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Membrane Bioreactor for treating petroleum refinery effluent: treatment performance, membrane fouling mechanism and fouling control

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Biorreator com membrana tratando efluente de refinaria de petróleo: performance do tratamento, mecanismos de incrustação da membrana e controle de incrustação

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ABSTRACT

The work developed discusses the potential use of MBR to treat refinery effluent and operational strategies that may mitigate fouling. At first, MBR performance was evaluated in terms of pollutants removal and fouling investigation in conditions of shock load. The results demonstrated that MBR was able to reduce effectively the pollutants, meeting guideline standards of disposal and reuse for non-potable ends. FTIR results showed that organic matter was removed by biological oxidation and/or retained by adsorption in the biological sludge or retention in the UF membrane. Furthermore, SMP was produced during treatment. In terms of membrane permeability, the results showed that the soluble fraction of mixed liquor contributed significantly to membrane fouling due to the presence of SMP fraction. Secondly, the sludge filterability was studied as an important parameter to evaluate sludge properties and the potentiality of membrane fouling in MBR. Three filterability assessment methods described in the literature were compared regarding their capability to sense sludge quality variation and reproducibility treating petroleum refinery effluents. This study showed that, among the methods evaluated, *Time To Filter* was the most effective to assess the filterability both in terms of its capability to detect sludge quality variation and reproducibility. The results have also shown that filterability is directly related to membrane fouling potential, and can be used as a tool to monitor and control fouling process in MBR. Significant filterability correlations among colloidal TOC, EPS and floc size were found. The third study assessed the long-term use of cationic polyelectrolyte to improve the sludge filterability, as well as membrane fouling control in bioreactor membrane while treating refinery effluents. Corrective and preventive cationic polyelectrolyte dosages have been added to the MBR in order to evaluate the membrane fouling mitigation in both strategies. The results have confirmed that the use of this product increased sludge filterability, and reduced membrane fouling. During monitoring time stress events occurred due to increase in oil and grease and phenol concentrations in the MBR feed. The preventive use of cationic polyelectrolyte allowed a more effective and stable sludge filterability with lower consumption without decreasing MBR pollutant removal overall performance.

RESUMO

O trabalho desenvolvido aborda o uso do BRM tratando efluente de petróleo e estratégias operacionais que possam minimizar a incrustação. Primeiramente, avaliou-se o desempenho do BRM em termos de remoção de poluentes e investigou-se o comportamento da incrustação em ocorrências de cargas de choque. Os resultados demonstraram que o BRM foi capaz de reduzir efetivamente os poluentes, alcançando padrões de descarte e reuso. Os resultados de IV mostraram que a matéria orgânica é removida por oxidação biológica e/ou retenção por adsorção no lodo biológico ou retenção pela membrana. Além disso, verificou-se que o SMP é produzido durante o tratamento. Em relação à permeabilidade da membrana, verificou-se que a fração solúvel do lodo biológico contribui significativamente para a incrustação da membrana devido a presença de SMP. No segundo estudo a filtrabilidade do lodo foi estudada como um importante parâmetro para a avaliação das propriedades do lodo e o potencial de incrustação da membrana em BRM. Foram comparados três métodos de determinação da filtrabilidade relatados na literatura em termos de capacidade de detecção de variações da qualidade do lodo e da reprodutibilidade, avaliando a aplicação deste parâmetro como ferramenta para o monitoramento e controle de incrustação de BRM. O estudo mostrou que o método *Time To Filter* foi o mais eficiente para medição da filtrabilidade, tanto em termos de capacidade de detecção de variação da qualidade do lodo, como em reprodutibilidade. Verificou-se também que a filtrabilidade está diretamente relacionada ao potencial de incrustação na membrana. Encontraram-se correlações significativas da filtrabilidade com os parâmetros COT coloidal, EPS e tamanho de floco. No terceiro estudo, avaliou-se a utilização de um polieletrólito catiônico a fim de melhorar a filtrabilidade do lodo e consequentemente controlar a incrustação da membrana. Dosagens corretiva e preventiva do polieletrólito foram realizadas nos BRM a fim de avaliar o melhor controle da incrustação nas duas estratégias. Os resultados confirmaram que o uso do produto aumenta a filtrabilidade do lodo e reduz a incrustação da membrana. Durante o período de monitoramento ocorreram choques de carga com altas concentrações de óleos e graxas e fenol na alimentacão. O uso preventivo do polieletrólito catiônico permitiu uma filtrabilidade mais efetiva e estável sem prejudicar o desempenho do BRM quanto à remoção de poluentes.

SUMMARY

LIST OF PUBLICATIONS

CONGRESS PUBLICATIONS:

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LIST OF SYMBOLS AND ABREVIATIONS

µ	Dynamic viscosity
BP	By products
BR	Biological removal
BS	Biological Sludge
COD	Chemical Oxygen Demand
CST	Capilarity Suction Time
DFCm	Delft Filtration Characterization Method
EC50	Median Effective Concentration
EC50 30 min	Median Effective Concentration in 30 minutes
EPS	Extracellular Polymeric Substances
EPSc	EPS concentration in terms of polysaccharide
EPSp	EPS concentration in terms of protein
FT	Filter test
FTIR	Fourier transform infrared spetroscopy
HTR	Hidraulic Retention Time
MBR	Membrane Bioreactor
MCE	Mixed cellulose ester
MFI	Modified Fouling Index
ML	Mixed Liquor
MLSS	Mixed Liquor Suspended Solids
MLSSV	Mixed liquor volatile suspended solids
MPE	Membrane performance enhancer
MR	Membrane retention
NH_3–N	Ammoniacal nitrogen
NR	Not removed
NTU	Nephelometric turbidity units
O&G	Oil and Greases
P	Permeate
PVDF	Polyvinylidene Difluoride
R	Spearman correlation coefficient
RE	Refinery effluent

REGAP	Refinery Gabriel Passos
S	supernatant of mixed liquor
s	Standard Deviation
SA	Sludge adsorption
SFI	Sludge Filtration Index
SMP	Soluble Microbial Products
SMPc	SMP concentration in terms of polysaccharide
SMPp	SMP concentration in terms of protein
SS	Suspended Solids
t	Filtration Time
TDS	Total Dissolved Solids
TMP	Transmembrane Pressure
TOC	Total Organic Carbon
TTF	Time to Filter
UF	Ultrafiltration
V	Permeate Volume
VC	variation coefficient
$\bar{x}$	Median Value
α	specific resistance
φ	Diameter

1. INTRODUCTION

1.1 Contextualization and problem

The petroleum refining industry transforms crude oil in more than 2500 products, including liquefied gas, gasoline, kerosene, jet fuel, diesel fuel, lubricants, amongst others. A great demand for water is required in the processes, especially for distillation, desalination and cooling systems (YAVUZ *et al.,* 2010).

The estimated water consumption per barrel of oil to be processed is 246-341 L, which generates an effluent of approximately 0.4-1.6 times this value (ALVA-ARGAEZ *et al*., 2007). The amount of liquid effluent generated by this industrial typology and its features depends on the settings of each process. In general, the refinery wastewater contains COD levels of about 300-600 mg / L, phenol grade from 20-200 mg / L, benzene levels from 1-100 mg / L, besides of heavy metal levels like chromium, from 0.1 to 100 mg / L, lead from 0.2-10 mg / L, and other pollutants such as oils, greases and ammonia at high concentration (WBG, 1999). Due to these pollutants, the effluent is considered a major source of contamination of the aquatic environment (WAKE, 2005).

Conventional treatment of petroleum refinery effluent is often accomplished through a combination of methods to remove the oily portion and the contaminants before the disposal. A standard water treatment system can include a sour water separator, a gravity oil-water separator, a floater, some biological treatment and a clarifier (WBG, 1999). A generic sequence for the effluent treatment and the objectives of each phase are shown in Figure 1.

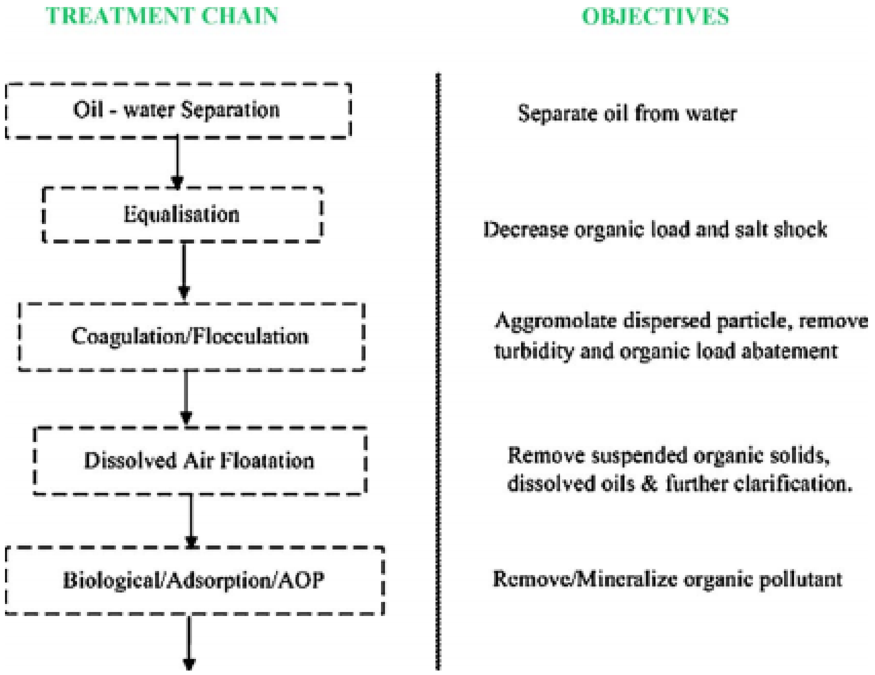

Figure 1 -Schematic diagram of generic sequence for treating petroleum refinery effluent. (Source: Diya'uddeen *et al.*, 2011)

However, the increased cost in water collection and treatment, the effluent discharge and, in some cases, the low availability of water, combined with the imposition of environmental laws increasingly restrictive as well as the industry pressure for sustainable development, have driven oil refineries to deploy wastewater reuse systems.

Several solutions have been suggested to optimize the effluent treatment process. Some studies presents methods that include chemical precipitation (HOSSEINI *et al.*, 2003; ALTAŞ and BÜYÜKGÜNGÖR, 2009), eleltrocoagulation (YAVUZ *et al.*, 2010, YAN *et al.*, 2011), fenton oxidation (HASSAN *et al.*, 2012), photocatalytic oxidation (KHAN *et al.*, 2014, SHAHREZAEI *et al.*, 2012), adsorption (EL-NAAS *et al.*, 2010), membranes (TAKHT RAVANCHI *et al.*, 2009; MADAENI e ESLAMIFARD, 2010; SALEHI *et al.*, 2014; WANG *et al.*, 2014), membrane bioreactor (BAYAT et al., 2014; VIERO et al., 2008; QIN et al., 2007; RAHMAN and AL-MALACK, 2006) amongst others.

Membranes bioreactors (MBR) is a technology which combines biological degradation process by activated sludge and a solid-liquid separation promoted by membrane filtration (LE-CLECH *et al.*, 2006). This technology has been widely used in the treatment of industrial wastewater for removal of organic matter and nutrients due to their increased pollutant removal efficiency compared to conventional processes. High mixed liquor suspended solids (MLSS) concentration in this technology has made it a suitable choice for the treatment of highly toxic wastewater such as petrochemical wastewater (BAYAT *et al.*, 2014).

Some advantages of MBR are: high efficiency removal of micro-pollutants and persistent organic pollutants, low sensitivity to load variation, low sludge production, high sludge age, total removal of suspended solids, among others (JUDD, 2006). However, the possibility of fouling that reduces flow through the membrane has been limiting the use of this process, especially when treating industrial effluents, which, due to the high load variations tends to amplify this problem.

The membrane fouling is caused by the adsorption of solute molecules on the membrane surface, pore clogging obstruction by suspended particulate material and the deposit of suspended material on the surface of the membrane forming a cake (JUDD, 2006). This process is influenced by a number of factors related to feeding, membrane operating conditions, and is determined by the membrane tendency in being encrusted by components of the liquid accumulated in the external and internal membrane structures (LE-CLECH *et al.*, 2006). The membranes fouling affects directly the permeate flow and the pressure differential in the system resulting in greater energy requirements, higher frequency of the membrane cleaning, shorter life of the membrane and, consequently, greater operating costs. Therefore, monitoring and fouling control are essential for the technical and economic use of MBR in treating effluents.

In this context, the present work addresses operational strategies that can minimize fouling in the use of MBR technology treating petroleum refinery effluent, evaluating the performance and quality characteristics of the biological sludge used, checking tools to control fouling process and enabling therefore the knowledge of instruments that will allow greater control of the membrane fouling process. This fact will enable a more conscious use of technology resulting in lower energy requirements, lowering the frequency of membrane cleaning, longer membrane lifetime and, consequently, lower operating costs.

1.2 Objectives

1.2.1 General Objective

The general objective of this study was to evaluate the MBR performance in terms of pollutants removal, fouling investigation and control in the petroleum refinery effluent.

1.2.2 Especific Objectives

- Evaluate MBR performance at long term monitoring in terms of nutrients and organic matter removal treating petroleum refinery effluent.
- Investigate pollutants removal/retention mechanisms in MBR;
- Investigate membrane fouling mechanisms;
- Evaluate the sludge filterability test as a parameter to monitoring membrane fouling;
- Select the filterability method with higher reproducibility for MBR treating Petroleum refinery effluent;
- Investigate the influence of sludge quality in MBR sludge filterability;
- Evaluate the use of a permeability improving agent as a tool fouling control;
- Evaluate the effect of permeability enhancer dosage in the MBR performance in the removal of organic matter and nutrients;

The first three specific objectives are related to the dissertation´s second chapter. The following three are linked to the third chapter. The two last objectives are mainly associated to the fourth chapter.

1.3 Structural form

Besides this introduction (Chapter 1), the final considerations (Chapter 5) and recommendations (Chapter 6), this dissertation is structured in three chapters in an article format. The choice of an article format indicates that the chapters are interdependent but can also be read separately.

In Chapter 2 the performance of submerged membrane bioreactor (MBR) was evaluated in terms of nutrients and organic matter removal and fouling investigation in conditions of shock load. To get a better insight into the mechanism of pollutants removal and the causes of membrane fouling in the MBR, detailed physicochemical characteristics of effluent, mixed liquor and permeate and morphological and filtration characteristics of mixed liquor were also studied.

Chapter 3 discusses the filterability parameter of biological sludge in MBR, showing that the measurement of this parameter is an important tool for assessing the quality of biological sludge and the potential of fouling formation in MBR. It is also discussed the lack of standardization of its determination method making it difficult to understand its interference with the MBR performance and also the comparison of results. Thus, this first article aims to compare three filtration methods measurement reported in the literature (*Time to Filter, Filter Test* e *Sludge Filtration Index*) in terms of detection capability of the sludge quality variations and its reproducibility, evaluating the implementation of this parameter as a tool for monitoring and controlling the fouling in the MBR treating oil refinery effluent and investigating the influence of sludge quality in the filterability of the same for MBR.

In Chapter 4 is discussed the long-term use of cationic polyelectrolyte to improve the sludge filterability, and as well to control membrane fouling in membrane bioreactor while treating refinery effluents. Different dosages of strategic were also evaluated concern- the MBR without cationic polyelectrolyte addition performance in terms of sludge quality and performance in the removal of organic matter and nutrients.

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2. POTENTIAL USE OF SUBMERGED MEMBRANE BIOREACTOR TO TREAT REFINERY EFFLUENT: COMPREHENSION OF MBR DYNAMIC TO REMOVE ORGANIC MATTER AND FOULING CHARACTERISTICS

2.1 Introduction

Petroleum refinery effluent combine effluents from different typical refinery plants such as cracking, reforming, topping and lube manufacturing processes. Such processes require high water volumes, and therefore they account for high effluent outflow. Usually, 246 to 340 liters of water are required to process a crude oil barrel, which corresponds to a production of average effluent volume ranging from 0.4 to 1.6 times the amount of the oil processed (Alva-Argáez *et al.*, 2007). Additionally, such effluents contain a great variety of organic and inorganic pollutants, including sulfides, ammonia, cyanides, aliphatic hydrocarbons (up to C_{12}), and polyaromatic hydrocarbons such as ethylbenzene, toluene, benzene and 1-methylethyl benzene and phenolic compounds that, when released into the environment can result in serious environmental consequences (Wake, 2005).

A typical refinery effluent treatment plant comprises a primary treatment by which a combination between physical and physicochemical processes are performed to remove free oil (floating oil), suspended solids and colloidal substances, followed by a secondary treatment to remove effluent contaminants and to acceptable levels for its discharge into water streams (Diya'uddeen *et al.*, 2011).

The most extensively used processes for refinery effluent secondary treatment are biological processes, specially the activated sludge conventional process that allow the production of an effluent that usually meets the law standards. However, the increase of water catchment and treatment and effluents discharge costs and, in some cases even the scarcity of water supply, and moreover stricter protective environmental laws and pressure of the sector for environmentally-friendly development have compelled petroleum refineries to implement reuse effluent treatment systems.

In such background, the membrane bioreactors (MBR) technology that consists in combining biologic processes with membrane separation processes has arisen as a good alternative to petroleum refinery effluent treatment for being capable to produce high quality effluent that suited to be reused in refining processes (Fallah *et al.*, 2010).

