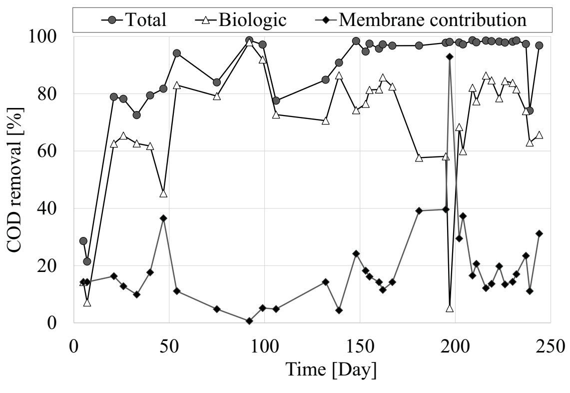

Figure 3.2 COD removal efficiency throughout experiments

Referring to hydrocarbon removal, Figure 3.3 shows the aromatic hydrocarbons removal efficiency throughout experiments. By analysing Figure 3.3, it is possible to observe a quite high removal efficiency until day 127 92% on average). Nevertheless, by experimental day 147 it was noticed a huge decrease of removal efficiency.

This result can be related to a twofold reason: on one hand, a worsening of biomass flocculation properties while, on the other hand, mixing problems were experienced in the wastewater storage tank, with a decrease of the inlet concentrations (providing, as a consequence, a decrease of system removal efficiencies).

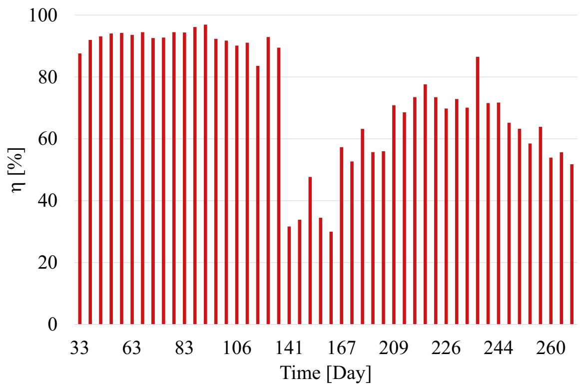

Figure 3.3 Aromatic hydrocarbons removal efficiency

Moreover, in the last portion of experiments TPH were also measured at the inlet and outlet of the MBR plant. Concerning the observed removal efficiency, the MBR system showed high performance, with an average value higher than 85%. Nevertheless, around experimental days 237 and 239 it was observed a significant decrease of removal efficiency, down to 47% at day 239. This result could be due to mixing problems in the wastewater storage tank. However, the overall performance of the MBR system towards TPH removal was satisfactory, thus suggesting the potential application of this configuration for the treatment of wastewater contaminated by hydrocarbons. In Figure 3.4 the TPH removal efficiencies obtained during experiments are shown.

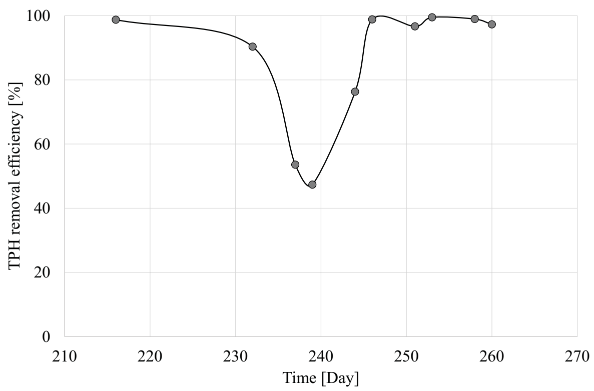

Figure 3.4 TPH removal efficiency pattern during experiments

3.3 Nitrification efficiency

Referring to nitrification, the average value of ammonium removal was close to 70% (Figure 3.5), highlighting a satisfactory activity of nitrifying species, also confirmed by respirometric batch tests, as better outlined in the following section. The removal efficiency showed slight fluctuations, mainly due to the reduction of the inlet NH_4-N concentrations, related to a drawback within the wastewater storage tank. Moreover, the observed results highlighted the absence of nitrite accumulation, suggesting the occurrence of a complete nitrification process throughout experiments, with nitrate concentrations at the outlet generally consistent with the inlet ammonium (Figure 3.5).

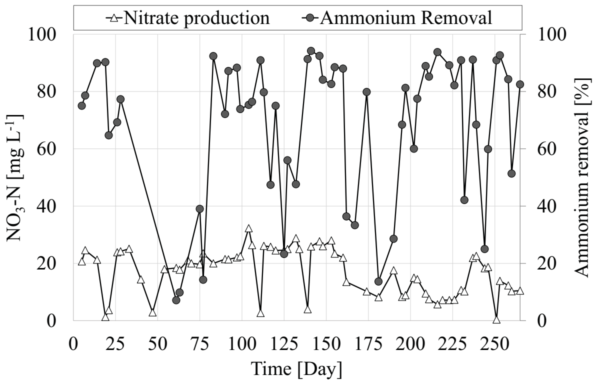

Figure 3.5 Nitrate production and ammonium removal efficiency throughout experiments

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 the MBR plant. The obtained kinetic and stoichiometric parameters are consistent with previous results reported in the technical literature for MBR systems, also considering the presence of hydrocarbons as organic substrate source. Table 3.1 summarizes the biokinetic and stoichiometric parameters obtained during experiments.

