

POTENTIAL APPLICATION OF MEMBRANE BIOREACTOR (MBR) TECHNOLOGY FOR TREATMENT OF OILY AND PETROCHEMICAL WASTEWATER IN VIET NAM - AN OVERVIEW

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Summary

Oily and petrochemical wastewaters generated from various activities such as crude oil production, oil refinery, petrochemical industry, metal processing, car washing, etc., are one of the sources of high environmental pollution. These wastewaters were not effectively treated by the conventional activated sludge process due to their toxic and refractory characteristics. In recent years, membrane bioreactor (MBR) technology has been widely applied in various industrial wastewater treatments around the world. Therefore, it would be interesting to employ this technology for treating oily and petrochemical wastewaters in Viet Nam. This paper evaluates the feasibility of using the MBR technology to treat oily and petrochemical wastewaters. The discussions are mainly focused on the operational characteristics, fouling characteristics, fouling control strategies, and costs of the MBR technology in the treatment of these types of wastewaters. It is hoped that this paper could provide useful information for researchers and engineers to develop this novel technology to treat oily and petrochemical wastewaters in Viet Nam.

1. Introduction

Oily and petrochemical wastewater (OPW) is complex in composition. It contains high concentrations of biologically inhibitory substances such as petroleum, amines, phenols, polycyclic aromatic hydrocarbons, benzene and its derivative, among others [1 - 3]. This wastewater must be treated before discharging into the environment, otherwise its high mineral and organic content may severely pollute coastal waters, estuaries, rivers, the seashore and soil [4, 5].

Conventional oily wastewater treatment methods, including gravity separation and skimming, air flotation, coagulation, de-emulsification and flocculation and absorption all have intrinsic disadvantages such as low efficiency, high operation cost, corrosion and recontamination problems [6, 7]. More importantly, most of these conventional methods cannot efficiently remove the micron or submicron sized oil droplets. Conventional activated sludge (CAS) process is commonly used to decompose organic substances in wastewater because of its low cost and reasonable efficiency. The OPW is also currently treated by CAS with pre-treatment of oil/water separation [8]. However, it should be noted that the OPW is low in N and P compounds, the CAS process

cannot operate efficiently, as bulking and foaming tend to occur [9]. Furthermore, the high salt concentration of OPW affects the metabolism of the micro-organisms in activated sludge, attenuating endogenous respiration [10]. Similarly, in Viet Nam, OPW was usually treated by using the conventional technologies, such as: coagulation, flocculation, sedimentation, flotation, and biological methods (anaerobic and aerobic). Overall, the treatment efficiency was still low [11 - 13]. Physical treatment of oily wastewater, by such methods as a gravity separator, dissolved air flotation, etc., was not effective in removing the pollutants completely, instead they just transferred them to a more concentrated phase [5]. Moreover, the physical treatment cannot remove the soluble fraction of the wastewater which may contain toxic components such as polyaromatic hydrocarbons [3]. Biological treatment of gas station wastewater is feasible as it contains a portion of easily biodegradable components and, when mixed with domestic wastewater, it receives the essential nutrients such as nitrogen and phosphorus in the form of ammonia and phosphates, which are favourable for the growth of micro-organisms [6]. However, removal efficiency of conventional biological processes is low due to the inhibitive effects of toxic substances and hydrophobic characteristics of the oil components present in them.

Large space requirements also limit the application of conventional biological treatment [10].

In recent years, the membrane bioreactor (MBR), which couples a microfiltration (MF) or an ultrafiltration (UF) membrane with a bioreactor, has received great attention in wastewater treatment [14, 15]. The MBR offers several advantages over the CAS processes. These include excellent quality of treated water, which can be reused for industrial processes or for many secondary household purposes, small footprint size of the treatment plant, and reduced sludge production and better process reliability [1]. So far, MBR has been used for industrial wastewaters such as food processing, pulp and paper, textile, tannery, landfill leachate, and pharmaceutical wastewaters. Also, the European Commission has decided to promote the development of the MBR technology whilst funding four projects entirely dedicated to research, development, capacity building and technological transfer in regards to this promising wastewater treatment process. The four projects, namely AMEDEUS, EUROMBRA, MBR-TRAIN and PURATREAT, are supported by three different financial instruments set up by the European Commission within the sixth Framework Program and were implemented in parallel from October 2005 up to December 2009. By the end of 2009 the total number of MBR systems applied

to wastewater treatment was about 4,400 around the world [15].