Rahman and Al-Malack (2006) studied the use of crossflow membrane bioreactor to treat petroleum refinery effluent. In their study, the authors assessed the performance of the technology using two different concentrations of MLSS (Mixed Liquor Suspended Solids), that is, 5000 and 3000 mg/L. The results showed that, independently on MLSS concentrations, the effectiveness of COD removal was over 93%.

Qin *et al.* (2007) investigated the feasibility of using submerged membrane bioreactors by evaluating refinery effluent treatment performance, and as well the possibility of reusing the water produced during the process. COD concentration dropped down from 700-1200 mg/L at feeding to 50 mg/L in the product, while the ammonia concentration dropped down from 56-132 mg/L to 0.10-0.95 mg/L, and from 14-20 mg/L to a 1 – 4 mg/L of oil and grease content in the product. To discharge the treated product, all parameters were within specified standard ranges. About reusing the water in the process, specifically in the cooling towers, all requirements have been met, except the total dissolved solid contents that, due to the high sodium and sulfate concentrations, have not met the requirements of such application, and then it was required to segregate streams containing high TDS concentrations.

Viero *et al.* (2008) also analyzed the use of submerged membrane bioreactors to treat petroleum refinery effluents, specifically in oily streams containing high phenol concentrations. Compared to a conventional biological system, the use of a MBR improved the COD and TOC removing efficiency by 17% and 20%, respectively. Besides it, and in spite of the biodegradation difficulties placed by the high oil and grease and phenol concentrations, the treatment by MBR has proved to be highly efficient to remove phenol and organic contents.

Nevertheless, the fouling formation over the membrane, which decreases its cross-flow velocity or increases the membrane cross-flow pressure, makes membrane cleaning procedures and replacement more frequent, besides raising power consumption and operational cost (Lin *et al.*, 2013), has been restraining the use of this process, specially to treat refinery effluents that, due to their high load variations, are prone to aggravate this inconvenience.

Fouling formation on the membranes is caused by the adsorption of solute molecules over their surfaces, obstruction of pores by suspended particles and deposition of suspended substances over membrane surface that forms a sludge cake (Judd, 2006). This process is influenced by many factors related to feeding, the membrane and operational conditions, and it's determined by the membrane tendency to be fouled by the contents of the liquid that accumulates on the inner and outer membrane structures (Le-Clech *et al.*, 2006).

Many studies have striven to correlate permeability declination caused by fouling formation to sludge properties. Chang *et al.* (2002), Judd (2006) and Drews (2010), for example, presented a review of the parameters associated with the sludge properties, that's to say, floc size, volatile suspended solid concentration, EPS (Extracellular Polymeric Substances), SMP (Soluble Microbial Products), among others – and showed how they are related to MBR fouling formation likeliness. As discussed in these works, due to the biologic system complexity, the conclusions have been often controversial, so they can not be directly transferred to other systems.

Fouling process characterization may be accomplished by some essays such as, for example, characterization essays and quantification of the resistance to transport due to different fouling process types. The total resistance to filtration defined by Darcy's law, has usually been analyzed by using the resistance in-series model to describe the role of each fouling mechanism such as cake deposition, gel layer formation, pore blocking, free or bound EPS, adsorption or formation of condensation polarization layers (Diez *et al.*, 2014).

Another essay carried out to evaluate the fouling formation potential is the Modified Fouling Index (MFI). MFI can be used to predict the fouling potential of the feed in membrane systems, and assumes that the particulate fouling of membranes is dominated by cake filtration. MFI is determined by the gradient of the general cake filtration equation for constant pressure in a plot of t/V versus V (Javeed *et al.*, 2009).

Additionally, to monitor or check the likeliness of fouling formation on the membrane, other essays may be performed, as the assessing membrane permeability (Sabia *et al.*, 2014), sludge filterability (Rosemberger & Kraume, 2003, Alkmim *et al.*, 2014), and also by determining the concentration of compounds excreted by bacteria, i.e., Soluble Microbial Products (SMP) and Extracellular Polymeric Substances (EPS) that, according to some researchers, are the main responsible for membrane fouling formation in MBR systems (Pan *et al.*, 2010; Lee *et al.*, 2001).

The literature reports many studies on MBR use to treat industrial effluents, specially petroleum refinery effluent treatments. However, only few have been carried out in the long run of monitoring, and have taken into account the influence of the load variation and the composition of the effluent on the MBR performance to remove pollutants and the potentiality of fouling formation over the membranes.

Thus, this work aims to evaluate MBR performance in a pilot project to treat petroleum refinery effluent treatment, and has been primarily focused on the removing efficiency of organic substances and nutrients, and as well on analyzing fouling formation under load variation conditions and effluent composition. To have a clearer view of pollutant removing process, and membrane fouling formation causes in the MBR, detailed physicochemical characteristics of effluent, mixed liquor and permeate, and as well morphological and filtration characteristics of mixed liquor have also been studied.

2.2 Materials and methods

2.2.1 **Petroleum refinery effluent**

The effluent used in this study was from REGAP - Gabriel Passos Refinery Plant - located in the city of Betim, state of Minas Gerais, Brazil. It’s a Petrobras petroleum refinery that produces turpentine, asphalts, coke, sulfur, gasoline, LPG, diesel, and aviation kerosene. The effluent was transferred to the pilot plant after being pretreated by an oil-water separator, flotation in the first monitoring stage, from the 1st to the 237th day, and in the second stage, from the 238th to the 400th day, by an oil-water separator, flotation and sand filter

2.2.2 Experimental Apparatus and Operational Conditions

MBR pilot plants comprised a 90L biological tank connected in series to a 30L membrane tank in which PVDF hollow fiber modules with middle size pores up to 0.040 µm submersed with an 0.9 m2 area (Figure 2).

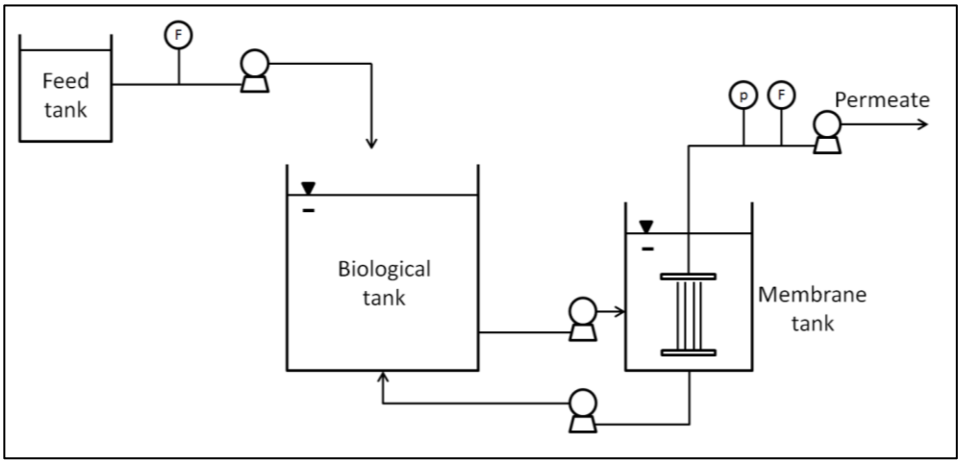


Figure 2 – MBR schematic drawing

The plant were operated and monitored for 400 days under the same operating conditions: hydraulic retention time of 8 hours, sludge retention time of 45 days, permeate flux of 16 $L.m^{-2}.h^{-1}$, backwash of 15 seconds and flux of 25 $L.h^{-1}$ every 600 seconds of filtration, biological tank aeration of 3.6 L/h and membrane tank aeration of 3.0 L/h. The sludge pH has kept constant nearly 7 with a dose of a 200 ppm sodium carbonate solution and phosphor demand supplied by a 1.5 $g.L^{-1}$ sodium triphosphate solution.

2.2.3 Effluent characterization and pollutant removal evaluation

The effluent from the refinery and the permeate from the MBR were characterized according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005) regarding the following physicochemical parameters: DQO (5220B), COT (5310B), alkalinity (2320B), ammonia (4500-NH3-B), phenol (5530D), color (2120B), turbidity (2130B), nitrite (4500-NO2-B), nitrate (4500-NO2-B), conductivity (2510 – B), chloride (4500-Cl -B), oils e greases (5520 D). The parameters of color, turbidity and TOC (Total Organic Carbon) have been analyzed by the following devices: Hach DR 3900 Spectrum Photometer, Hach 2100AN Turbidimeter, Shimadzu TOC-VCPH analyzer, respectively. The samples used to characterize the effluent were collected three times a week during the monitoring period.

The refinery effluent and MBR permeate were also characterized for acute toxicity by *Aliivibrio fischeri* bioluminescence bacterium using a Microtox® Model 500 Analyzer (SDI). The results were presented in EC50 – (Median Effective Concentration).

2.2.4 Investigation into the mechanisms of removal and retention of organic substances by FTIR (Fourier transform infrared spectroscopy)

To evaluate the MBR pollutant removing and retaining dynamic, 200mL samples of feeding and permeate, biologic sludge, and supernatant biologic sludge after sedimentation were dried out in a dehumidifying chamber at a temperature of 100°C for 24 hours. Dry solid samples were analyzed by a FTIR spectrometer (Shimadzu IR-prestigio-21 model Infrared device in ATR module). The samples were analyzed by direct exposure of the sample compressed by radiation in the ATR module in the range from 400 to 4.000 cm^{-1}, and resolution of 4.0. Readings were done based on percent transmittance.

2.2.5 Fouling formation evaluation

To monitor the fouling formation process, sludge samples were periodically collected and characterized regarding their filterability by Time to Filter (TTF) method (Thiemig, 2011) that, according to previous study, has proved to be the most reproducible method for this sort of effluent treatment (Alkmim *et al.*, 2014), concentration of EPS (Extracellular Polymeric Substances) and SMP (Soluble Microbial Products) determined by extraction thermal method introduced by Morgan *et al.* (1990) that was characterized with regard to the content of carbohydrate (Dubois *et al.*, 1956), proteins (Lowry *et al.*, 1951), and DQO, floc size (Laser Scattering Particle Size Distribution Analyzer HORIBA - LA-950V2) and colloidal TOC (Yang *et al.*, 2010).

The pressure and permeate flux data was daily collected. The filtering resistance caused by fouling formation was assessed based on the model proposed by Choo and Lee (1998).

MFI (Modified Fouling Index) measurements have also been performed to find out fouling characteristics. A batch cell (8400, Amicon, USA), with an ultrafiltration membrane (Nominal molecular weight limit 100 kDa, polyethersulfone, 31,7 cm^2, Amicon, USA), was used to measure the permeate volume under a constant pressure of 10 psi. Two samples were applied to fractionate the membrane foulants into soluble and suspended solids (SS) compounds. First, the mixed liquor (ML) of the MBR sludge containing the soluble and SS components was filtered. Second, for the soluble component, the supernatant of the mixed liquor centrifuged at 4500 rpm for 10 min, was filtered. Last, the SS component was calculated by subtraction of the soluble component from the ML. The MFI was calculated from the plot of t/V versus V using the filtration equation at constant pressure (Equation 1). The MFI is defined as the gradient of the linear relationship between t/V and V (Equation 2) (Dillon *et al.*, 2001).

$$\frac{t}{V} = \frac{\mu R_m}{\Delta P} + \frac{\mu \alpha C}{2\Delta P} V \qquad \text{Eq. 1}$$

$$MFI = \frac{\mu \alpha C}{2\Delta P} \qquad \text{Eq. 2}$$

where t is the filtration time (s), V is the permeate volume per unit filtration area (mL), μ is the dynamic viscosity of the permeate (Pa*s), Rm is the intrinsic membrane resistance (m−1), P is the applied transmembrane pressure (kPa), α is the specific resistance (m/kg), and C is macromolecular concentration in the bulk solution (mg/L).

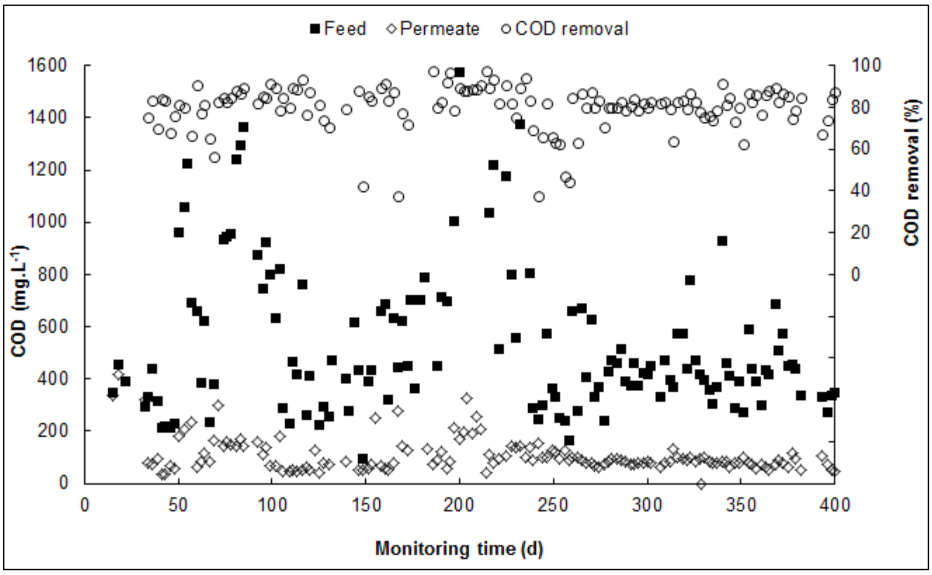
2.2.6 **Statistic Evaluation**

Kruskal Wallis' test was used to check for the existing significant differences between the evaluated parameters, followed by nonparametric multiple comparisons among groups. To find out the correlation between the evaluate parameters, Spearman's coefficient of correlation between variables was determined with further correlation significance analysis by hypothesis testing. STATISTICA 8.0 software was used for all statistical analyses.

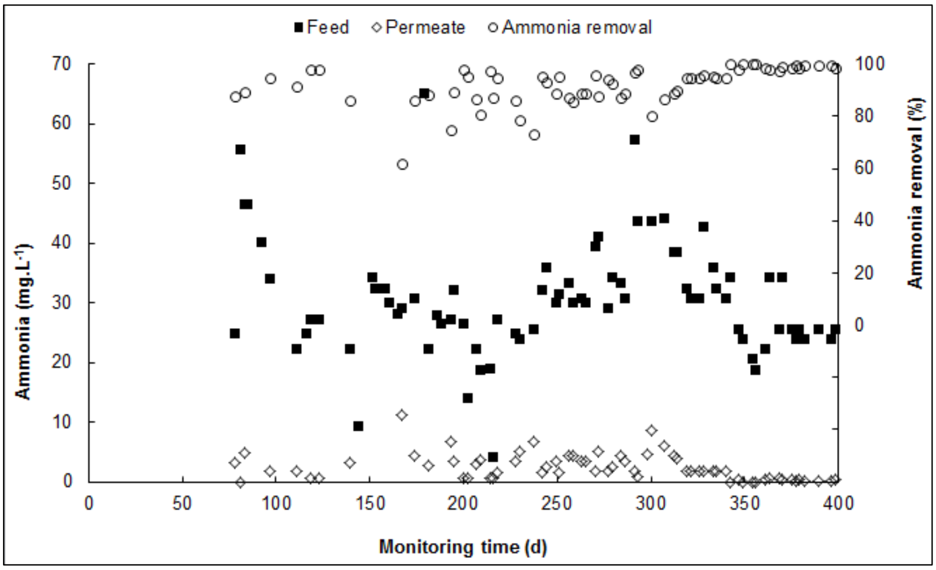
2.3 Results and discussion

2.3.1 **MBR pollutant removal efficiency**

Figure 3 shows the performance of MBR system with respect to the removal of COD and NH3–N during the two experimental stages. During the first stage (pre-treatment with only oil-water separator and flotation (from the 1st to 237th day), the refinery effluent COD concentration ranged between 213 and 2935 mg/L with an average value of 828 mg/L and standard deviation of 619 mg/L (Figure 3 (a)). The average value of the corresponding permeate COD was 126 mg/L and standard deviation of 81 mg/L which gives an average removal efficiency of 82 % and standard deviation of 11%. During the second stage (form 238th day 400th day), a considerable decrease in the refinery effluent COD concentration was observed with values ranging between 164 and 930 mg/L with an average value of 406 mg/L and standard deviation of 136 mg/L due to the improvements in the pre-treatment process. The average value of the corresponding permeate COD was 85 mg/L and standard deviation of 20 mg/L, which corresponds to an average removal efficiency of 87 % and standard deviation of 10%, which was greater than the removal efficiency attained in the first stage. The significant differences of MBR performance of COD removal in both stages was confirmed by statistical analyses based on Kruskal Wallis test method followed by nonparametric multiple comparisons among groups with p value < 0,05.



(a)



(b)

Figure 3 -Performance of the MBR for (a) COD removal and (b) NH3-N removal.

The variation in ammonia–nitrogen concentration in the refinery was notable during the monitoring time [Figure 3 (b)], although no significant differences were observed between stages 1 and 2 according to Kruskal Wallis followed by nonparametric multiple comparisons among groups (p-value < 0.05). Ammonia concentration in the refinery effluent varied between 14 and 65 mg/L with an average value of 31 mg/L and standard deviation of 10 mg/L. However, there is an increased ammonia removal during stage 2 relative to stage 1. The average value of the corresponding permeate ammonia in the first stage was 3.2 mg/L and standard deviation of 2,63 mg/L which corresponds to an average removal efficiency of 87 %; while in the second stage the corresponding permeate ammonia was 2.2 mg/L and standard deviation of 1.9 mg/L which corresponds to an average removal efficiency of 94 %. MBR performance difference in both stages was confirmed by statistical analyses based on Kruskal Wallis test method followed by nonparametric multiple comparisons among groups with p value < 0,05.

