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Investigation of Membrane Filterability in Membrane Bioreactors for Treating Oil Refinery Wastewater

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Abstract
The evaluation of critical flux and pollutant removal in a lab-scale submerged membrane bioreactor (MBR) was performed for the wastewater of a domestic oil refinery. The flux step method and its behavior vs. transmembrane pressure (TMP) were studied to determine the critical flux of the membrane and the effect of TiO_2 nanoparticles (NP) incorporation into polyvinylidene fluoride (PVDF) matrix on the membrane filterability. The effectiveness of MBR for treating effluent stream of dissolved air floatation (DAF) unit of the Tehran oil refinery wastewater plant was studied, and the results showed that TiO_2 NP improved the efficiency of phenol removal. Ultimately, according to this study, 70 % enhancement in the critical flux of the PVDF/TiO_2 membrane was obtained as a result of TiO_2 NP tendency to reduce the fouling of PVDF membranes.

Key words: Membrane Bioreactor, Critical Flux, PVDF Membranes, TiO_2 Nanoparticles, Oil Refinery Wastewater.

Introduction
Oil and gas industries produce a large amount of wastewater, which is considered as the major source of pollution in this field and contains different components such as oil, salts, aromatics, organic acids etc. There are two main approaches to overcome the pollution problems that are called: (1) reinjection to the discharging wells and (2) treatment [1]. Because of water shortage problems in most oil field areas, treatment has received more attention. In this way, the treated water can be reused after the removal of contaminants. Methods and equipment like gravity separators (API), hydrocyclones, centrifuges, and membranes have been already used to remove oil from petroleum refinery wastewater [1]. A process that has recently gained more attention in the treatment of refinery wastewater is membrane bioreactor (MBR) [2-6], which can be an alternative to the activated sludge and coagulation/flocculation steps in conventional wastewater treatments.
MBR with about thirty-year background in the field of wastewater treatment was developed based on the combination of the membrane filtration and the activated sludge process [7]. High-quality effluent, the possibility of reusing treated water, no need for a secondary clarification, and smaller footprint are remarkable advantages that motivated researchers to consider the application of MBR in the treatment of various industrial wastewater [3,7-12]. However, membrane fouling is still the major challenge of the technology and has been the subject of numerous researches that have studied the various aspects of the issue and different approaches of its reduction or control [10, 13-16].
Generally, there are different strategies to reduce the fouling of the membranes in MBRs which include: the methods to optimize (1) the operating conditions (e.g., sludge retention time (SRT), hydraulic retention time (HRT), the mixed liquid suspended solids (MLSS)) and (2) the aeration as a way to remove sediments from the membranes, (3) the efficient ways of fouled membrane cleaning and the suitable chemicals thereof, (4) the improvement regarding biological issues. In addition, new fouling mitigation methods in MBRs such as application of electricity or vibration, and development of the so-called "engineered membranes" most of them containing nanoparticles (NP) designed and fabricated to be less prone to fouling are the other options for reducing the fouling of the membranes in MBRs [13,17].

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Silver, zinc oxide, and titanium dioxide (TiO_2) nanoparticles, carbon nanotubes, graphene, graphene oxide, fullerenes, and their derivatives were applied in various forms to mitigate the membrane fouling in the MBRs [13]. The effect of hydrophilicity enhancement to reduce membrane fouling in MBRs has been pointed in various researches [18,19]. Other characteristics, such as the antimicrobial or photocatalytic ability of such nanoparticles, show a synergistic effect in fouling control. Despite of the complications related to the UV irradiation in a turbid environment of bioreactors and the packaging of the membrane modules in the MBRs, as well as limited photocatalytic activity of TiO_2 embedded membrane, unique properties of TiO_2 have made it attractive for researchers [20-24].
One of the important operational factors in MBR fouling is the critical flux, that is defined as the flux above which the cake layer formation on the membrane surface is seen [25,26]. Hence, to prevent the cake layer formation on the surface of the membrane, it is important to determine the critical flux and operating at a flux below which. In such circumstances, the rate of TMP increase is not high enough to require chemical cleaning of the membrane. This results in the sustainable operation of MBR and enhancement in the critical flux of MBRs. Moreover, not only does it have a direct impact on the sizing criteria and lead to design smaller MBR plants, but it also reduces the number of membrane cleaning during MBR operation [27].
In this research, the critical flux and filterability of the TiO_2/PVDF membrane were investigated in MBRs for treating oily wastewater. To the best of our knowledge, it has not been studied in previous literature.