However, there are limited investigations on the treatment and reuse of OPW using MBR technology [16, 17]. The MBR technology is also quite new in Viet Nam. So, it would be interesting to review the available studies of MBRs treating the OPW around the world which could be applied for OPW treatment in Viet Nam in the future.

This study, therefore, was aimed to provide an overview of the MBR technology used to treat the OPW. The present work provides information on the following aspects: fundamentals of MBR technology; factors affecting the MBR treatment of OPW. The potential application, operational conditions and costs of MBRs are also discussed. It is hoped that the information presented in this paper will be helpful for researchers and engineers in developing novel and efficient methods for OPW treatment in Viet Nam.

2. MBR technology and applications of MBR for OPW treatment

2.1. Characteristics of the MBR systems

The two main MBR configurations are shown in Fig.1. Fig.1a shows an MBR in which membranes are installed outside the aerobic tank. In this configuration the liquid-solids mixture is pumped around a recirculation loop which contains a membrane unit. The permeate is discharged and the retentate is returned to the aerobic tank. The second and third configurations of MBR have membranes which are either submerged in the aerobic tank or in the membrane tank (Fig.1b). In the submerged configurations, the air was supplied for biological processes and membrane scouring [18]. The submerged MBR is the configuration that is most often applied in wastewater treatment [15, 19].

Microfiltration (MF) and Ultrafiltration (UF) membranes are frequently employed in MBR applications for industrial wastewater treatments. The membrane configurations used are mainly tubular, hollow fibre and flat sheet (Fig.2). The membrane materials can be classified into three major categories: polymeric, metallic, and inorganic (ceramic). Ceramic membranes can be backwashed, effectively providing high resistance to corrosion and fouling control

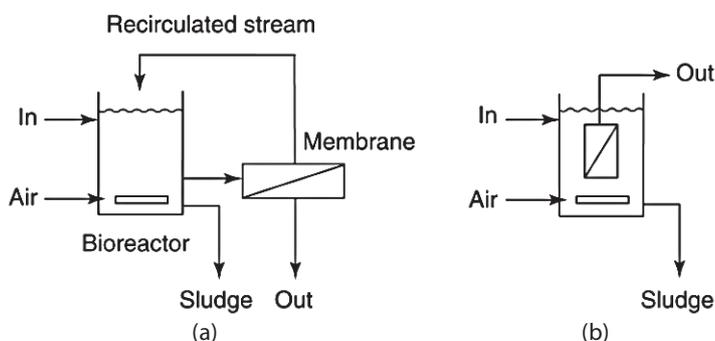


Fig.1. MBR process configurations: (a) sidestream, (b) immersed [20]

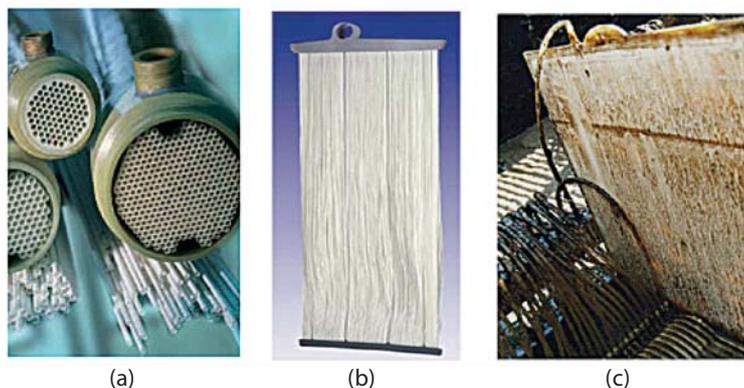


Fig.2. MBR membrane configurations: (a) multi-tube, (b) hollow fibre (c) flat sheet [21] (with permission from Elsevier publisher, License No: 3058350479403)

[22]. However, they are more expensive than polymeric membranes, such as polyvinylidene fluoride (PVDF), polyethersulfone (PES), polyethylene (PE), and polysulfone (PSf) membranes, which seem to be most widely used in present applications. The pore size of membranes used ranged from 0.01 - 0.45µm [23]. There are essentially two modes of operation of an MBR regarding operating flux: sustainable flux and intermittent operation. Modern practice appears to favour the intermittent operation at sustainable flux that limits rapid and severe membrane fouling [24]. The sustainable fluxes ranged from 25 - 140 and from 3.7 - 85 LMH for external and submerged configurations, respectively.