The average pH in the reactor suggests that most part of the ammonia nitrogen content found during the monitoring period was in ammonium cation (NH_4^+) form as a higher amount of ammonia (NH_3) occurs when the pH value is above 9.25 (BENJAMIN, 2002). In such condition, ammonia removal by volatilization becomes negligible, which suggests that nitrification was the main ammonia removal mechanism. Gray (2004) added that nitrification is favored by slightly alkaline conditions, at an optimal pH value between 8.0 and 8.4, which reinforces the nitrification mechanism as the one responsible for the maintenance of low concentrations of $N\text{-}NH_4^+$ in the permeate.

The lower removal ratio of ammonia during the first stage may be attributed to the lower growth rate of nitrifying bacteria as these bacteria need more time to get established and reach concentrations sufficient to nitrify the ammonium (Terada *et al.*, 2013). In the first stage the concentration of NO_3-N in the permeate (61±30 mg/L) corresponds to 93% of total nitrogen, while in the second stage the concentration of NO_3-N in the permeate (107±28 mg/L) corresponds to 98% of total nitrogen, which reinforces the lower growth rate of nitrification in the first stage in relation to the second stage.

The high removal rate observed in the second stage (99%) and the ammonia concentration in the permeate below 1 mg/L, important in enabling the reuse of the treated effluent, may be associated with the full retention of solids by MBR membrane, which allows its operation with high sludge concentration, and also the persistence of some nitrifying organisms or organisms capable to slowly degrade compounds that are hard to degrade, so that there is no loss of activity in the process and high removal rates of organic substances and ammonia are achieved (Alvarez-Vazquez *et al.*, 2004; Renou *et al.*, 2008).

The removal of COD and ammonia may be correlated to the sludge concentration (MLSSV) (Spearman R of -0.16367 and p-level of 0.10024 for COD removal and MLSSV correlation, and Spearman R of -0.25528 and p-level of 0.06506 for ammonia removal and MLLSSV correlation). The results of COD and ammonia removal demonstrate the importance of having an efficient pretreatment on the MBR treatment performance efficiency. Table 1 shows the physicochemical characterization results and refinery effluent toxicity after pretreatment (feed) and after MBR treatment (permeate), and also the treatment performance associated with the pollutant removal ratio.

Table 1 – Physicochemical and toxicological characterization of the MBR feeding and permeate

Parameter	Unit	Feed[a]	Permeate[a]	Pollutant Removal Rate (%)[a]
Alkalinity	$mg.L^{-1}$	496 ± 141	70 ± 100	86
Ammonia	$mg.L^{-1}$	30 ± 31	2 ± 2	95
Chloride	$mg.L^{-1}$	268 ± 161	292 ± 159	-
COD	$mg.L^{-1}$	440 ± 554	84 ± 64	83
Color	Hazen	148 ± 124	18 ± 14	87
Conductivity	$\mu S/cm^2$	2,1 ± 0,5	1.9 ± 0.5	4
Nitrate	$mg.L^{-1}$	0.83 ± 0,55	64 ± 46	-
Nitrite	$mg.L^{-1}$	0.66 ± 0,15	0.66 ± 2.25	-
O&G	$mg.L^{-1}$	30 ± 225	0.22 ± 0.47	99
Phenol	$mg.L^{-1}$	13 ± 9	0.09 ± 0.04	99
TOC	$mg.L^{-1}$	91 ± 35	19 ± 4	80
Toxicity	EC 50 30 min	8 ± 2	Non-toxic	100
Turbidity	NTU	48 ± 320	0.35 ± 0.96	99

The MBR system reduced the color of refinery effluent value from 148±124 Hazen unit to 18±14 Hazen unit corresponding to an average removal of 87%. The color remotion in the MBR may be associated with the remotion of humic substances occurred by both, biologic oxidation or by the membrane filtration. Meanwhile, the average concentration of refinery effluent turbidity was reduced from 48±320 NTU to 0.35±0.96 NTU corresponding to an average removal of 99%. Furthermore, MBR system achieved full removal of total suspended solids (TSS) from the effluent.

The high alkalinity removal observed (86%) may be related to the ammonia removal by the system, species capable of neutralizing acids and provides alkalinity to effluents, or other ions with the same property, besides the consumption of alkalinity for neutralizing acids produced during the degrading process.

MBR system shows high stability and efficiency to remove oil and grease even over eventual period of incidental oil and grease overload in the effluent. The average value of refinery effluent during the first stage was 155 ± 264 mg/L, and the corresponding permeate oil and grease concentration was 0.45±0.5 mg/L, which corresponds to an average removal efficiency of 99.8%, while in the second stage the average value of refinery effluent during the first stage was 20 ± 17 mg/L, and the corresponding permeate oil and grease concentration was 0.16±0.08 mg/L, which corresponds to an average removal efficiency of 99.9%.

MBR also has proved to be highly efficient to remove phenol, and then to reduce phenol concentration in refinery effluent value from 13±9 mg/L to 0.09±0.04 mg/L corresponding to an average removal of 99%.

The excellent MBR performance to remove pollutants may be confirmed by the full acute toxicity removal of the refinery effluent evaluated by Microtox test using *Aliivibrio fischeri* bioluminescence bacterium. It could be inferred that the toxic and refractory organics were mainly transformed into readily biodegradable intermediates, thus wastewater toxicity was simultaneously decreased.

2.3.2 Mechanism of pollutant removal and retention

FTIR spectra of refinery effluent, permeate, mixed liquor and supernatant are provided in Figure 4. The main peak wave number in the FTIR spectrum and relevant groups giving peaks at these wave numbers are shown in Table 2.

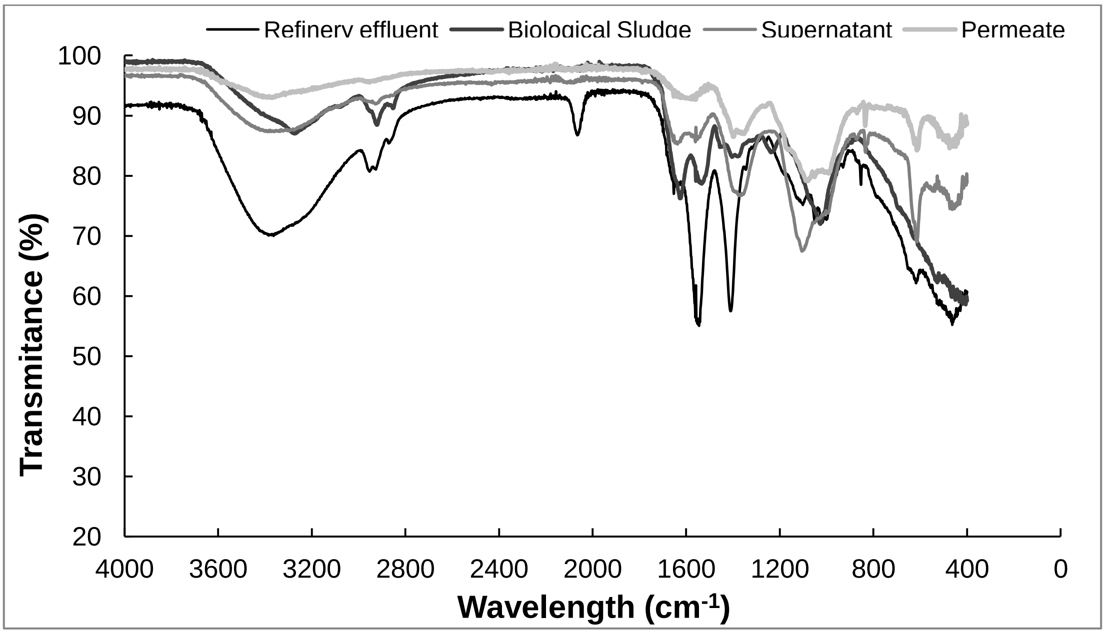


Figure 4 - FTIR spectrum of refinery effluent, mixed liquor, supernatant of mixed liquor and permeate

Table 2 – Main peak wave value in the FTIR spectrum, relevant groups and their corresponding wave peak values

Peak wave value in the FTIR spectrum (cm^{-1})	**Occurrence**				**Removal/ Retention via or origin**	**Relevant groups giving peaks at these wave values**	**Reference**
	RE	**BS**	**S**	**P**			
3277-3300	X	X	X	X	NR	N–H stretching Hydroxyl group in polysaccharides	Pan *et al.* (2010)
2953	X	X			SA	C-H asymmetric stretching in CH3, characteristic of polysaccharides	Coates (2000) and Pan *et al.* (2010)
2916	X	X	X		SA/MR	Aliphatic CH2 and/or the C–H Stretch of alkanes	
2864	X	X			SA	Symmetric C–H Aliphatic Stretch of alkanes	Coates (2000)
2056	X				BR	C-H stretching vibrations of alkenes and alkynes	Ibrahim *et al.* (2013)
1653	X				BR	Amide I (proteinaceous materials)	Leenheer *et al.* (2001)
1620		X	X		BP	Amide II (protein secondary structure- possibly SMPp)	
1556	X	X	X		SA/MR		Pendashteh *et al.* (2011)
1413	X	X	X	X	NR	Symmetrical stretches of –COO– overlapped by amides absorption band of Amino acids and/or aromatic compounds	Coates (2000) and Pendashteh *et al.* (2011)
1248	X				BR	Phenol, C–O stretch	Coates (2000)
1093	X		X		MR	Symmetric and asymmetric CO stretch of polysaccharides or polysaccharides-like substances	Pendashteh *et al.* (2011) and Pan *et al.* (2010)
1076				X	BP	C–C stretching	
1045	X			X	NR	di-substituted benzene	Ibrahim *et al.* (2013)
1012	X	X			SA	Aliphatic phosphates (P–O–C stretch)	
995	X				BR	Phosphates and/or C–H Alkenes Inorganic salts and/or intermediate compounds of the biological oxidation of the aromatic hydrocarbon)	Coates (2000)
923	X				BR	Carbo-acid (COOH)	Shon *et al.*, 2006
864	X		X	X	BP	Calcium carbonate	Lee and Kim (2009), Pendashteh *et al.* (2011)
609	X		X	X	NR	Sulfur (C–SO$_2$–, S–C) (The Presence of S Containing amino acids in proteins)	Shon *et al.*, 2006 and Coates (2000)

RE: Raw effluent; BS: Biological sludge; S: supernatant; P: permeate; NF: not removed; SA: sludge adsorption; BR: biological removal; BP: By-products; MR: membrane retention;

The FTIR analysis of the refinery effluent showed many hazardous components such as polyaromatic hydrocarbons at 1413 cm^{-1}, C-H stretching vibrations of alkenes and alkynes at 2056 cm^{-1}, nitric acid at 3277-3,300 cm^{-1}, amide at 1653 and 1556 cm^{-1}, phenol at 1248 cm^{-1}, di-substituted benzene at 1045 cm^{-1} and sulfur containing groups 609 cm^{-1}. These species were also detected in other studies involving refinery effluents (Ibrahim *et al.,* 2013). The peak that's the closest to the wavelength 864 cm^{-1} shows the presence of calcium carbonate. The impact of calcium ions on membrane fouling formation in submerged MBR membranes remains controversial. It has been reported that the interaction of hydrophobic organic compounds such as soluble microbial products (SMP) and extracellular polymeric substances (EPS) with calcium improved bioflocculation (Nagaoka *et al.*, 1996). Additionally, calcium may play an important role as a coagulant to produce colloidal flocs via charge neutralization (Kim and Jang, 2006). In this regard, external fouling formation promoted by calcium deposition over the membrane surface may come to be significant, if the colloidal flocs are larger than the membrane pore size. Calcium carbonate may also contribute to membrane scaling. Given to that, the concentrations of dissolved inorganic solutes increase in the direction of the feed flow, while the concentrations of sparingly soluble salts exceed their solubility limit, and then their crystallization may occur either directly over the membrane surface or in the bulk. $CaCO_3$ particles are cohesive and lay down a deposit of $CaCO_3$ particles over the membrane surface, which may be physically irreversible (Kim and Jang, 2006).

Some compounds detected in the effluent are biodegradable, and are removed by the biologic oxidation, evidenced by the disappearance of the peaks in the permeate, mixed liquor and supernatant spectrum at the wavelengths of 2056, 1653, 1248, 995, 923 cm^{-1}, or intensity decrease of the peaks 1413 e 1556 cm^{-1}. The higher intensity of the peak 2916 cm^{-1} (C-H asymmetric stretching in CH_2) and the intensity decrease of peaks 2953 cm^{-1} (C-H asymmetric stretching in CH_3) and 2864 cm^{-1} (C-H symmetric stretching in CH_2) in the sludge, supernatant and permeate in relation to the effluent indicates changes from long aliphatic chains in wastewater to less abundant and more branched structures after going through biological treatment process.

It is been noted that other compounds are retained by MBR due to their adsorption on biological sludge evidenced by the reduction or absence of the peak on the permeate spectrum, and detection of the peak on the biologic sludge spectrum, i.e., peaks recorded at wavelength of 1012, 2864 and 2953 cm^{-1}. The biological process could be divided into two stages. Firstly, the organic matter is adsorbed by sludge, and then organic substrates cell surfaces undergo oxidation by microorganism within sludge (Zhang *et al.*, 2014). The degradation of adsorbed compounds depend on their biodegradability as the HRT (Hydraulic Retention Time) of these compounds inside the MBR is longer than the HRT set to the MBR. The recalcitrant compounds are eliminated from the MBR along with the sludge discharge to control the cellular retention time. The adsorption of toxic recalcitrant compounds on the sludge requires a differentiated management of the discharged sludge. It is noteworthy that the adsorption of these compounds can also change the sludge characteristics and influence the sludge fouling potential.

Another mechanism involved in the removal and retention of refinery effluent compounds is their retention by the membrane evidenciated by the detection of some peaks in the biologic sludge supernatant spectrum and their absence in the permeate spectrum, i.e., peaks at wavelengths of 1093, 1556 and 2916 cm^{-1}. The retention of organic compounds with molecular size smaller than the pore size may occur due to the fact that, during operation, a cake is formed over the membrane surface. Such cake is formed by microorganisms, cellular matter, proteins, etc., and works as a dynamic layer that favors filtration efficiency improvement by reducing the effective pore size of the membranes (Berube *et al.*, 2006).

Some compounds are not removed or retained during the process being found in the permeate, sludge and supernatant, i.e., peaks recorded at wavelengths of 609, 864, 1045, 1413, and 3277-3300 cm^{-1}. It is noteworthy that these residual compounds may correspond to effluent compounds and/or degradation byproducts that may contribute to membrane fouling. Shariati *et al.* (2011) evaluated the use of a membrane sequencing batch reactor to treat synthetic petroleum refinery wastewater and, by analyzing the fouling material deposited over the membrane by FTIR, found polysaccharides, proteins and possibly aliphatic and aromatic hydrocarbons, or the intermediate compounds produced by their biodegradation.

It is also observed the production of microbial products in the medium as shown by the appearance of some peaks not observed in the feed spectrum and detected in the biologic sludge or supernatant. The peaks near the wave values of 1076 cm^{-1} indicate the presence of materials resembling polysaccharides, whereas the peaks at 1620 cm^{-1} demonstrate the presence of substances resembling proteins (Jarusutthirak and Amy, 2006) usually found in

SMP and EPS. Some of these products are retained by the membrane, while others permeate through the membrane contributing to residual COD or TOC. Such residual organic matter, although not affect the fulfillment of the law standards, can hinder the reuse of the effluent in the process.

Another substantiation of SMP and EPS production is the higher peak intensity observed at the wavelength value of 1093 cm^{-1} that correspond to the symmetric and asymmetric CO stretch of polysaccharides or substances resembling polysaccharides, and 609 cm^{-1} that correspond to the presence of S containing amino acids in the proteins in the supernatant spectrum related to the effluent spectrum. Manu authors report the presence of sulfur compounds associated with the presence of EPS (Higgins *et al.*, 2008). An unobserved peak at 1093 cm^{-1} in the permeate spectrum suggests the retention of polysaccharides or substances resembling polysaccharides by the membrane, while sulfur compounds pass through the membrane as it’s been observed in the permeate. Such SMPs play an important role in membrane fouling formation and flow rate decrease in wastewater reclamation and reuse processes.

2.3.3 **Membrane performance**

For suspension filtration like biological sludge in MBR, the permeation flux will decrease proportionally to the time as a result of the increase in total resistance resulting from membrane fouling formation due to deposition of particles on the membrane, or adsorption into the membrane pores. Because MBR process in this study was operated on constant flux basis, an increase in TMP will take place during the whole experiment due to the fouling formation phenomenon as shown in Figure 5. The stable TMP during the second stage was due to the better pretreatment the have provided the conditions to the obtention of higher quality sludge. Many studies have related permeability decrement caused by fouling formation to sludge properties. For example, Chang *et al.* (2002), Judd (2006) and Drew (2010) presented a review of sludge parameters – floc size, MLSS, EPS, SMP, among others, and how they relate to MBR fouling formation likeliness.

In this regard, two characterization parameters of sludge properties have been underscored, that is, filterability and colloidal TOC. Alkmim *et al.* (2014) carried out a study in which they observed that the fouling formation over the membrane, and its consequent permeability decrease may be predicted by measuring sludge filterability, which shows that filterability is directly related to the membrane permeability. Fan *et al.* (2006) observed that colloidal TOC may be related to the critical flux, a parameter used to control the fouling formation process and filterability, and also defined as a flow rate below which the membrane fouling formation will not take place (Field *et al.*, 1995). An increase in colloidal TOC content in the sludge will cause critical flux decrement.