The obtained results highlighted a good level of biomass activity, in terms of both heterotrophic and autotrophic species. Figure 3.6 reports the specific OUR (SOUR) values for heterotrophs (Figure 3.6a) as well as the nitrification rates (Figure 3.6b) for nitrifying bacteria during experiments.

Heterotrophic Day	Y_H mg VSS mg COD^{-1}	$\mu_{H.max}$ d^{-1}	K_S mgCOD L^{-1}	OUR_{max} mgO_2 $L^{-1}h^{-1}$	SOUR mgO_2 $gVSS^{-1}h^{-1}$
84	0.61	1.18	5.00	11.97	5.99
107	0.63	1.16	4.50	18.65	7.77
119	0.69	2.36	7.82	18.65	7.77
133	0.66	2.03	3.18	12.65	6.01
161	0.61	1.21	0.78	13.58	5.60
181	0.72	2.12	27.96	13.87	5.81
210	0.58	2.96	30.05	21.08	8.81
238	0.59	2.52	5.00	28.43	11.54
280	0.70	2.13	13.64	15.93	6.19
Autotrophic Day	**Y_A mg VSS mg N^{-1}**	**$\mu_{A.max}$ d^{-1}**	**K_N mgN L^{-1}**	**OUR_{max} mgO_2 $L^{-1}h^{-1}$**	**Nitrification rate mgN L^{-1} h^{-1}**
84	0.19	0.22	0.01	9.86	1.94
107	0.18	0.26	0.10	12.31	2.33
119	0.12	0.21	0.35	17.32	3.24
133	0.42	0.43	0.10	17.74	3.39
161	0.17	0.27	0.13	16.66	2.83
181	0.19	0.24	0.28	12.86	2.02
210	0.16	0.15	0.22	11.42	1.65
238	0.21	0.16	0.10	16.26	2.37
280	0.12	0.10	0.11	9.14	1.56

Table 3.1 Summary of respirometric batch test for the evaluation of kinetic and stoichiometric parameters

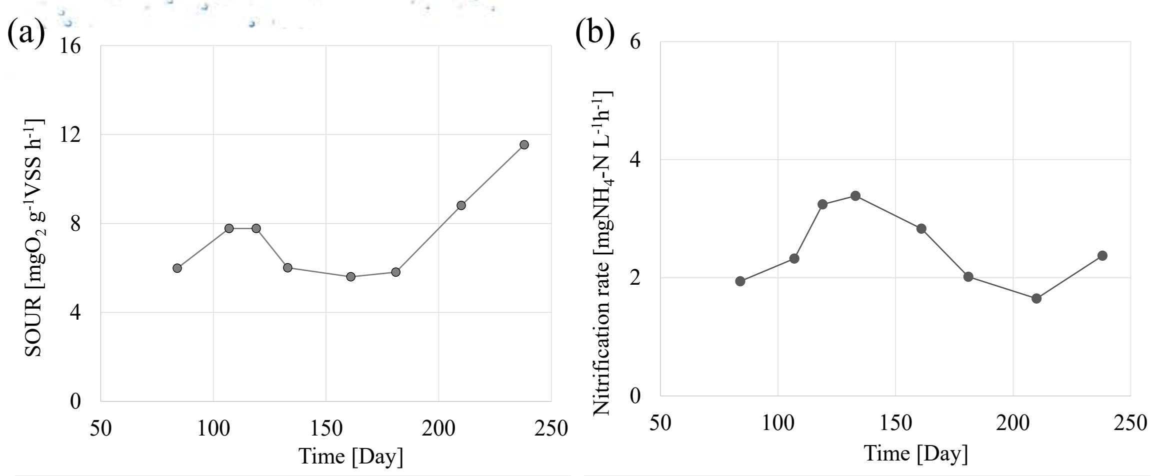

Figure 3.6 SOUR (a) values for heterotrophic species and nitrification rates (b) for autotrophic species

3.5 EPS production

Figure 3.7 reports the EPS_{Bound} (Figure 3.7a) and the SMP (Figure 3.7b) concentrations during the overall experimental campaign. Referring to EPS_{Bound}; it was noticed a slight decrease in the system until experimental day 54. This result could be related to a sort of inhibitory stress exerted by hydrocarbons, with a reduced metabolic activity, thus preventing the production of polymeric substances. Nevertheless, after sodium acetate was added in the influent as rapidly biodegradable substrate, a significant increase of EPS_{Bound} concentrations was observed in the MBR plant, mainly as proteins contribution.

Conversely, the SMP production and release in the bulk liquid was almost negligible throughout experiments.