2.2. Characteristics of oily and petrochemical wastewater

Although OPW has a complex composition, it's characteristics can be presented by basic parameters, such as COD, BOD, SS, NH₄⁺-N, TN, TP, heavy metals, pH, color and turbidity parameters. The typical characteristics of OPW can be summarised as shown in Table 1.

As can be seen in Table 1, despite the substantial variation in results, these data provide a useful guideline for MBR system design. The OPW was high strength wastewater which can contain mixtures of hydrocarbons and oils. OPWs represent one of the most concerning sources of pollution due to their toxic and refractory characteristics. These compounds are poorly biodegradable. The currently available conventional biological wastewater treatment techniques are mostly incapable of complete elimination of the refractory hydrocarbons [31]. Therefore, introducing and developing advanced and high-efficiency wastewater treatment and reuse technologies will have profound significance in sustaining the development of oil refineries. Nevertheless,

tightening effluent regulations and increasing the need for reuse of treated water have generated interest in the treatment of OPW using MBR technology.

2.3. Application of MBR in oily and petrochemical wastewater treatments

Biological treatment technology for treating wastewater containing hydrocarbon is a favourable method and interest has focused on the application of suspended growth biological systems such as the activated sludge process, but high operating expense, weak tolerance to shock loading, and fewer settle-ability problems at high loading rates are still limiting the development of the wastewater process [20].

It should be noted that MBR is a modification of the CAS process, where the activated sludge is concentrated in a bioreactor which is connected to a membrane filtration unit. Due to the high removal efficiency of oily pollutants and the complete retention of suspended solids by the membrane unit, the MBR system shows good potential for application in industry for process wastewater recycling purposes [31].

In this part, some important examples of the MBR technology applied to oily and petrochemical wastewaters are presented. The feasibility of an MBR process to treat petrochemical-contaminated wastewater by using synthetic wastewater containing either fuel oil or lubricant oil and a surfactant was studied [31]. The MBR used in this study was composed of an activated sludge reactor connected to an external tubular cross-flow ultrafiltration unit, as shown in Fig.3.

In the study, a removal efficiency of 99.9% for fuel oil as well as lubricant oil could be achieved at the conditions

Table 1. Characteristics of oily and petrochemical wastewaters [1, 6, 25, 26, 27, 28, 29, 30]

Parameters	Type of oily and petrochemical wastewaters [from different sources]							
	[1]	[6]	[25]	[26]	[27]	[28]	[29]	[30]
pH	-	6.5 - 6.8	2.5 - 2.7	7.80 - 8.79	-	-	-	11.5
COD (mg/L)	72.1 - 296.1	500 - 1,000	55,000 - 60,000	250 - 613	4,345 - 6,864	124	280 - 215	22,250
BOD (mg/L)	90 - 188	-	30,000 - 32,000	-	919 - 1,360	52	112 - 119	-
SS (mg/L)	245 - 950	90 - 300	20 - 300	108 - 159	253 - 889	60	-	613
NH ₄ ⁺ -N (mg/L)	12.05 - 19.79	-	-	56 - 125	-	-	13.5 - 19	-
TP (mg/L)	0.82 - 2.96	-	102 - 227	< 0.5	-	-	5.0	-
O & G (mg/L)	20 - 87	400 - 1,000	360	35 - 55	-	78	17	641

of an HRT of 13.3hr, influent with 500 - 1,000mg/L hydrocarbons. The permeate quality was so high that the effluent can be reused in the industrial process. The results clearly showed that the MBR process enhanced permeate quality due to biodegradation of pollutants.

Wastewater from gas stations is characterised by a high concentration of oil-water emulsion which cannot be effectively removed by a conventional gravity separator. An experimental investigation on the treatability of oily wastewater from gas stations using MBR system was studied [32]. The experimental schematic diagram is presented in Fig.4. The results obtained from this study revealed that MBR systems could achieve good removal efficiency with stability against shock loading. Optimum operating conditions were found to be at a hydraulic retention time of 4hr and an oil loading rate of 1.8kg oil/m³.day.

Another important study was that of a UF process followed by an MBR system facility used for treatment of OPW from an automobile engine manufacturing plant [27]. After the upgrading, 90% COD and complete oil, grease and phenolics removals were achieved. This contrasts with the widely fluctuating results in the past. Although most of the reported studies have been conducted on the aerobic MBR and excellent COD removal has been obtained, utilisation of anaerobic MBR in oily and petrochemical wastewater treatment has some inherent benefits. The use of anaerobic MBR for OPW has

also been studied [33]. In this study, an OLR of up to 25kg/m³.day was observed with an effluent COD normally lower than 500mg/l, corresponding to over 97% COD removal. The OLR was much higher (0.5 - 3kg/m³.day) than that obtained in aerobic ones.