In this study there was a negative correlation between permeability values and filterability (Spearman R = -0.151, p-level = 0.024) indicating that the better the filterability (shorter filtration time), the better the membrane permeability. Regarding colloidal TOC, it was found also a negative correlation (Spearman R = -0.238), i.e., the higher is the colloidal TOC value, the lower the membrane permeability.

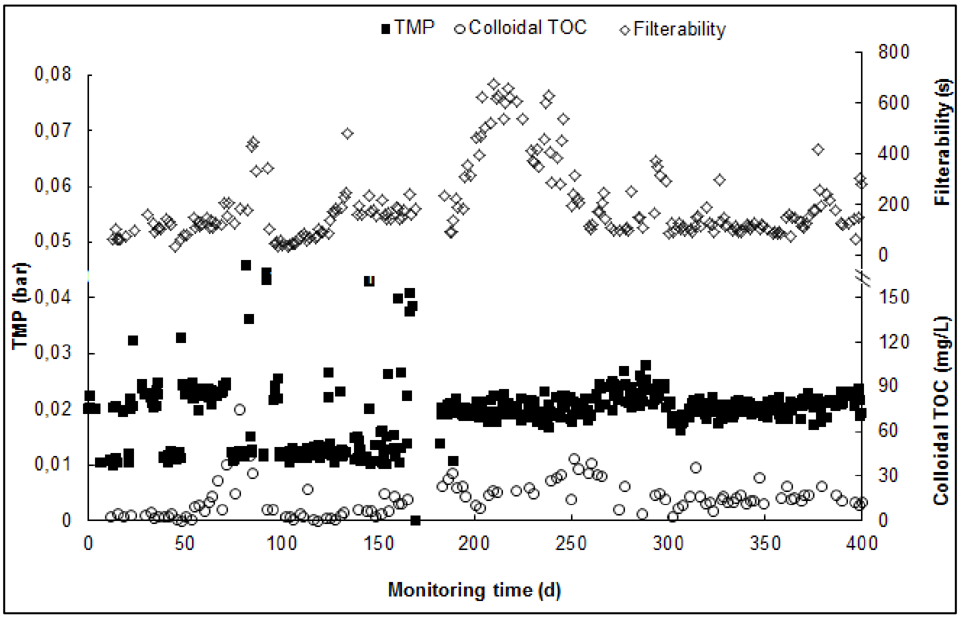


Figure 5 – Behavior of TMP, Colloidal TOC and Filterability over the monitoring time.

In the first stage, filterability values ranged from 65 to 674 s with average around 226±174 s while in the second stage, filterability values ranged from 36 to 421 s with average around 153±71 s (Figure 5). According to GE Water & Process Technologies (2009), filterability values below 200s found by the Time to filter methodology are taken as good filterability values. High filterability values are related to events such as load or composition variation in refinery effluent s that occur very often at petroleum refinery plants, which makes the maintenance of MBR membrane permeability a tough challenge at treating this kind of effluent. Over the monitoring time period, seven events of shock load were reported for high oil and grease concentrations, ammonia an phenol, which have impacted the sludge quality, increased the colloidal COT and filterability values, and consequently the membrane fouling, which increased the TMP required to keep a steady flux, and also affected the MBR performance to remove COD and ammonia (Table 3).

Table 3 – Load variations occurred over the monitoring time period and their influence on MBR parameters

Time (days)	**Event description**[a]	**Filterability**[b] **(s)**	**TMP**[b] **(bar)**	**Colloidal TOC**[b]**(mg/L)**	**COD Removal**[c] **(%)**	**Ammonia Removal**[c] **(%)**
64 -71th	High O&G concentration - 82 (24) mg/L	**177 ±36 (123 ± 17)**	**0,024 ± 0,001 (0,022 ±0,001)**	27 ± 10 (10 ±3)	61 (84)	-
81-92th	High NH_3 concentration - 46 (27)mg/L	**389 ± 59 (171 ± 32)**	**0,044 ± 0,004 (0,012 ±0,001)**	38 ± 9 (19 ±9)	81 (84)	-
102-104th	High O&G concentration - 74 (26) mg/L	64 ± 18 (46 ± 11)	**0,013 ± 0,001 (0,012 ±0,001)**	3 ± 1 (3 ±1)	78 (85)	89 (87)
179-207th	High Phenol concentration - 19 (2) mg/L	**254 ± 75 (175 ± 46)**	**0,021 ± 0,001 (0,013 ±0,002)**	**26 ± 4 (14 ±3)**	79 (89)	74 (86)
194-253th	High O&G concentration - 240 (25) mg/L	**646± 23 (114 ±44)**	**0,022 ± 0,001 (0,019 ±0,001)**	**30± 3 (14 ±4)**	55 (83)	79 (88)
291 - 295th	High Alkalinity[d]	**333 ± 37 (151±26)**	**0,024 ± 0,001 (0,021 ±0,001)**	18 ± 2 (6±2)	79 (80)	80 (98)
370-377th	High Phenol concentration - 40 (9) mg/L	**250 ± 99 (114 ±6)**	**0,022 ± 0,001 (0,020 ±0,001)**	**18 ± 3 (15 ±2)**	74 (87)	98 (99)

a – Values between brackets correspond to the average of the parameters evaluated within the four-day period the events have occurred.
b – Values in bold letters have different significance between the values evaluated before and after the events ($p<0,05$) at a significance level up to 0.05%.
c – It wasn't possible to carry out statistics tests regarding COD and ammonia removal due to the insufficiency of data.
d - pH reading error – The pH sensor was located in membrane tank, and the sodium triphosphate solution was added to the biological tank. By this way, there was a response time until the sensor sensed the sludge pH stabilization in the biological tank, allowing a higher amount of sodium triphosphate which increased the alkalinity.

The presence of phenol in petroleum refinery effluent makes biological sludge bioflocculation process more difficult by causing its deflocculation and more turbidity so that the microorganism activity is reduced (Rebhun and Galil, 1988). High concentrations of such pollutant may bring forth some toxicity to the microorganisms that promotes cell lysis, which leads to low sludge filtration rate and low system performance that come to impair the system as a whole (Viero *et al.*, 2008).

The high concentration of O&G in the effluent may cause a number of problems to its biological treatment, including the decrease the exchange of substrate, products and oxygen between bacterial cells and the environment by depositing a lipid layer around the biological flocs. Furthermore, it may cause the emergence of foam and a high number of filamentous microorganisms with unwanted properties. Likewise, a poor microbiological activity associated with an excessive concentration of O&G prevents sedimentation and causes biomass losses. These negative effects are also associated with clogging and stinks, and besides being frequently associated with a decrease in the treatment system efficiency (Cammarota and Freire, 2006).

The soluble microbial products (SMP) and the polymeric extracellular substances (EPS) may potentiate the membrane fouling and diminish their filtration rates. The EPS are secreted by the cells or produced during cell lysis and are made up of insoluble materials such as capsular polymers, gels, polymers, and organic materials. EPS are important to determine biomass physicochemical properties such as floc structure, floc load and hydrophobicity. SMPs are released by cells in response to some environmental and/or operational condition during cell lysis, corresponding to the largest part of the effluent from biological processes (Laspidou and Ritmann, 2002). Figure 6 shows the SMP and EPS concentration profiles regarding polysaccharides and proteins over the monitoring time period.

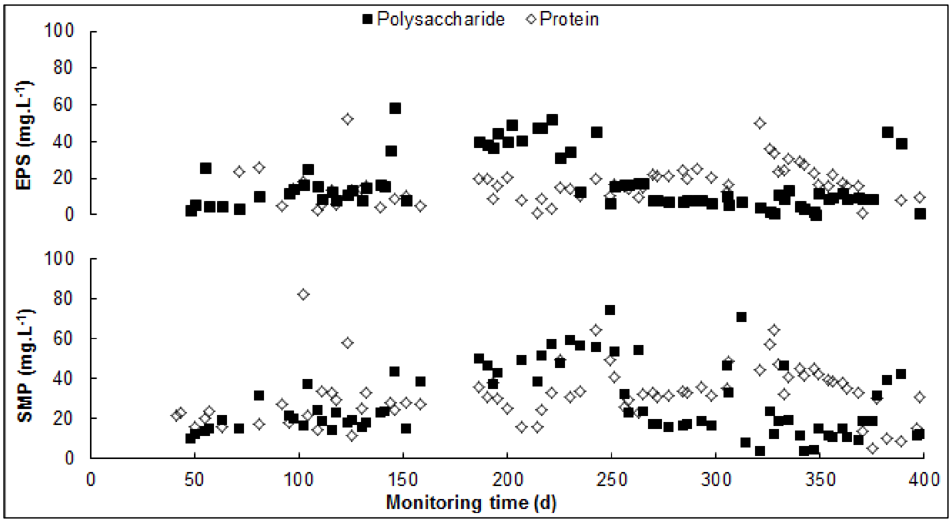


Figure 6 – Behavior of SMP and EPS over the monitoring time period

The SMP concentration of polysaccharides (SMPc) varied between 3.7 and 105 mg/L with an average value of 28±19 mg/L, while the (SMPp) concentration of protein varied between 4.7 and 82 mg/L with an average value of 32±14 mg/L. EPS concentration of polysaccharide

(EPSc) varied between 1 and 58 mg/L with an average value of 17±15 mg/L, while the EPS concentration of protein (EPSp) varied between 2.7 and 53 mg/L with an average value of 17±15 mg/L. SMP and EPS value variations occur mostly in periods of stress events corresponding to a response to any high concentrations of oil and grease, phenol and others. It’s been noticed that there was a significant positive correlation between SMPc and EPSc and sludge filterability and particle size, and EPS concentration of TOC, with Spearman correlation coefficients of about 0.4037 and 0.3223 for SMPc and EPSc respectively. That way, it has been found that by increasing SMPc and EPSc concentration the sludge filterability decrease takes place.

Several researchers have been pointing out that polysaccharides-like substances in the fraction contribute more to fouling than the protein-like substances (Rosenberger *et al.*, 2006; Yigit *et al.*, 2008; Lyko *et al.*, 2007).

According to the literature, polysaccharides contribute to the cohesion of the cell, playing an important role in maintaining the structural integrity of biofilms (Christensen, 1989). Other studies have also correlated polysaccharide concentration and fouling rate in MBR (Rosenberger *et al.*, 2006; Fan *et al.*, 2006).

2.3.4 **Fouling characteristics**

In order to identify the fouling formation process more clearly, the characteristics of fouling were occasionally analyzed by MFI (Modified Fouling Index) test of mixed liquor and sludge supernatant, and then compared it to the fouling resistance, floc size, MLSSV, colloidal TOC, SMP and EPS measurement (Table 4).

Table 4- Fouling characteristics related to sludge

Operating time (days)	Fouling resistance (m-1)	Sludge MFI (s.L^{-2})	Supernatant MFI (s.L^{-2})	Filterability (s)	Floc size (µm)	MLSSV (mg.L^{-1})	Colloidal TOC (mg.L^{-1})	SMP (mg.L^{-1})	EPS (mg.L^{-1})
306	1.20E+10	3.00E+05	2.21E+05	105	26.5	4790	21.3	106	26.6
312	3.70E+10	2.03E+05	1.90E+05	94	26.6	6360	18.3	97	132.2
377	7.00E+10	9.24E+05	6.90E+05	421	27.2	4810	20.9	234	69.6
382	3.60E+10	3.86E+05	2.40E+05	242	28.3	5860	20.3	142	24.7

By evaluating MFI results, it has been found that in all cases evaluated, MFI values concerning supernatant correspond to the most of the MFI of the biologic sludge. The percentage of the supernatant MFI compared to the sludge MFI ranged from 62% to 94%, which proves that the soluble fraction of the mixed liquor is the main contributor for the membrane fouling, as shown in other studies (Arabi and Nakhia,2009; and Jang *et al.*,2007).

It was noticed that on the day that the fouling resistance reached its highest value (377th day), sludge MFI also reached its highest value, which demonstrates the influence of the sludge quality on membrane fouling process. The high fouling potential of the sludge on that day may be associated with the high SMP concentration, compared to the other days such fouling was monitored, which confirms the previous findings that made clear the correlation between SMPc and filterability. SMP may accumulate over the membrane surface or penetrate the membrane pores, increasing filtration resistance. According to Meng *et al.* (2009), due to the membrane rejection, SMP are more easily accumulated in the MBR, which causes a decrease in sludge filterability, a fact proven by the lowest filterability value recorded, i.e., 421s. FTIR results above discussed confirm the retention of polysaccharides and polysaccharides-like substances by the membrane, which contributes to membrane fouling.

Furthermore, the linear regression between data related to MFI of the mixed liquor and the supernatant, and the variables related to colloidal TOC, SMP and EPS, MLSSV and floc size provided a good adjustment only for the MFI of the mixed liquor and supernatant and SMP. R2 values obtained from linear regression between the MFI of the mixed liquor and SMP (R2= 0.98), and MFI of the supernatant and SMP (R2= 0.94) reinforces the contribution of SMP to higher fouling formation likeliness of the sludge soluble fraction. These results suggest that for the membrane fouling control in MBR treating refinery wastewater, one alternative is the control of SMP concentration in the medium.

2.4 Conclusions

- MBR technology was able to effectively reduce the COD, NH_3–N, turbidity, color, phenol and toxicity to meet disposal and reuse of non-potable water standard requirements.

- Organic substances were removed by biological oxidation and/or retained by adsorption in the biological sludge or by in UF membrane, while SMP was produced during treatment.

- Soluble fraction of mixed liquor contributes significantly to membrane fouling due to the presence of SMP content.

- Pretreatment is important to ensure optimal treatment performance, and to keep membrane fouling under control as shock loads of oil and grease, phenol and alkalinity was highly frequent in refinery effluent.

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3. THE APPLICATION OF FILTERABILITY AS A PARAMETER TO EVALUATE THE BIOLOGICAL SLUDGE QUALITY IN A MBR TREATING REFINERY EFFLUENT

3.1 Introduction

Membrane bioreactors (MBR) are effluent treatment systems that include separation processes performed by membranes and biological processes[1]. Although membrane fouling remains as a disadvantage of this technology, the smaller footprint and the better product quality make MBR more effective than other biological wastewater treatment methods such as, for example, the conventional activated sludge method[2].

Membrane fouling directly affects the permeate flux, besides increasing the transmembrane pressure system, which demands for higher power consumption, higher cleaning frequency, smaller membrane lifetime, and therefore higher operational cost. Membrane fouling is influenced by a series of factors related to the feed, membrane and operating conditions, and it is caused by the deposition of mixed liquor suspended solids (MLSS) over internal and external membrane structures due to interactions between sludge compounds and the membrane[2].

Membrane permeability is the most important parameter used to monitor MBR process. However, Gil *et al.*[3] stated that results only based on this parameter allows for inaccurate conclusions about the process as it will not provide specific information on what factors have actually been determining.

Many studies have tried to relate the permeability decline caused by fouling to the sludge properties. For example, Chang *et al.* [4], Judd[1] and Drew[5] presented a review regarding sludge parameters – floc size, MLSS, EPS (Extracellular Polymeric Substances), SMP (Soluble Microbial Products), among others, and how they are related to MBR fouling potential. As discussed in this works, due to the biologic system complexity, the conclusions found have been often controversial, and therefore they cannot be directly transferred to other systems.

Biologic sludge from MBR shows different compositions and characteristics. One of these characteristics is its filterability, which stands for the resistance placed by the fluid to pass through a permeable/porous like a membrane, indicating the propensity for membrane fouling caused by biologic sludge. Therefore MBR fouling is a process, and filterability is a specific characteristic of the sludge.

According to Rosemberger and Kraume[6], According to Rosemberger and Kraume[6], the filterability is directly influenced by the sludge properties such as concentration of suspended solids, temperature, viscosity, distribution of particle sizes, and concentration of univalent and bivalent cations. Thus, the study of this parameter associated with other sludge properties may be used as a tool to control and prevent membrane fouling.

The effects of sludge properties have been often controversial in different studies. Lee *et al.*[7] showed that due to the dynamic layer formation on the membrane surface, high suspended solid concentrations improve the system filterability, while Nagaoka *et al.*[8] found a negative effect caused by suspended solids due to their high viscosity that could affect filtering process hydrodynamic.

Mikkelsen & Keiding[9] found that sludge containing more fractions of EPS tend to form more flocs, improving the filterability. Then again, Kim *et al.*[10] and Nagaoka *et al.*[8] reported a filterability decreasing with increasing EPS concentration. Houghton *et al.*[11], pointed out an optimal EPS range to improve sludge filterability.

Studies based on sludge disintegration by using ultrasound showed that filterability decreases considerably as suspended particles sizes decrease[12]. Nevertheless, experiments carried out Sun *et al.*[13] show that ozonization of biopolymeric agglomerates by reducing their sizes, would improve their filterability.

Filterability discusses much about sludge properties, but not necessarily much about the system as the tests are usually comprise only a simple filtration. It is not always the system geometry used for the test resembles MBR geometry, which may lead to some apparently controversial conclusions.

Many studies have shown the application of filterability tests to monitor and control incrustation on MBR[14, 10, 15, 16]. However, different methods have been employed such as *Capilarity Suction Time - CST*[17], *Time to Filter* - TTF[18], *Filter Test* – FT[17], S*ludge Filtration Index* – SFI[19], and *Delft Filtration Characterization Method* - DFCm[20]. The lack of filterability method standardization has impaired the understanding the influence of filterability on MBR performance, and so the comparison among results. Even though, sludge filterability is an important characteristic that provide valuable information on membrane bioreactor filtration processes, and as its determination is considerably easier to be carried out, it may be a suited parameter to monitor and control fouling process.