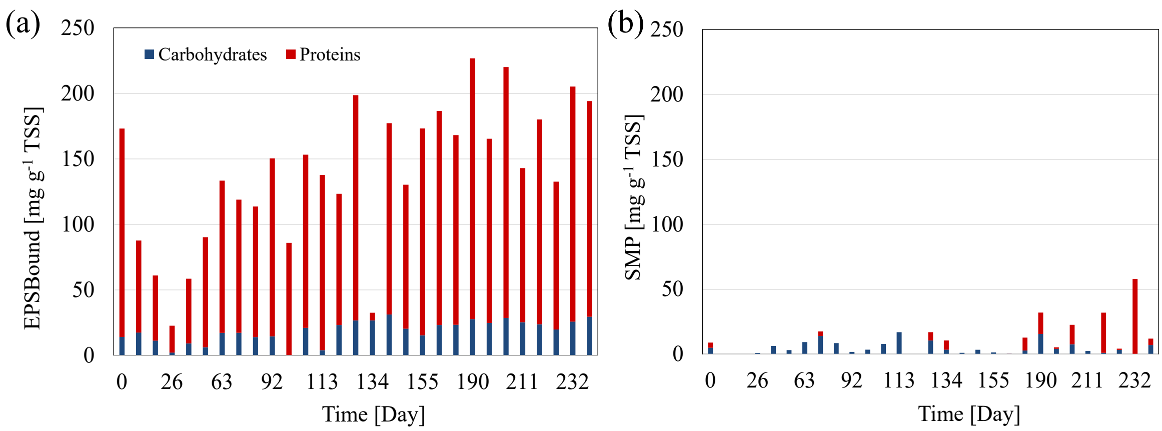

Figure 3.7 EPS_{Bound} (a) and SMP (b) values during experiments.

3.6 Membrane fouling analysis

In Figure 3.8 the results related to the fouling monitoring are reported. In particular, Figure 3.8a shows the total resistance over time, whereas Figure 3.8b reports the resistances related to specific fouling mechanisms, obtained from the application of the RIS model.

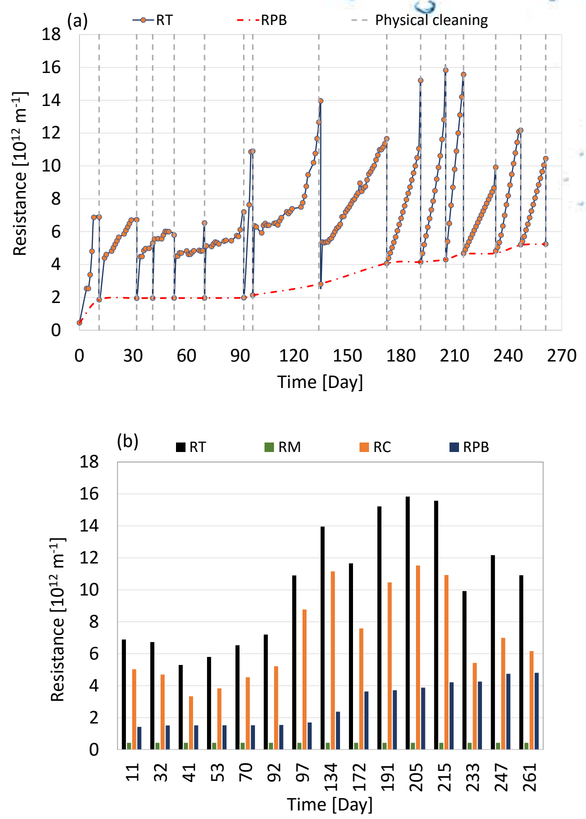

Figure 3.8 Trend of the total resistance (a); results related to the RIS model application

By analysing Figure 3.8a one can observe that the total resistance ranged between 0.45 10^{12} m^{-1} to 15.9 10^{12} m^{-1}. It was observed an increase of R_T until experimental day 215. Conversely, in the last 30 days a decrease of the total resistance was observed. This result is likely due to the fact that oil fouling on the membrane surface has become less stable and started to be effectively removed by the shearing force from the high cross-flow fluid (Zhu et al., 2014). Furthermore, a progressive pore fouling occurred as shown by the red line in Figure 3.8a. During pilot plant operation, in order to limit the R_T value (thus avoiding the critical flux achievement as suggested by the membrane manufacturer) 15 physical cleaning were carried out (Figure 3.8a, Figure 3.8b). As reported in Figure 3.8b the application of the RIS model showed that the main fouling mechanism was due to cake deposition, that is removable with cleaning operations (either physical or chemical). Indeed, the major compound of R_T is represented by the resistance due to the cake layer. However, a gradual transfer of foulants from the membrane surface (cake layer deposition) directly to the pores (pore blocking) was observed, with an increase of the resistance due to pore blocking (partially removable with chemical cleanings only).

Conclusions

The plant provided good performance both in terms of COD removal and nitrification, thus showing a sort of biomass adaptation to hydrocarbons. Such a result has been also confirmed by the biomass respirometric tests, that highlighted a good development of biomass respiratory activity.

Membrane fouling analysis showed a reduction of the total resistance during the last period; this result was most likely due to the hydrocarbon which caused an irreversible fouling due to the oil deposition on membrane surface.

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