A hybrid of anaerobic and aerobic processes with membrane filtration was conducted to investigate the treatment process of OPW [1]. A schematic diagram of the process flow and pilot plant setup is presented in Fig.5. The results showed that the removal rates for COD and BOD were stable and averaged 92%. The average removal rates for NH₄⁺-N, oil and turbidity were shown to be 93.7%, 75.3% and 94.6%, respectively. The removal rates for TP, TSS, SS and phenol were shown to be greater than 98.5%, 97.9%, 93.8% and 99.9%, respectively. This demonstrated that MBR technology had a superior treatment effect on the above contaminants.

3. Design and operational conditions for MBR systems

3.1. Hydraulic and sludge retention times

Overall, OPW contains a high organic strength resulting in high COD loads. Therefore long hydraulic retention times (HRT) are needed to achieve high biological performance of the MBR system. Typical anaerobic and aerobic HRTs for MBRs used for OPW treatment were in the range of 2 - 10 days and 0.5 - 3 days, respectively [1].

Sludge retention time (SRT) is another important

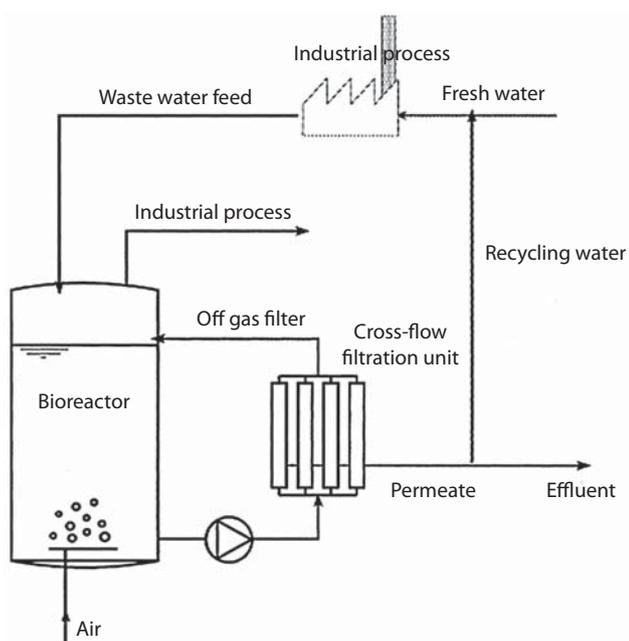


Fig.3. Schematic of the MBR system used for OPW [31] (with permission from Elsevier publisher, License No: 3058350739834)

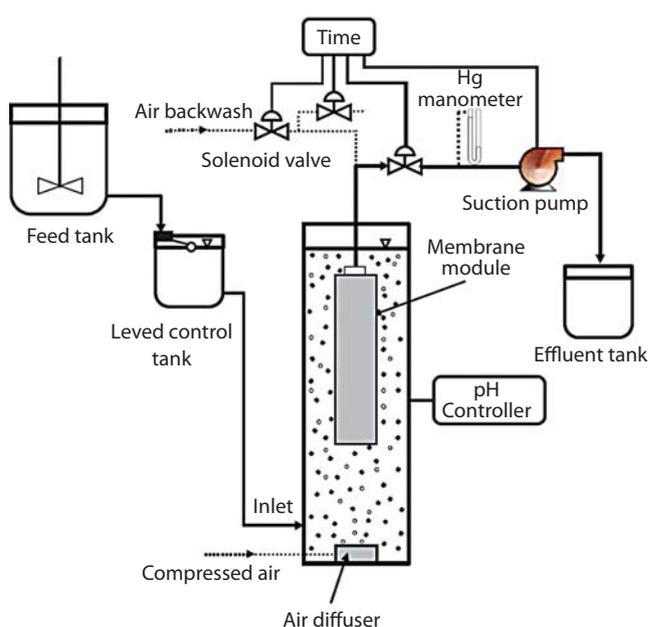


Fig.4. Experimental setup for the MBR [32] (with permission from NRC Research Press, License No: 3058351422976)