In this context, this work aim to evaluate the filterability test use as a tool to monitor and control membrane fouling in MBR. Furthermore, different methods were used to compare filterability measurement findings regarding their capability to sense sludge quality variation their reproducibility, and as well correlate the most reproducible test results and sludge quality parameters.

3.2 Methodology

3.2.1 **Selection of Filterability methods**

Periodically, over 184 days, samples of sludge of a MBR used to treat refinery effluent were collected, and the filterability of determined by using three different methods to compare them. The MBR evaluated comprised an external submerged ultrafiltration membrane bioreactor. The membrane was a PVDF-based (polyvinylidene difluoride) polymer had the conformation of a hollow fiber, and had an average pore opening of 0.04 µm. Both, biologic and membrane tank have aeration systems.

Altogether, 32 sludge samplings were carried out, while the methods evaluated were *Time to Filter* (TTF), *Filter test* (FT), and *Sludge Filtration Index* (SFI). All tests were triplicated for each of the samples. All samples were homogenized before performing the tests.

Filterability tests based on Time to Filter method (TTF) were performed by using the assembly schematically shown in the Figure 2(a). The assembly had a 100 mL graduate beaker, a 1000 mL Büchner flask, Buchner funnel with a diameter of 9 cm and e filter paper (Whatman glass microfiber 934-AH, φ 90 mm, pore size retention 1.5 µm). The filtering procedures were performed by using a vacuum pump that supplied a pressure of nearly 51 kPa. To carry out the trial, 200 mL of sludge were used. The time required to filter a 100 mL was recorded. The filterability value based on this method is given by the Equation 1:

$$TTF = \frac{\text{Filtration time}}{\text{100 mL of Filtrate}} \qquad \text{(Eq. 1)}$$

For filterability tests performed by the Filter Test method (FT), it was used an assembly as shown in the Figure 2(b). For these trials, it was used a Whatman quantitative filter paper, Grade 42, pore size retention 2.5µm with a diameter of 185 mm folded up into 8 folds so that it would fit into the funnel as shown in the Figure 2(b). 50 mL of biologic sludge sample were collected and filtered through a filter paper. The countdown started right after the beginning of the filtering process, and the volume was recorded after 5 minutes. The filterability value found by this method is given by the Equation 2:

$$FT = \frac{\text{Filtrate Volume}}{\text{5 minutes}} \qquad \text{(Eq. 2)}$$

For the filterability tests based on the Sludge Filtration Index method (SFI), it was used an assembly as shown in the Figure 2(c). 500 mL of sludge sample were collected from the bioreactor being studied. The sample temperature was adjusted to 20ºC by an ice bath. The funnel trials, it was place a Macherey Nagel MN 85/70 BF filter paper with pore size retention of 0.6µm. The sludge sample was homogenized and poured into the filter, and it was then stirred up at 40 rpm as shown in the Figure 2(c). The countdown started with the permeate volume collected from the beaker reached 100 mL, and stopped when the volume of 150 mL was reached. The filterability value measured by this method was calculated based on the time recorded in seconds in relation to the suspended solid concentration (SS) as given by the Equation 3:

$$SFI = \frac{\Delta t}{SS}\left[\frac{s}{\%SS}\right] \qquad \text{(Eq. 3)}$$

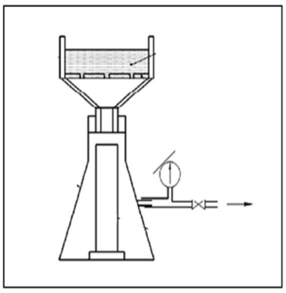
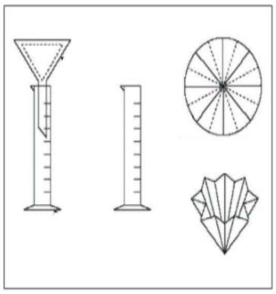
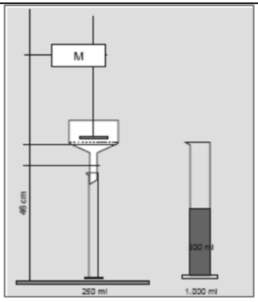
Time To Filter	**Filter Test**	**Sludge Filtration Index**
 (a) Source: THIEMIG [17] – Adapted	 (b) Source: THIEMIG [17] – Adapted	 (c) Source: THIEMIG [19]

Figure 7 – Assemblies used for sludge filterability tests.

The findings of the tests were compared for sludge filterability variation sensing capability over the reproducibility monitoring time. Sludge quality variation sensing capability was evaluated by means of an analysis of the temporal behavior of the tests. In order to select the method that would allow for the highest reproducibility of the petroleum refinery sludge, the variation coefficient (VC) value sets resulted from the methods being tested were compared. To that, each test was triplicated for a determined sample, and the values found were analyzed by means of Dixon's Q test [21] to exclude the values deemed to be substantially different from the others. Then, the variation ratio was calculated from the median value of $\bar{x}$ and the standard deviation of *s* of the replicated tests as given by the Equation 4.

$$VC = 100x\frac{s}{\bar{x}} \qquad \text{(Eq. 4)}$$

As seen in the Equation 4, the variation coefficient represents the dispersion of a data set in relation to its median value. So, when its calculated based on the replicated test results, the lower its value is, the lower data dispersion is, and higher it is its stability degree and, in such a case, higher the reproducibility degree is according to the test being studied. Besides it, for being dimensionless, it allows for reproducibility comparison among the value sets of different measurement units, which explained its utilization to compare the filterability test results found in this work.

The substantiation of significant existing differences regarding reproducibility of filterability tests measured based on variation coefficient was evaluated by means of hypothetical test of multiple independent samples. To that, nonparametric tests were carried out, which do not depend on the frequency of the population being studied. So, to check for the significant existing differences among the median values of the variation coefficient, *Kruskal-Wallis test* was applied followed by a nonparametric test for multiple comparison among groups. All statistical analyses were performed by using STATISTICA 8.0 software.

3.2.2 **The influence of the sludge filterability on membrane fouling process**

To evaluate the influence of the sludge filterability on MBR fouling process, a MBR used to treat a petroleum refinery effluent was monitored, which was then associated with the permeability monitoring data. The sludge filterability was evaluated according to the Time to Filter method (TTF).

3.2.3 **Influence of sludge properties on sludge filterability**

The biologic sludge properties being evaluated as possible filterability influencers were concentration of mixed liquor volatile suspended solids (MLSSV)[18]; SMP and EPS was determined by Thermal methods for EPS extractions introduced by Morgan et al.[22]; concentration of total colloidal organic carbon (colloidal TOC) was quantified by using TOC analyzer software (SHIMADZU TOC-VCPN) and determined according to the method proposed by YANG et al.[23]; particle size distribution (Laser Scattering Particle Size Distribution Analyzer HORIBA - LA-950V2).

In order to verify the influence of biologic sludge properties on filterability, it was evaluated the existence of a correlation coefficient among the parameters previously mentioned along with the respective filterability values found by applying the method that had shown higher reproducibility. To that, the Spearman correlation coefficient among the variables with further correlation significance analysis by means of the Hypothesis Test. STATISTICA 8.0 software was used to perform statistic tests.

3.3 Results and Discussion

3.3.1 **Selection of Filterability methods**

After carrying out Dixon’s Q test, no data was deemed to be significantly different from the other values, and all them were taken into account to compare methods regarding their sludge quality variation sensing capability and reproducibility. The Figure 8 shows the temporal filterability result series chart for the different tests being analyzed.

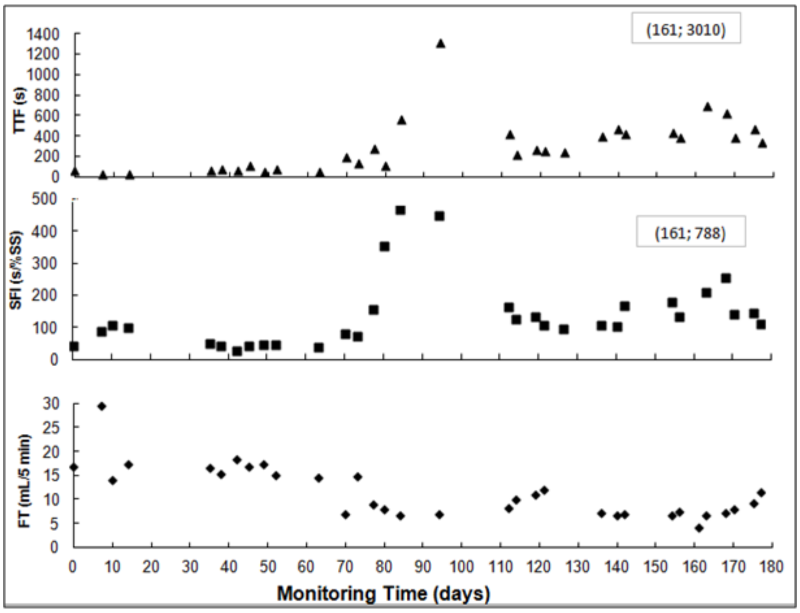


Figure 8 – Temporal comparison among the three filterability methods being analyzed. The highlighted values stand for the outliers.

By comparing the results found, it was noticed that the FT method was unable to sense significant result differences sensed by using other methods being evaluated. It was observed that the filterability values found by applying the FT method showed an almost constant behavior, while the other tests showed significantly different values, particularly between the 70th and the 100th monitoring days. That finding indicated that, possibly in the case of the system being studied, SFI and TTF methods showed to be more sensitive to sludge quality variation compared to the Filter Test.

In order to determine which method would be the most reproducible to analyze the biologic sludge obtained from an MBR used to treat a petroleum refinery effluent, it was performed a variation coefficient (VC) analysis of them. Kruskal-Wallis nonparametric hypothesis test was carried out to check whether the variation coefficients of the different filterability tests had median values significantly different at a significance level of 0.05. So it was found that there were significant differences among the median values, multiple nonparametric comparison procedures were adopted.

Such test allows for a simultaneous comparison between the variation coefficient data, aimed to identify which median values that taken two a time, would significantly differ from each other at the significance level of 0.05. The Table 5 shows the multiple comparison test results, which were applied after verifying a significant existing difference among the groups found by applying Kruskal-Wallis test.

Table 5 - Kruskal-Wallis statistic tests that showed significant differences among groups at a significance level of 5%.

Test Types	Result that showed significant differences
Filter Test (FT)	Among TTFs
Time to Filter (TTF)	Among all the tests
Sludge Filtration Index (SFI)	Among TTFs

By evaluating the results, it was observed that there were significant differences between the VC median values of the TTF method compared to the other methods, while there was no significant difference between the median values of the FT and SFI methods. The Figure 9 shows that the variation coefficient values of TTF method were significantly lower than the other test, which shows that such a test is the most stable of all the methods evaluated, and it is the one that features higher reproducibility to evaluate the filterability of biologic sludge used to treat petroleum refinery effluents.

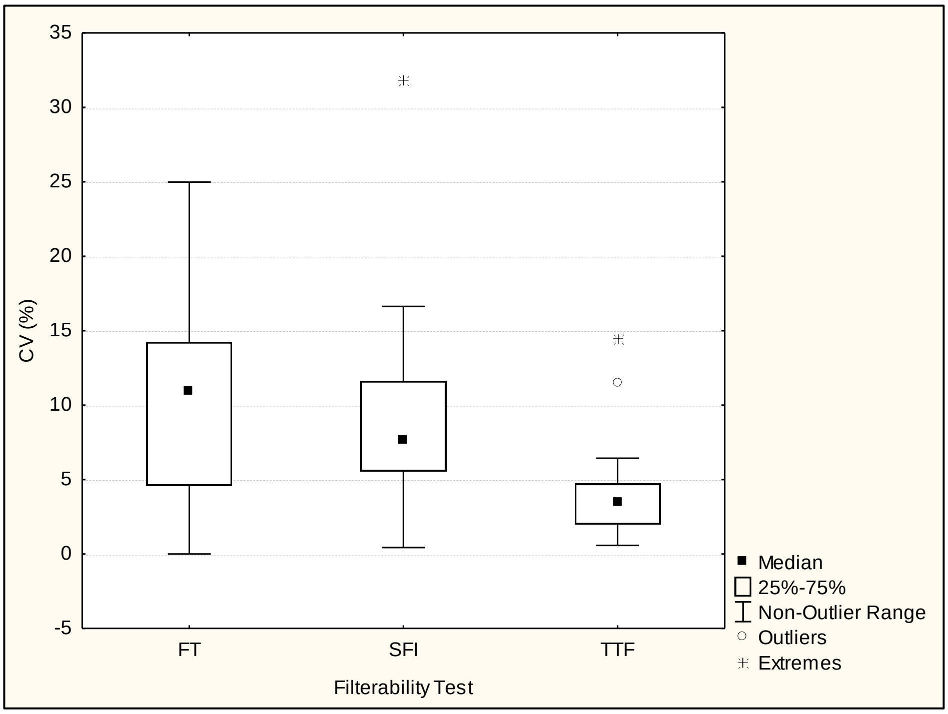


Figure 9 - Box-plot Chart showing the range of variation coefficients of different filterability methods.

In his study, Thiemig[19] compared the utilization of the three filterability methods in relation to their reproducibility. *Sludge Filtration Index, Filter Test, and Capilarity Suction Test* methods were compared for municipal sewage sludge treatment by means of analysis of variation coefficient (VC) tests. The method that had the worst result was the FT test, which confirmed the results found in the study performed. According to the author, this result is related to a small amount of sludge used for the test, which may cause higher variability of the results due to sampling errors.

Although the SFI method showed a sensing capability similar to the TTF method , for the biologic sludge being evaluated, its reproducibility was lower, which indicates that TTF method was the most proper for filterability evaluation of all them.

3.3.2 **Filterability as a parameter to evaluate the sludge fouling potential in a MBR**

In order to prove the quality of the reactional liquid has a direct influence on membrane fouling, MBR filterability and permeability Time to Filter (TTF) method results were evaluated as shown in the Figure 10.

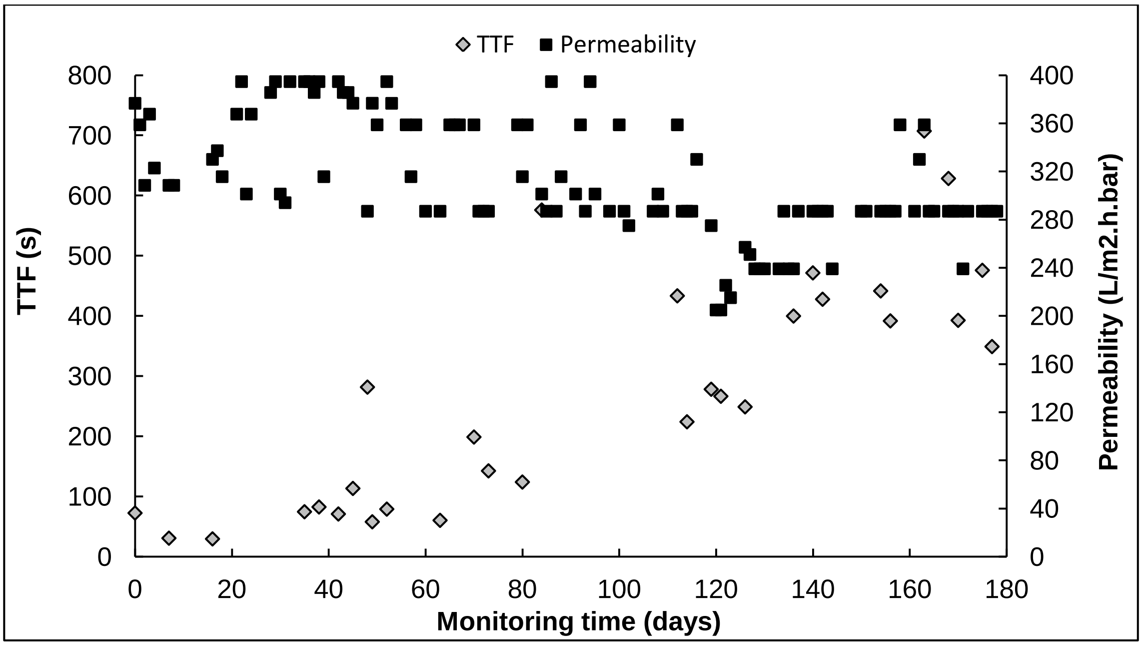


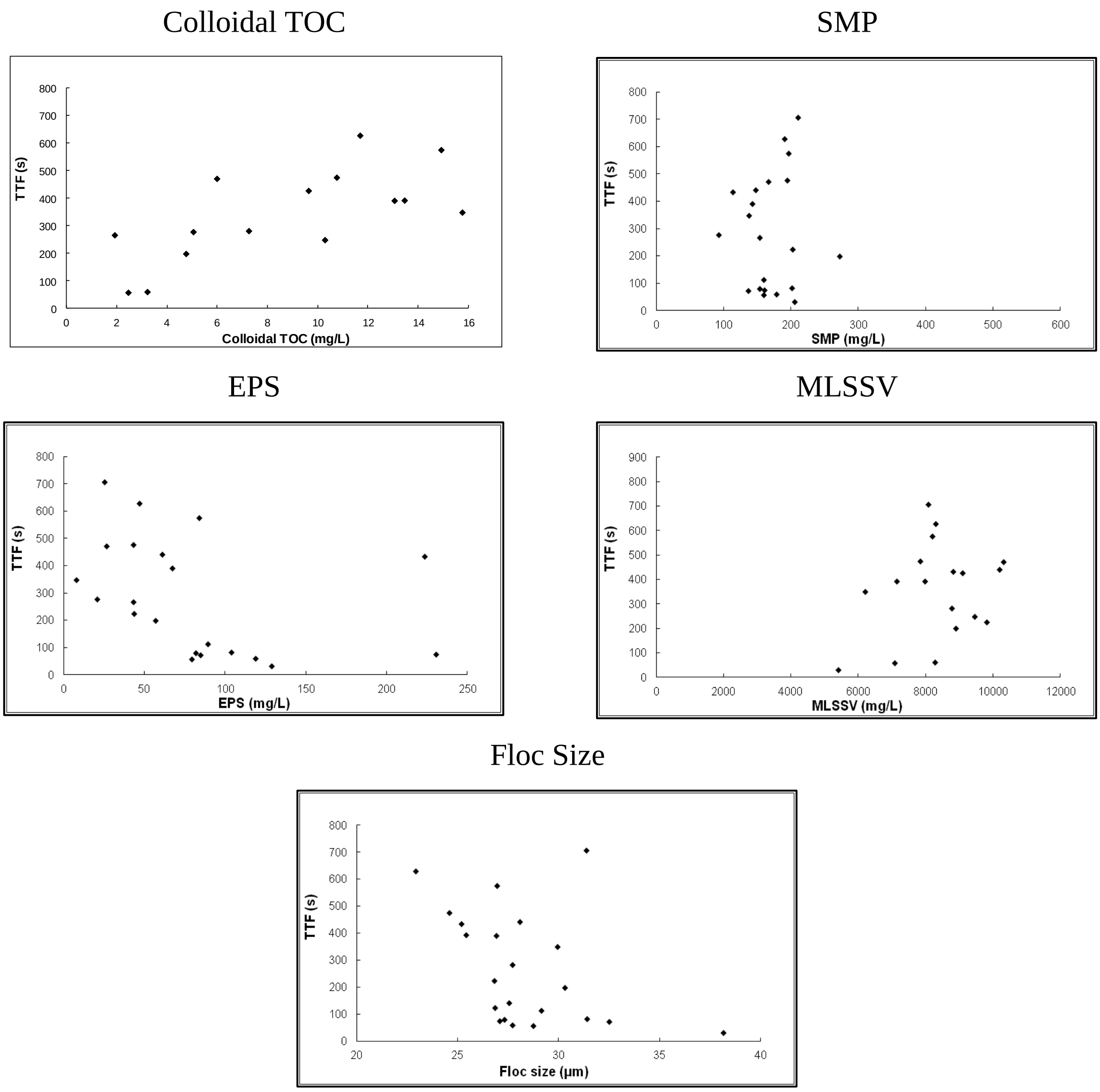
Figure 10 – Permeability and filterability profile by operation monitoring time.

As it may be seen in the Figure 10 that over the monitoring time the permeability decrement was followed by sludge filterability decrement (longer filtration time). So, it may be realized that filterability parameter, and as well other sludge parameters, can be used to forecast and monitor MBR fouling process. Besides it, being aware of the way other sludge parameters influence filterability may confirm the use of this parameter, which is easier to be used to monitor MBR performance.

3.3.3 Influence of sludge characteristics in sludge filterability

In order to evaluate the influences of sludge properties on filterability behavior, it was analyzed the possible existence of a correlation between these parameters. The following parameters were evaluated: colloidal TOC, SMP e EPS (characterized in terms of COD), MLSSV and particle size.

The Figure 11 shows the relationship between the sludge parameters and the filterability.


Colloidal TOC

SMP

EPS

MLSSV

Floc Size

Figure 11 - Graphic of possible correlation between the parameters analyzed and sludge filterability found by TTF Test.

In order to evaluate the existence of such correlations, and to find out whether they are significant, the Spearman correlation coefficient (R) was determined, and the correlation significance test was carried out. The results found are shown in the Table 6.

Table 6 - Spearman correlation coefficient (R) values and correlation significance analysis. *(The highlighted values correspond to the significant correlations)*

Variable Pair	Classification - Spearman Correlation Marked correlations are significant = $p<0.05$	
	Spearman (R) Correlation coefficient	**p-value**
TTF & MLSSV	0.301471	0.239624
TTF & colloidal TOC	***0.714286***	***0.004104***
TTF & SMP	0.144415	0.543548
TTF & EPS	***-0.625564***	***0.003178***
TTF & Floc Average Size	***-0.628120***	***0.001331***

Based on the values obtained, it was found that there is a correlation between filterability determined by the TTF method and colloidal TOC parameters, EPS and Floc average size.

Regarding colloidal TOC parameter, the correlation coefficient found was about 0.7, which a statistically significant value at the significance level of 5%. That way, it was realized that colloidal TOC affects sludge filterability significantly so that the higher is the concentration, the longer the time required to TTF is, which indicates a sludge quality decrement.

Fan *et al*. [25] observed that colloidal TOC may be related to critical flux, a parameter used to control fouling process, and as well filterability, and defined as flux below which the membrane fouling would not take place[24]. An increase of colloidal TOC in the sludge causes a critical flux decrement. Such a phenomena is related to the increment of the potential fouling of biological sludge, which may also be related to filterability reduction. Therefore, colloidal TOC likewise filterability may be suggested as prompt, reliable and easy to use indicators to evaluate the process behavior and control MBR membrane fouling process.

It was noticed that there was also a significant correlation between sludge filterability and particle size, and EPS concentration in terms of TOC, with correlation coefficients of about -0.63 in both cases. That way, it was found that by increasing EPS concentration and floc average size there was a sludge filterability improvement. In literature there is no consensus about the relation between the EPS concentration, floc size and membrane fouling process. However, this answer may be associated with the contribution of EPS in the floc formation, which improves sludge filterability. Floc size increase favors higher filterability, form less dense and compact cakes, which have a little impact on the membrane fouling process[25]. According to Mikkelsen & Keiding[9], EPS parameter is the most important regarding the sludge structure and accounts for floc stabilization, and by increasing its concentration will make the flocs less sensitive to the shearing and there will be a smaller dispersion degree of them, which would bring forth a filterability improvement as it was found in the results presented.

Over the monitoring time, it was noticed the increment of concentration of solids in the system varying from about 8 to 9 g/L, while it was observed a sludge filterability decrease, which suggested that such parameters may be related (Figure 5). However, no statistically significant correlation was found among them. Le-Clech et al. [26] studied the effect of mixed liquor suspended solids (MLSS) concentration on the critical flux behavior. Regarding MLSS, no substantial difference was found on critical flux for a shift from 4 and 8 g/L. However, the greatest critic flux values obtained for 12 g/L were appointed as indicative of the formation of a protective gel layer on the membrane surface. Rosenberger *et al.* [27] stated that the general trend of MLSS increase on fouling process in municipal applications seemed to cause less fouling at very low MLSS concentrations (<6 g/L), no impact at medium MLSS concentrations (8–12 g/L), and more fouling at very high MLSS concentrations (>15 g/L).

That way, the effect of solids on fouling process are not clear due mostly to the complexity and variability of sludge biomasses. Thus, the variation of solids evaluated in this work has not been enough to determine the effect of the concentration of solids on filterability. No significant correlation between filterability and concentration of SMP was found in the system. According to Drews[5], two samples with the same SMP concentration may exhibit very different fouling behavior because its nature as a surrogate parameter means that individual components can be present in largely varying amounts and the physical-chemical environment (Ca concentration, pH, temperature) affects properties of SMP compounds which are relevant for fouling process such as size, shape, charge, gelling potential and hydrophobicity. Therefore the fouling potential measurement regarding SMP concentration could have multiple, complex and interacting influences that could not be assessed independently on each other in full-scale trials, and often are even more difficult to be separated in the lab.

Based on the results obtained, it was noticed that filterability along with other sludge parameters may be used to forecast, monitor and control fouling process in the system being studied.

3.3.4 **Filterability test towards sustainability in MBR operation**

The stable long-term operation of membrane processes is imperative. Performance declination is both, inconvenient and costly. The major limitation is membrane fouling process that influences the selection of conditions for long-term sustainable operation[28]. That way, fouling process control allows for the process optimization, which cuts down power consumption, and extends membrane lifetime as maintaining membrane cleanliness demands further capital equipment (Capex) and operating costs (Opex)[29].

Therefore, filterability has the potential to forecast and control fouling process, and it is an easily determined parameter when compared to other factors reported in the literature. Sludge filterability decrement may be a warning to help implement some strategies to improve sludge quality such as adding permeability improvers, coagulants or adsorbents, effluent pretreatment, and other procedures carried out before a significant membrane fouling membrane takes place, which will reduce the chemical cleaning demand, and the MBR operational cost. As pointed out by Gil *et al.*[3], a good sludge filterability allows for a more sustainable and reliable MBR performance, and low power consumption.

3.4 Conclusions

The study showed that from the three filterability methods examined, namely Time to Filter (TTF), Filter Test (FT) and Sludge Filtration Index (SFI), TTF test was the most efficient to measure filterability for its greater capability to sense sludge quality variations, and as well for its higher reproducibility. The FT was the one that attained the poorest outcome regarding the parameters being evaluated.

Based on the permeability monitoring results together with filterability, it was reasoned that filterability may be used as a tool to monitor and to help control MBR membrane fouling process, which demonstrates that reactional liquid quality has a direct influence on membrane surface fouling process.

By checking the filterability behavior for sludge properties, significant filterability correlations among colloidal TOC parameters, EPS and floc average size were found. So, the filterability has the potential to forecast and control the fouling process so that its use along with other parameter will allow for process optimization, lower power consumption and longer membrane lifetime, which will contribute to MBR sustainable operation.

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4. LONG TERM EVALUATION OF DIFFERENT STRATEGIES OF CATIONIC POLYELECTROLYTE DOSAGE TO CONTROL FOULING IN MEMBRANE BIOREACTOR TREATING REFINERY EFFLUENT

4.1 Introduction

Refining is a highly water consuming process, and thus it accounts for a massive effluent production. Usually, 246 to 340 liters of water are spent to refine a barrel of crude oil, which produces an effluent volume that varies from 0.4 to 1.6 times larger than the volume of processed oil as a by-product according to Alva-Argáez *et al.*[1]. Besides the large effluent volume produced, it’s worth also emphasize the wide variety of organic and inorganic compounds found in it. The increase in costs of the water, water and wastewater treatment, and in some cases, even the water supply shortage together with the limits set by environmental law that have become increasingly restrictive, the pressure of the sector for eco-friendly sustainable practices have pushed petroleum refineries to implement wastewater treatment systems.

To treat refinery effluents a combination of conventional physical, chemical and biological processes have been applied, however such systems have not been capable to produce water according to the quality standard required to be reused, and therefore the wastewater treatment plants must strive to implement improvements in order produce higher quality reusable water. Membrane bioreactors (MBR) have been widely implemented to treat industrial effluents due to their higher capability to remove organic matters and inorganic pollutants from wastewater compared to conventional processes. The main MBR advantages are their high capability to remove micro pollutants, persistent organic pollutants, and additionally, their low sensitivity to the load variation, low sludge production, high sludge age, full suspended solid removal, among other advantageous outcomes. Nevertheless, membrane fouling formation remains as a restricting factor for the implementation of this wastewater recycling technology.

Membrane fouling formation take place due to the adsorption of molecules of solutes and matters over the membrane surface, consequent pore clogging caused by such suspended particles and material that end up making an obstructive cake [2]. Fouling process is influenced by a series of factors related to the system feed, membrane and operating conditions, and it’s determined by the membrane trend to be fouled by compounds carried by the liquid that accumulate over the internal and external membrane structures [3]. Fouling formation has a direct effect upon the permeate flux and/or the system pressure differential, which comes to require higher power consumption, more frequent cleaning procedures, membrane shorter lifetime and therefore, raise the system operating overall cost. Thus, monitoring and furthermore, controlling fouling formation process is all-important to make effluent treatment by MBR technically and economically feasible.

Many studies have endeavoured to associate the permeability decrease caused by fouling formation with sludge properties. For example, Chang *et al*. [4], Judd [2] and Drews [5] presented a review on sludge parameters regarding floc sizes, Volatile Suspended Solids (VSS), EPS, SMP, among others, and how they relate to bioreactor membrane fouling formation likeliness. According to these works, due to the biologic system complexity, such conclusions have often been controversial, and therefore they may not be directly applied to other systems.

To mitigate MBR membrane fouling formation, many methods may be applied such as low flux operation, crossflow filtration (membrane aeration), and physical cleaning procedures like relaxation, backwash or pulse, and chemical cleaning procedures. Another alternative is the addition of certain chemicals that modify the mixed liquor, both sludge flocs and mixed liquor supernatant, through mechanisms like adsorption, coagulation and/or flocculation, to significantly reduce membrane fouling formation without changing membrane surface characteristics.

The use of agents to control fouling formation over the membranes such as diatomaceous earth, powdered activated carbon, Fe^{3+} or Al^{3+} salts, inorganic polymeric substances, organic polyelectrolytes, natural organics has been discussed in many studies [6-9].

Some biopolymers have been developed as membrane performance enhancer agents to react with the biomass in MBR. They usually feature a cationic net that reacts with the biomass, decreasing the amount of biopolymers, increasing particles sizes, changing the cake structure on the membrane surface, and allowing for a uniform distribution of the compounds over the cake layer regarding bacterial cells, polysaccharides and proteins. They may be used as a operating tool aimed to improve sludge microbiologic condition, ensure high and stable permeability, promote an operating flux increase, reduce pressure difference through the membrane, reduce the amount of fine particles disperse in the medium, reduce the cleaning frequency requirement, and reduce the EPS and SMP concentration without impairing the biologic treatment and oxygen transference to the medium [10-12].

According to bench and pilot scale studies carried out by Yoon e Collins [12], polysaccharide levels were reduced by half, while the flux increased significantly. Different from the membrane filtration with no such agent addition, fouling formation proportions over the membranes were found to be almost constant regardless the flux, and vary from moderate to higher than the critical flux.

Dizge *et al.* [13] carried out a study in which they evaluated the influence of adding comercial membrane performance enhancer agent, MPE, on the filterability and on MBR fouling reduction. They used four types of membranes of different compositions, namely cellulose acetate, polyethersulphone, mixed cellulose ester (MCE) and polycarbonate with two pore sizes, i.e., 0.45–0.40 and 0.22–0.20 µm in order to evaluate the effects of MPE addition in different situations. It was observed that, in every situation there was a considerable performance enhancement of the membrane filtration, and was also found that the adherence of biological flocs to the membrane took longer to take place by adding antifouling agents, which improved considerably the initial flux, and as well increased permeate volume.

In literature, most articles on the use of membrane performance enhancers to control MBR membrane fouling have reported the effectiveness of these products on bench scale, and often on batch mode, or on short-term filtration processes treating domestic wastewater or synthetic domestic wastewater. However, Iversen *et al.* [14] remarked that dewaterability measurements and short-term filtration tests have sometimes overestimated, or even incorrectly predicted the effects of fouling reducers on real MBR operations. In their investigation, synthetic polymers such as MPE 50 and Adifloc KD452, for example, showed similar, but much smaller effects in pilot scale trials in comparison to batch tests. Another even more striking example is related to the starch. This natural polymer showed a very high dewaterability improvement, and short-term filterability in batch experiments, while a detrimental effect on the permeability trend was found in more extended pilot scale trials.

Furthermore, the optimal chemical dosage determination has usually been based on MLSS concentration, however the optimal concentration not only depends on MLSS but also on some other mixed liquor characteristics. Therefore, the implementation of more advanced dosing strategies, e.g., based on actual sludge characteristics or fouling propensities is required. Besides that, it’s important to study the impact of chemical addition on MBR performance in terms of biomass activity and organic and nutrient removal, since although several studies highlighted the role of flocculants on membrane fouling reduction in MBR system, as discussed above, there are insufficient data on flocculating agents influence on pollutant removal efficiency.

Moreover the evaluation of the use of membrane performance enhancer applied to MBR treating industrial effluent is rarely addressed in the literature, especially for cases of effluent with high complexity and variation of composition and load so frequent as occurs in the effluent generated in petroleum refineries.

In this context, this article aims to evaluate the long-term use of a cationic polyelectrolyte to improve the sludge filterability, and control fouling formation on the bioreactor membrane while treating effluents from refineries. Different strategic dosages of were also evaluated concerning the MBR performance without cationic polyelectrolyte addition.

4.2 Materials and methods

4.2.1 **Effluent sampling and characterization**

The effluent taken for the study has come from a Brazilian petroleum refinery. Such refinery produces turpentine, asphalt, coke, sulfur, gasoline, LPG, diesel, Kerosene-type jet fuel. The effluent is transferred to pilot facilities after being treated by an oil-water separator and flotation device. Table 7 shows the main physicochemical characteristics of the effluent from the refinery after pre-treatment.

Table 7 - Refinery effluent physicochemical characterization

Parameter	Unit	Median	Minimum	Maximum
COD	$mg.L^{-1}$	630,19	221,27	2934.66
TOC	$mg.L^{-1}$	95.91	48.11	142.60
Fluoride	$mg.L^{-1}$	0.12	0.05	0.28
Chloride	$mg.L^{-1}$	167.28	24.87	627.07
Nitrite	$mg.L^{-1}$	0.34	0.32	0.41
Bromide	$mg.L^{-1}$	0.87	0.32	1.26
Nitrate	$mg.L^{-1}$	0.75	0.33	2.67
Phosphate	$mg.L^{-1}$	2.39	1.00	63.17
Sulfate	$mg.L^{-1}$	3.04	0.24	31.66
Ammonia	$mg.L^{-1}$	27.23	9.28	64.98
Conductivity	mS/cm^2	1.38	1.05	2.52
Phenol	$mg.L^{-1}$	19.42	12.96	22.84
Oil and Greases	$mg.L^{-1}$	47.13	18.40	1130.00
Color	Hazen	226.64	73.46	473.73
Turbidity	NTU	104,00	21,70	1544,00

The effluent from the petroleum refinery is typically characterized by the presence of organic matter, oils and greases, ammonia and sulfide. The parameter value variation is due to the effluent constitution variation caused by specific process changes such as maintenance stoppages, equipment replacement, among other reasons.