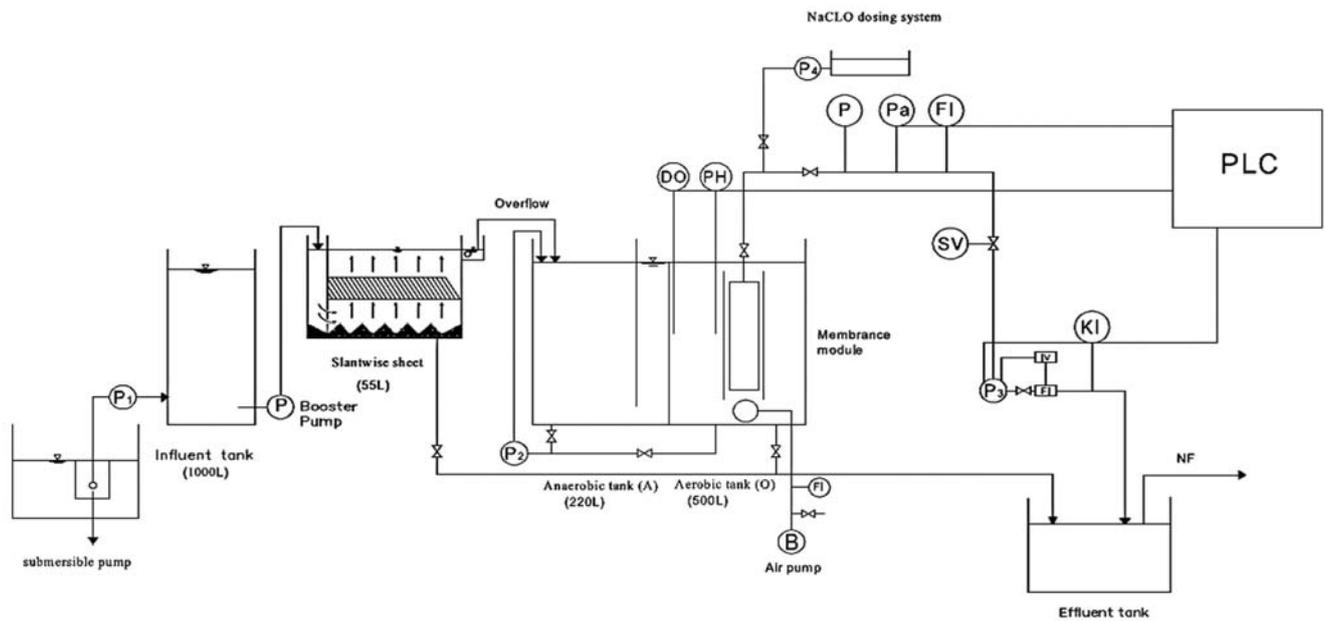


Fig.5. Schematic diagram of the A/O MBR for wastewater treatment [1] (with permission from Taylor & Francis, License No: 3058340986675)

operational parameter. MBR was normally operated with long SRTs and low F/M ratio for reduction of sludge production. However, an increase in SRT would induce an increase in MLSS in the reactor which could have an effect on membrane fouling and could reduce the microbial activity [34]. The proper SRT for MBR systems should be controlled at 20 - 50 days, but highly depends on HRT and the feed characteristics. Typical MLSS values are in the range of 12,000 - 15,000mg/L in submerged MBR [17].

3.2. Operational pH and temperature

Most MBR systems are operated at near neutral pH. However the pH of the OPW is varied largely as shown in Table 1. Therefore, neutralisation and equalisation at a desired pH would be required. The bioaugmentation of an alkaline-tolerating culture in a CAS system that suffered from shocks up to pH 12 is possible [35]. So, similar attempts could be made in MBRs because they are all activated sludge processes.

Most aerobic MBRs are operated at ambient temperatures around 20 - 30°C, whereas anaerobic ones are usually operated at elevated temperatures of 30 - 40°C. An increase in temperature could affect the organic removal efficiency. However, MBRs operated at thermophilic temperatures always show a deterioration of membrane flux although a high flux is anticipated because the flux is inversely proportional to the fluid viscosity [18, 36]. Attention should be paid to improve the membrane flux under thermophilic conditions.

3.3. Membrane fouling control

Membrane fouling represents one of the most challenging issues constraining the more extensive applications of MBRs. Briefly, membrane fouling could be caused by pore clogging by colloidal particles, adsorption of soluble compounds and biofouling, deposition of solids as a cake layer, and the spatial and temporal changes of the foulant composition during a long-term operation [37]. All the parameters involved in the design and operation of MBR processes affect membrane fouling. These factors can be classified into four categories: feed characteristics, biomass characteristics, membrane characteristics, and operational conditions [38]. Optimisation of reactor and module design was also found beneficial to membrane fouling control. With respect to aeration, bubbling requirements for MBRs are typically split into fine bubbles for aeration and larger coarse bubbles for fouling control [39].