4.2.2 Batch treatment test

MPE 50, a modified cationic polymer supplied by Nalco, was used as a membrane enhancer performance in this study. Initially, an optimal dosage of MPE 50 was determined. The optimal dosage was determined by means of a Jar-test in which each jar was filled up with 500mL of sludge and MPE 50 dosages of 100, 150, 200, 250, 300, 500 mg/L for jars from 1 to 6, respectively. To determine MPE 50 concentration optimal value it was carried out an evaluation of the filterability of the sludge, colloidal TOC, sludge floc size, SMP and EPS concentrations for different MPE 50 dosages.

4.2.3 **Effects of different cationic polyelectrolyte dosing strategies**

Two MPE 50 dosing strategies to improve permeability were evaluated. The first strategy, named corrective use was an application of a single MPE 50 dose when the sludge quality decay was signalized by filterability decrease. The second one, named preventive use, was a continuous MPE 50 application to prevent possible permeability decrease resulting from sludge quality decrease caused by effluent composition variations.

For such an evaluation, three MBR pilot scale plants were used, (i) Reference MBR (an MBR operated with no MPE 50 addition); (ii) an MBR with MPE 50 corrective agent use; and (iii) an MBR with MPE 50 preventive agent use. All plants comprise 90L biological tank connected in series to a 30L membrane tank in which PVDF hollow fiber modules with middle size pores up to 0.040 µm submersed with an 0.9 m^2 area are installed. All three plants were operated and monitors during 220 days under the same operating conditions: hydraulic retention time of 8 hours, sludge retention time of 45 days, permeate flux of 16 $L.m^{-2}.h^{-1}$, backwash of 15 seconds and flux of 25 $L.h^{-1}$ every 600 seconds of filtration, biological tank aeration of 3.6 L/h and membrane tank aeration of 3.0 L/h. The sludge pH has kept constant nearly 7 with a dose of a 200 ppm sodium carbonate solution and phosphor demand supplied with a 1.5 $g.L^{-1}$ sodium triphosphate solution.

In case of corrective use of membrane performance enhancer, a MPE 50 volume corresponding to the dosage set as optimal was added to the reactor when there was a sharp filtration rate decrement, while in case of preventive use of membrane performance enhancer, a initial dose of MPE 50, corresponding to the optimal dose, was added to the reactor, while an equivalent enhancer dose corresponding to the exceeding amount of the discharged sludge and its biodegradable portion (1%) was daily replaced to the MBR.

To evaluate the biologic sludge behavior with MPE 50 added, sludge samples were periodically collected and characterized regarding their filterability by Time to Filter (TTF) method [15] of which, according to previous study, proved to be the most reproducible one for this sort of effluent treatment [16], concentration of EPS (Extracellular Polymeric Substances) and SMP (Soluble Microbial Products) determined by extraction thermal method introduced by Morgan *et al.* [17] that was characterized with regard to the content of carbohydrate [18], proteins [19], and DQO, floc size (Laser Scattering Particle Size Distribution Analyzer HORIBA - LA-950V2) and colloidal TOC [20]. Digital images were obtained using a capture system and image analysis, consisting of binocular Olympus CX31 microscope (Olympus Optical do Brazil Ltda, São Paulo, SP) and camera (SC30 Color CMOS Camera for Light Microscopy, Olympus Optical Ltd. Brazil, São Paulo, SP).

The pressure and permeate flux data was daily recorded to monitor the fouling formation progress. The filtering resistance due to fouling formation was determined based on the model proposed by Choo and Lee [21].

Monitoring possible significant differences from the three MBR (reference MBR, MBR with corrective use of MPE 50 and MBR with preventive use of MPE 50 regarding their filterability, SMP and EPS, Colloidal TOC, sludge floc sizes and the behavior in relation to the load impacts, was carried out by hypothesis test for multiple independent samples. To do that, nonparametric tests, which do not depend on the frequency distribution of the population being studied, were used. Thus, to monitor possible existence of significant differences between the medians and variation of coefficient values, a *Kruskal Wallis* test was performed followed a nonparametric test for multiple comparison among the groups. To check the correlation among the evaluated parameters of the three plants, the *Spearman* correlation coefficient was determined among the variables, followed by further analysis of the correlation significance by means of hypothesis test. For all statistical analyses, STATISTICA 8.0 software was used.

4.2.4 **The effect MPE 50 use on MBR pollutant removal performance**

In order to evaluate the effect of MPE 50 on MBR performance, was analyzed the quality of effluent (feed) and permeate of each MBR, verifying the MBR efficiency to remove COD, TOC, Ammonia, Phenol, color, turbidity and oil and greases. The analyses were carried out according to the recommendation of the "*Standard Methods for the Examination of Water and Wastewater"* [22].

4.3 Results and discussion

4.3.1 Batch treatment test

Different MPE 50 doses varying from 0 to 500 mg/L were evaluated (Table 8).

Table 8 - Results of optimal MPE 50 dosage addition tests

MPE 50 Concentration (mg/L)	Filterability (s)	Floc Size (μm)	Colloidal TOC (mg/L)	SMP			EPS		
				COD (mg/L)	Carbohydrate (mg/L)	Protein (mg/L)	COD (mg/L)	Carbohydrate (mg/L)	Protein (mg/L)
0	457.56	28.8	58.32	193.86	77.62	31.31	34.58	52.38	3.50
100	82.38	63.61	38.41	138.19	82.07	20.06	15.25	48.56	2.88
200	65.03	91.9	29.97	130.82	57.36	16.63	29.06	50.57	1.00
250	21.88	124.58	26.82	101.78	70.85	16.94	14.33	50.63	2.25
300	17.78	152.37	25.46	105.44	80.45	19.44	32.74	48.85	0.06
400	26.59	175.26	23.82	86.13	53.77	16.00	1.45	8.11	5.06
500	15.13	227.49	22.96	91.65	17.94	16.94	0.07	2.11	4.13

As expected and according to the literature, it was found that the cationic polyelectrolyte increased floc size, while decreased colloidal TOC, SMP and EPS concentrations. Such event may be explained by the formation of larger flocs produced by a charge neutralization mechanism. When a cationic polymer is added to the mixed liquor and adsorbs onto the microbial flocs of prevailing negative surface charge, the surface charge of such flocs changes their charges from negative into neutral. By attracting each other these neutralized flocs may produce larger flocs [8]. During that flocculation process, small particles are supposedly entrapped by the flocs.

Apparently, the efficiency of the cationic polyelectrolyte regarding SMP and EPS reduction not only depends on the total amount of the different SMP and EPS species present, but also on specific SMP and EPS characteristics. It was found that protein removal was higher than carbohydrate removal at low cationic polyelectrolyte concentrations. This may be explained by the charged protein groups. However, at higher cationic polyelectrolyte concentrations, carbohydrate removal efficiency was higher than protein removal efficiency. Koseoglu *et al.* [8] found reductions by 36% and 9% in protein and carbohydrate concentrations, respectively, and by adding 500 mg/L of MPE 50 polyelectrolyte. Yoon *et al.* [12] also found that polysaccharide concentration was reduced by half by adding the same polyelectrolyte amount.

Although such findings have suggested that the highest cationic polyelectrolyte efficiency for the most part corresponded to the highest tested concentration in terms of floc size increase, colloidal TOC, SMP and EPS reduction, it may be concluded that from a given substance concentration (250mg/L) there was no significant sludge filterability change, which indicates that such concentration is enough to improve sludge quality.

Some authors take as reference to define the optimal MPE 50 dosage the amount that allows for the greatest SMP and EPS reduction. However, studies previously carried out with identical effluent indicated filterability parameter as a promising response variable to monitor MBR membrane fouling formation of a specific effluent, and found no significant influence of SMP and EPS concentration on membrane fouling formation in this specific case [16]. Thus, the concentration of 250 mg/L was taken as the optimal dosage as there is no need of a higher MPE 50 dosage to ensure a more effective SMP and EPS retention. Additionally, some authors have suggested that MPE 50 residues found in the supernatant, which were not bound to the flocs, could cause intense fouling by adsorbing over membrane surface and inside the pores [14].

4.3.2 **Effect of different strategies of MPE 50 use on fouling control**

As discussed above, the mainstream recommendation is to use MPE 50 continuously, and set the dosage depending on MLSS concentration and the portion carried away by the discharged sludge. To make the applicability of this tool feasible, it’s necessary to evaluate and implement more advanced dosing strategies to ensure more effective fouling control and stability without compromising the MBR performance to remove organic matter and nutrients, the good condition of the membrane itself, while keeping the lowest possible operational cost.

For that purpose, two MPE 50 use strategies were evaluated, i.e., corrective and preventive additions to control the fouling formation over a 220-day period to be compared to a MBR operation with no MPE 50 additions (reference MBR).

The effects of different dose strategies of MPE 50 on sludge properties were evaluated by monitoring the concentrations of colloidal TOC, SMP and EPS, and as well the sludge floc size, filterability (TTF), and fouling resistance. (Table 9).

Table 9 - Effects of fouling resistance, colloidal TOC, SMP and EPS, floc size and TTF

Parameter[a]	Unity	Reference MBR1	MBR with corrective use of MPE 50	MBR with preventive use of MPE 50
Colloidal COT	mg.g^{-1} MLSSV	2.71	2.76	1.61
SMP –Carbohydrate	mg.g^{-1} MLSSV	8.65	6.81	7.51
SMP – Protein	mg.g^{-1} MLSSV	8.33	3.66	4.07
SMP – COD	mg.g^{-1} MLSSV	24.71	26.90	18.55
EPS – Carbohydrate	mg.g^{-1} MLSSV	8.10	5.10	2.69
EPS – Protein	mg.g^{-1} MLSSV	3.30	1.97	2.07
EPS – COD	mg.g^{-1} MLSSV	15.87	10.75	11.02
Floc Size	µm	26.84	24.75	27.73
Fouling Resistance	10^{7}.m^{-1}.g^{-1} MLSSV.L	6.89	3.44	4.41
Filterability (TTF)	s.g^{-1} MLSSV.L	38.46	71.27	22.81

a- Parameters in bold letters show significant differences from the evaluated values in different MBR ($p<0,05$) at a significance level up to 0.05%.

A significant difference was found from the results regarding fouling resistance, SMP related to protein content, EPS related to carbohydrate, Colloidal COD, floc sizes and filterability when the data was evaluated by means of hypothesis tests of multiple independent samples by *Kruskal Wallis* test followed by multiple comparison nonparametric test of the groups.

Regarding sludge floc sizes, although from the statistical standpoint there was found significant differences from floc sizes in the MBR with and without MPE 50 addition, the difference observed was not relevant to evaluate the fouling formation potentiality compared to the data found in the literature and even in results found by batch tests carried out to determine MPE 50 optimal dosage [10, 11, 23]. Sludge floc size enlargement is expected as a result from load neutralization. When a cationic polymer is added to the biologic sludge, and it’s adsorbed by microbiologic flocs with prevailing surface negative charges, the superficial charge of such flocs change their charge from negative to neutral. This floc neutralization may attract other substances, which would cause the floc to enlarge [8]. The irrelevant floc enlargement found during continuous operation in this study may be due to the shearing caused by pumping the sludge from the biologic tank to the membrane tank, and vice versa, and also by the aeration rate applied.

Regarding EPS concentration, a significant difference was observed from the values found for MBR with MPE 50 added, and MBR with no MPE 50 addition compared to COD and carbohydrate measurement (Table 9) with a significant EPS reduction when MPE 50 was added. Such result was also attained by the study carried out by Lee *et al.* [23]. That result may be due to the fact that, during the flocculation process, small particles and metabolites such as EPS are entrapped by the floc, which causes a decrement of small particles and EPS available in the sludge [24].

Regarding SMP concentration in terms of COD, although SMP value in the MBR with preventive MPE 50 addition is lower than the one observed in the other MBR, such difference has not been found to be significant from the statistic standpoint, which's a behavior similar to the one observed for colloidal TOC. On the other hand, SMP concentration in terms of protein, it was observed a reduction of value in case of both, corrective and preventive MPE 50 addition. The greatest SMP portion reduction in terms of protein content in relation to SMP portion in terms of carbohydrate may be due to the loads of protein groups. Similar result was also observed by Guo *et al.* [25], Dizge *et al.* [13] e Koseoglu *et al.* [8].

Regarding the resistance caused by fouling formation, there were found significant differences from the MBR with no MPE 50 added, and other MBR with MPE 50 additions, which once more confirms the contribution of MPE 50 to the fouling formation reduction also shown for filterability values. Such finding was also noticed by Lee *et al.* [23] in their study, in which the stated that MPE 50 addition decreases the amount of biopolymers and increases the cake porosity and floc size, which would allow for littler membrane fouling formation. In the study carried out by Hwang *et al.* [11], it was notice a decrease in the resistance by more than three times attained by MPE 50 addition, and taking into account that resistance decrement caused by cake formation was the greatest responsible for the flux increase as such resistance with MPE 50 addition allowed a decrease by nearly 4 times. This occurrence may be explained by cake porosity increase when the MPE 50 is added. Dizge *et al.* [13] compared membrane resistance in cases of MPE 50 addition and no addition, and found a resistance decrease in all cases of MPE 50 addition.

Filterability parameter was the one that caused the greatest difference from MPE 50 strategies, i.e., with and without MPE 50 addition. Figure 12 shows sludge filterability profile over MBR operation times of in three MPE 50 usage conditions evaluated.

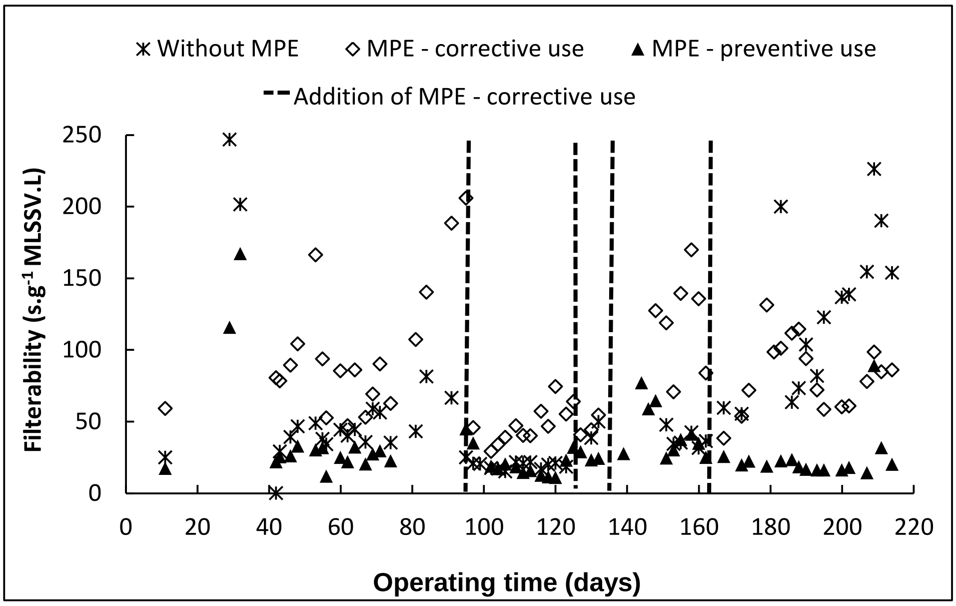


Figure 12 - Effects of different corrective and preventive MPE usage strategies on MBR sludge filtration rates (filterability).

It's been found that preventive MPE 50 addition has led to a better and more stable sludge filtration rate, which's been confirmed by statistical analyses, that is, hypothesis test for multiple independent samples based on Kruskal Wallis test method followed by nonparametric test of multiple comparison among groups, carried out in order to evaluate any possible significant difference from MBR filterability values. Significant differences have been found in all MPE 50 use conditions evaluated, i.e., with and without MPE 50 additions ($p<0,05$). MBR Sludge filterability with preventive use of MPE 50 resulted in the lowest median, that is, 23 s.g-1.L compared to values such as 38 and 71 s.g-1.L found for MBR with corrective MPE 50 addition and reference MBR, respectively. Higher MBR sludge filterability value with MPE 50 added may be related to sludge losses occurred within the period due to recirculation hose sludge leakage cause by possible cracks that result in a lower sludge MLSS concentration in the referential MBR. Although filterability value was normalized by sludge MLSS concentration, it's worth pointing out that not only MLSSV absolute value has an influence upon filterability values, but also its own composition. It was also checked whether there was a correlation of the sludge characterization regarding colloidal TOC, SMP, EPS and floc sizes and filterability data to provide support to understanding the factors associated with fouling potentiality mitigation such as MPE 50 addition. For such a purpose, the correlation coefficient of Spearman among the variables was determined, and also analysis of correlation significance was performed by hypothesis test (Table 10).