3.4. Costs for MBR systems

The overall costs of MBR systems are represented by the sum of the capital, operation, and maintenance costs. The capital costs mainly include costs of membranes, tanks and plant equipment. The operation costs are mainly costs of energy demand, sludge treatment and disposal, and chemical usage for membrane cleaning. The maintenance costs mainly refer to the cost of membrane replacement.

It should be noted that costs of energy demand, sludge treatment, and disposal for a large-scale hollow fibre

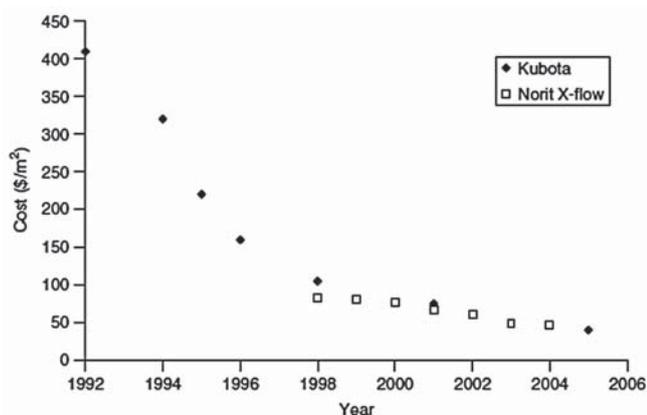


Fig.6. Microfiltration membrane replacement costs [43] (with permission from Elsevier publisher, License No: 3058351142243)

submerged MBR accounted for 79.6%, 17.9% and 2.5% of total operation costs, respectively [40]. Energy consumption rates between 0.2 and 2.4kWh/m³ were reported for the submerged operation of municipal and industrial wastewater treatments, and the aeration cost accounted for more than 80% of total energy consumption [17]. The aeration rate and membrane flux would significantly affect operational costs [21]. Therefore, the balance of flux and aeration rate represents a fundamental aspect of MBR design and operation. Membranes themselves represent a significant cost for the full-scale application of MBR systems. Membrane investment costs accounted for 25 - 50% of total capital costs, whereas the membrane replacement cost was about 25 - 33% of total operation and maintenance costs [18].

In general, the cost for MBR technology is higher than conventional activated sludge processes such as CAS and SBR due to the introduction of membranes. However, the membrane life could be up to 11 years [41]. So, if the membrane service time is extended, the costs of membrane replacement would be reduced significantly. In addition, the production cost of membranes decreases significantly year after year [42]. It appeared to have decreased exponentially over the past 10 - 15 years, with whole life costs decreasing from 400USD/m² in 1992 to below 50USD/m² in 2005 as shown in Fig.6 [43]. The rapidly decreasing membrane cost is an important driving force for the widespread application of MBRs.

4. Conclusions and Remarks

Based on the information reviewed from various literature sources it was concluded that MBR technology appears to be a prospective technology for OPW treatment. The treatment can be performed using the

Abbreviations

BOD: Biological Oxygen Demand
 CAS: Conventional Activated Sludge
 COD: Chemical Oxygen Demand
 DO: Dissolved Oxygen
 F/M: Food to Microorganisms ratio
 HRT: Hydraulic Retention Time
 MBR: Membrane Bioreactor
 MF: Microfiltration MLSS: Mixed Liquor Suspended Solids
 N: Nitrogen
 OLR: Organic Loading Rate
 OPW: Oily and Petrochemical Wastewater
 P: Phosphorus
 SRT: Sludge Retention Time
 TMP: Transmembrane Pressure
 UF: Ultrafiltration

submerged MBR or side-stream MBR. The OPW treated by using MBR can produce product quality that consistently meets the requirement for discharge.

However, MBR systems still face several challenges when applied to OPW treatment. It is worth noticing that application of the membrane fouling control strategies represents the involvement of the operational cost, energy, and manufacturing issues in the MBR systems. Therefore, some key remaining issues need to be addressed in the application of the MBR technology to the treatment of OPW such as the effect of high concentration of oil and grease in the feed on the biological process and membrane fouling; also the effect of pre-treatment on oil before the wastewater enters the MBR system. Besides, there is a scarcity of economic evaluation applied in the field based on full-scale applications. These limitations should be overcome to push the development of MBR technology in OPW treatment.

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