Table 10 - Results of correlation tests of characterization parameters regarding sludge and filterability

Pair of Variables[a]	Reference MBR		MBR with corrective use of MPE 50		MBR with preventive use of MPE 50	
	Spearman R	**p- level**	**Spearman R**	**p- level**	**Spearman R**	**p- level**
Colloidal TOC & Filterability	***0.736694***	***0.000002***	-0.066157	0.710087	-0.030405	0.864462
SMP (COD) & Filterability	***0.528653***	***0.024098***	0.354037	0.105985	0.062338	0.788364
EPS (COD) & Filterability	0.014919	0.951664	-0.149351	0.518188	-0.077588	0.724928
Floc Size & Filterability	-0.234742	0.280964	***-0.816609***	***0.000002***	-0.222387	0.307777

a- Values in bold letters showed significant correlation regarding the significance level up to 0.05

It’s been found significant correlations among filterability parameters between colloidal TOC and SMP (COD) only regarding the MBR evaluated with no MPE 50 added. Such result indicates that when MPE 50 is added, the sludge potential quality independent on its intrinsic characteristics.

More important than evaluating MPE 50 as a factor that allow for higher filterability average values, it’s MPE 50 capability to provide higher sludge quality stability in stress-inducing situations due to the variation of load or composition, mainly toxic compounds, for example. Such stressing conditions are very common at a refinery, and has been the main challenge to control MBR membrane fouling formation while treating this type of effluent. During MBR monitoring time reported in this study five events characterized as biologic stress-inducing factors or the combination of MBR biologic process and membranes. Table 11 shows the description of such event and its effect on filterability behavior of the three MBR in the period close to the event.

Table 11 - Description of the stress-related events occurred during the monitoring period

Time (days)	Event description	Filterability (s)[a]		
		Reference MBR	**MBR with corrective use of MPE 50**	**MBR with preventive use of MPE 50**
64th	High O&G concentration - 82 (24)[e] mg/L	**177 ±36** **(123 ± 17)**	**142 ± 33** **(63 ± 15)**	71 ± 6 (48 ± 14)
81-92th	High COD concentration - 1192 (744) mg/L [c]	**389 ± 59** **(171 ± 32)**	**703 ± 103** **(214 ± 63)**	**250 ± 63** **(70 ± 18)**
102-104th	High O&G concentration - 73 (25) mg/L	64 ± 18 (46 ± 11)	**136 ± 36** **(83 ± 12)**	**79 ± 6** **(121 ± 29)**
179-207th	High Phenol concentration - 19 (2) mg/L	**254 ± 75** **(175 ± 46)**	**507 ± 158** **(303 ± 102)**	107 ± 17 (102 ± 19)
186-204th	High O&G concentration - 519 (40) mg/L	**454 ± 114** **(175 ± 46)**	**583 ± 206** **(303 ± 102)**	90 ± 7 (102 ± 19)

a – Values between brackets correspond to the average of the parameters evaluated within the four-day period the events have occurred.

b – Values in bold letters have different significance between the values evaluated before and after the event ($p<0,05$) at a significance level up to 0.05%.

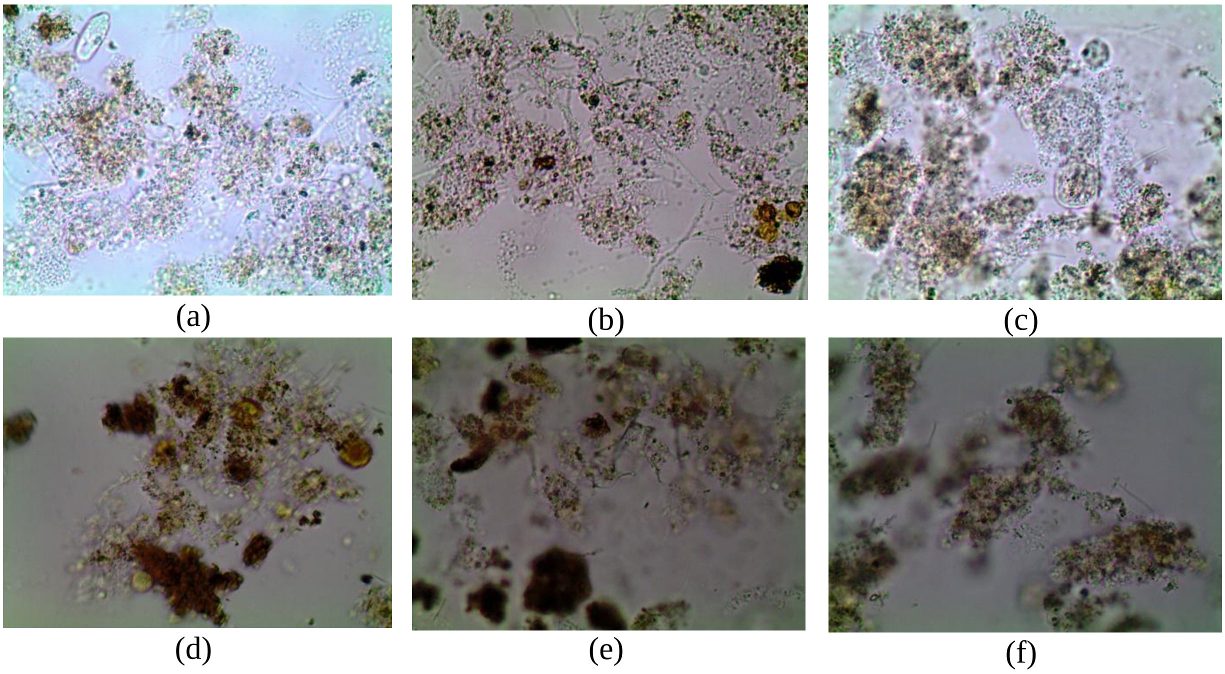
c – Over that period, phenol, oil and grease concentration values were not recorded, although it’s been estimated that, based on the data previous entries, an increase of COD was caused by the increase of these pollutants.

Amid the events observed, a more frequent occurrence of oil and grease loads was detected. Regarding MBR sludge stability associated with stress-inducing factors, it was notice that the preventive use of MPE 50 allowed for its lesser sensitivity to the load variations occurred as there was only one actual significant statistic negative difference between filterability values recorded before and after the event. Furthermore, in the case of such MBR even considering the stress-inducing factors, the filterability values have just got slightly over the filterability values considered unsuitable, i.e., (>200 s) [26]. In the case of the reference MBR with corrective MPE 50 addition, a significant difference was recorded in most of the stress-inducing factor occurrences that resulted in a significant decrease in the sludge quality with filterability values reaching values above 300 s, which’s considered critical.

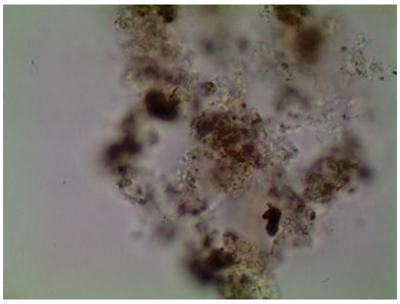
The presence of phenol in the petroleum refinery effluent makes the bioflocculation process of biological sludge more difficult by causing its deflocculation and more turbidity so that the microorganism activity is reduced [27]. High concentrations of such pollutant may bring forth some toxicity to the microorganisms, which promotes cell lysis that leads to a low sludge filtration rate and low system performance, which compromises such a system as a whole [28].

The high concentration of O&G in the effluent can lead to a number of problems to its biological treatment, including the reduction of substrate transference levels, products and oxygen between the bacterial cell and the environment through the production of a lipid layer around the biological flocs. Furthermore, it is possible the emergence of foam and a high number of filamentous microorganisms with unwanted characteristics. Likewise, a poor microbiological activity associated with an excessive concentration of O&G prevents sedimentation and causes biomass losses. These negative effects are also associated with clogging and the appearance of unpleasant odours, and are frequently associated with the reduction of the treatment system efficiency [29].

The images seen by using an optical microscope before a stress-inducing event shows an increase of biological floc density caused by MPE 50 addition [Figure 8 (c)] in comparison to the images of the sludge with no MPE 50 added [Figure 8 (a) and (b)]. After a stress-inducing event due to an oil and grease overload, it’s been noticed that reference MBR sludge and MBR with corrective MPE 50 added, which until that time had not received a MPE 50 dose addition, had some flocs presenting dark color, which suggests that they had been impregnated with oil and grease.


(a) (b) (c)

(d) (e) (f)



(g)

Figure 13 - Images of morphological characteristics of sludge obtained by optical microscopy (a) Reference MBR sludge (filterability = 180 s; MLSSV = 4,56 g/L), (b) Sludge of MBR with corrective MPE 50 added (filterability = 220; MLSSV = 4,35 g/L) and (c) sludge of MBR with preventive MPE 50 added (filterability = 89 s; MLSSV = 4,29 g/L) before a stress-inducing event; (d) Reference MBR sludge (filterability = 345 s; MLSSV = 5190), (e) Sludge of MBR with corrective MPE 50 added (filterability = 850 s; MLSSV = 4,51 g/L) and (f) sludge of MBR with preventive MPE 50 added (filterability = 126 s; MLSSV = 3,59 g/L) after a stress-inducing event; and (g) Sludge of MBR with corrective MPE 50 added after MPE 50 standard dosage addition (filterability = 62 s; MLSSV = 3,93 g/L) (Amplitude 100x)

These results suggest that MBR sludge with preventive MPE 50 added show lesser chemical attraction for oil and greases, possibly due to the hydrophilic character provided to the sludge by polyacrylamide polymers of the MPE 50. After adding a preventive MPE 50 dose [Figure 8 (g)], an agglomeration of flocs forming higher density flocs can be observed.

Regarding MPE 50 consumption occurred in different strategies, although it was expected a lower consumption in the MBR with corrective use of MPE compared to MBR with preventive use of MPE, the high occurrence rate of stress-inducing events observed over the monitoring period showed a higher MPE 50 consumption, i.e., 120 g in the MBR with corrective use of MPE 50, compared to MBR with preventive use of MPE 50 consumption, i.e., 96 g. In the case of the MBR using corrective MPE 50 4 doses of 250 mg/L of preventive MPE 50 were added to recover sludge filterability after stress-inducing events, while in the MBR using preventive MPE 50 only one dose of 250 mg/L was added and the replacement of the discarded portion and biodegraded (1%) that corresponded to as much as 0.3 g/d of MPE 50.

Therefore, it may be inferred that during the monitoring period the addition of preventive MPE 50 was more advantageous regarding MPE 50 consumption ration, and also regarding the sludge filterability optimization and stability. It’s worth pointing out that the lower MPE 50 consumption relates to this specific case. In case of a lower occurrence rate of stress-inducing events regarding the biomass, the corrective addition may prove to be the most cost-effective strategy.

4.3.3 MPE 50 addition influence on MBR pollutant removal performance

It is very important to ensure that biological treatment process will not be impaired by MPE 50 addition as the main aim of an MBR is to provide an effluent quality that meets the standards set by environmental law. Therefore, it is required to study MPE 50 addition impact on MBR performance in MBR system in terms of biomass activity, and organic and nutrient removal. Table 12 shows the main data associated with the main pollutants related to effluents that are inherent to the removal process of each MBR over the monitoring period.

Table 12 - Characterization and removal of pollutants

Parameter	**Unit**	**Feed**[a]	**Permeate**[a]			**Removing Pollutants (%)**[a]		
			MBR 1[b]	**MBR 2**[c]	**MBR 3**[d]	**MBR 1**[b]	**MBR 2**[c]	**MBR 3**[d]
COD	$mg.L^{-1}$	626.27	77.75	72.55	66.36	88.59	88.84	89.40
TOC	$mg.L^{-1}$	95.91	19.22	18.74	18.57	79.98	79.47	80.65
Ammonia	$mg.L^{-1}$	27.23	2.48	0.62	0.63	96.14	95.88	98.61
Phenol	$mg.L^{-1}$	19.42	0.07	0.09	0.07	99.66	99.60	99.86
Color	Hazen	226.64	19.96	21.19	21.87	87.57	89.60	88.48
Turbidity	NTU	104.00	0.46	0.40	0.41	99.85	99.75	99.78
O&G	$mg.L^{-1}$	47.13	0.20	0.20	0.20	99.99	99.96	99.94

a- Values corresponding to medians of concentration of parameter and removal
b- MBR With no MPE 50 added
c- MPE 50 – Corrective addition
d- MPE 50 – Preventive addition

It’s been found that there’s no significant difference between pollutant removal efficiency associated with the three MBR, which was confirmed by the statistical analyses, i.e., hypothesis test for multiple independent samples based on *Kruskal Wallis* test method followed by nonparametric test of multiple comparison among groups. Such results prove that MPE 50 addition enhances sludge filterability, and decreases the fouling formation potentiality without compromising the system pollutant removal performance.

Hwang et al. [11] also evaluated MPE 50 use as a Membrane Permeability Enhancer and observed that COD, TN and TP concentrations were very similar in both MBR, which indicates that MPE 50 addition has insignificant influence on the efficiency of biological treatment performance.

4.4 Conclusions

- MPE 50 addition increases sludge filtration rate and floc sizes, while decreasing SMP, EPS and colloidal TOC concentrations, and then decreases the membrane fouling in MBR.
- Preventive MPE 50 addition strategy allowed for a more efficient and stable sludge filterability in cases of high occurrence of stress-inducing events such as oil, grease and phenol overload, and furthermore it provided a lower MPE 50 consumption.
- It’s been demonstrated that, regardless MPE 50 addition, pollutant removal efficiency by MBR is highly effective, and no significant change has been associated with of MPE 50 addition.

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5. FINAL CONSIDERATIONS

Membrane Bioreactor technology (MBR) has great efficiency in removing pollutants treating refinery effluent. The COD and ammonia removal during the monitoring time was 83% and 95 % respectively. Furthermore, the effective removal of other pollutants was also observed. The MBR technology was able to remove all acute toxicity from the effluent.

Pre-treatment is considered an important stage for the best performance of MBR pollutant removal. Improvements in pre-treatment have led to a better pollutant removal, resulting in higher quality sludge and consequently a better filterability and fouling control.

In MBR the pollutants were removed by biological oxidation and/or retained by adsorption in the biological sludge or retention in the UF membrane.

The creation of microbial products (SMP and EPS) is attested during treatment, having an important role in membrane fouling and flux decline in wastewater reuse applications.

High filterability values are related to events such as load variation or refinery effluent compositions that occur very often at petroleum refinery plants, which makes the maintenance of MBR membrane permeability a tough challenge at treating this kind of effluent. High oil and grease, ammonia and phenol concentrations have impacted the sludge quality, increased the colloidal TOC and filterability values, and consequently the fouling formation, which increased the TMP required to keep a steady flux, and also affected the MBR performance to remove COD and ammonia.

MFI (Modified Fouling Index) values concerning supernatant correspond to the majority of the MFI biological sludge. This fact proves that the soluble fraction of the mixed liquor is the main contributor to membrane fouling formation, attested by the linear regression results among SMP and MFI biological sludge. These results suggest that a possible alternative to control MBR membrane fouling treating refinery effluents may be to control SMP concentration in the environment.

The permeability decrement was followed by sludge filterability decrement. Therefore, it may be concluded that the filterability parameter, as well as other sludge parameters, can be used to forecast and monitor MBR fouling process.

The *Time to Filter* filterability method, among the ones evaluated, was the most efficient to measure the filterability in terms of capacity to sense sludge quality variation and reproducibility. *The Filter Test* method presented the worst result according to the parameters analyzed.

Significant correlations among filterability and colloidal TOC, EPS and average floc size were found, suggesting that those parameters have a direct relation with membrane fouling on the case studied.

In evaluating the effects of adding the cationic polyelectrolyte (MPE 50) to the biological sludge, it was attested that this product acts to enhance the filterability of the sludge acting in its specific proprieties, as the enlargement of the biologic floc and the reduction of the colloidal particles as SMP and EPS. Moreover, it was attested that the addition of MPE reduces significantly the resistance caused by membrane fouling, which reinforces the contribution of this product in order to reduce the membrane fouling potential.

The preventive use of MPE enables a better and more stable filterability of the sludge. This strategy involves the continuous use of the enhancer to prevent possible decrease on the permeability due to the decrease of the quality of the sludge according of the variations on the effluent composition, enable a better and more stable filterability of the sludge.

When MBR was subjected to shock loads, events characterized by the significant increase on the concentration of oil and grease, phenols and ammonia in MBR feed, it was attested that the continuous dosage strategy resulted in less sensibility to these events, evidenced by the absence of significant differences between filterabilities before and during the event.

When MPE is added, the potential quality of the sludge is independent of its intrinsic characteristics. Furthermore, it was established that independent of the product addition, the efficiency on removing the pollutants was preserved, without significant difference between the removal of the pollutants when the product is added.

The MBR technology is efficient on treating petroleum effluents. As it has high efficiency in removing pollutants, it becomes a viable alternative to the reuse of the effluent treated due to its benefits in relation to conventional treatments. The study of control tools and membrane fouling minimization in this technology helps to understand the process as well as its optimization. Therefore, knowing the mechanisms of pollutants retention and removal, sludge filterability behaviour and the effect of permeability enhancers guarantee a better economic and technical viability on using the technology.

6. RECOMMENDATIONS

The following are suggestions for further research works

- Sludge filterability evaluation in MBR treating effluent from other industrial areas, making a comparative evaluation considering which method has the best reproducibility in a wide variety of contexts. That verifies which characteristics of the biological sludge would more interfere in the sludge filterability and consequently on the membrane fouling.

- A comparative study of membrane fouling dynamics either with or without MPE, describing and quantifying transportation resistances due to different types of fouling.

- Microbiological evaluation and description of biological sludge regarding bacteria morphotypes, considering possible outcomes when MPE is added.

- A comparative study between MPE and other agents used in membrane fouling control, such as power activated carbon, diatomaceous earth or Fe^{3+} or Al^{3+} salts.