Materials and Methods

MBR setup and wastewater specification

The experiments were performed using a membrane bioreactor setup, which is schematically illustrated in Figure 1. The system was equipped with two exactly the same features, including 5 L bioreactors, peristaltic pumps, and control instruments to provide the same test conditions for each membrane. The activated sludge was supplied by the MBR plant located in the wastewater treatment unit of the Research Institute of Petroleum Industry (Tehran, Iran). This plant was fed with real wastewater as a representative of aromatic wastewater containing phenol that was obtained from the effluent stream of the dissolved air flotation (DAF) unit of the wastewater treatment plant of Tehran oil refinery, Iran. The actual wastewater conventional treatment system of this petroleum refinery consists of three main steps: (i) primary step with an API oil-water separator followed by a dissolved air flotation (DAF) unit, to remove suspended solids and oil, (ii) secondary step with a biological system of aerated lagoons to remove mainly biodegradable organic compounds and ammoniacal nitrogen, and (iii) a stabilization lagoon to solids deposition. The specifications of three kinds of refinery wastewater corresponding to different weather and operational conditions in the Tehran oil refinery were presented in Table 1.

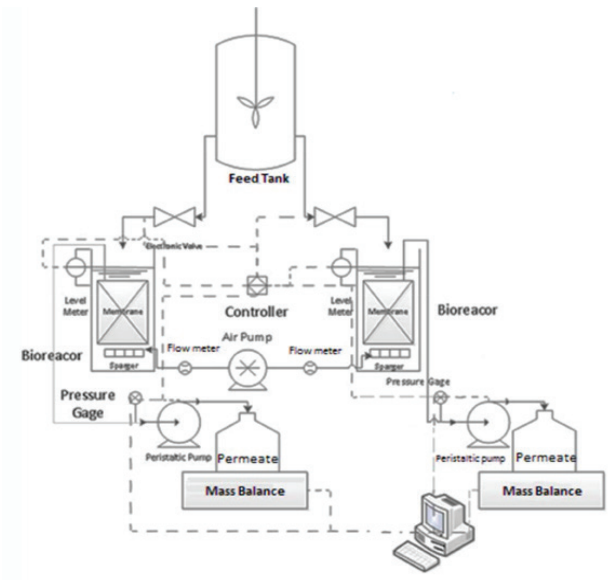

Fig. 1 MBR setup for investigation of the membrane filterability for oil refinery wastewater.

Table 1 Wastewater specification.

Wastewater type	Turbidity (NTU)	TSS ($mg.L^{-1}$)	TOC ($mg.L^{-1}$)	Oil & Greece ($mg.L^{-1}$)	Phenols ($mg.L^{-1}$)	COD ($mg.L^{-1}$)
1	69	184	157	37.35	292	353.5
2	95	230	138	19	424	343
3	40.5	188.5	200	34.5	320	451

The sludge was fed with real wastewater and sedimented to reach the mixed liquor suspended solids (MLSs) amount of 10 g/L. Generally, large particles do not have any significant roles in membrane irreversible fouling since most of them are removed by aeration during the MBR operation. However, the fine particles in the activated sludge and the wastewater have the main role inirreversible fouling. Hence, it is very important that the membrane-less prone to irreversible fouling and with appropriate pore size in the MBR plants be used. To find out the particle size distribution and charge characteristics of the activated sludge and wastewater, the particle size and zeta potential have been evaluated using Dynamic light scattering (DLS) analysis with a Malvern®, UK Zetasizer. The particle size distribution of activated sludge was determined after the microfiltration of the large particles by PTFE syringe filters. The particle size distribution and zeta potential of the refinery wastewater and activated sludge are shown in Figures 2 and 3, respectively.

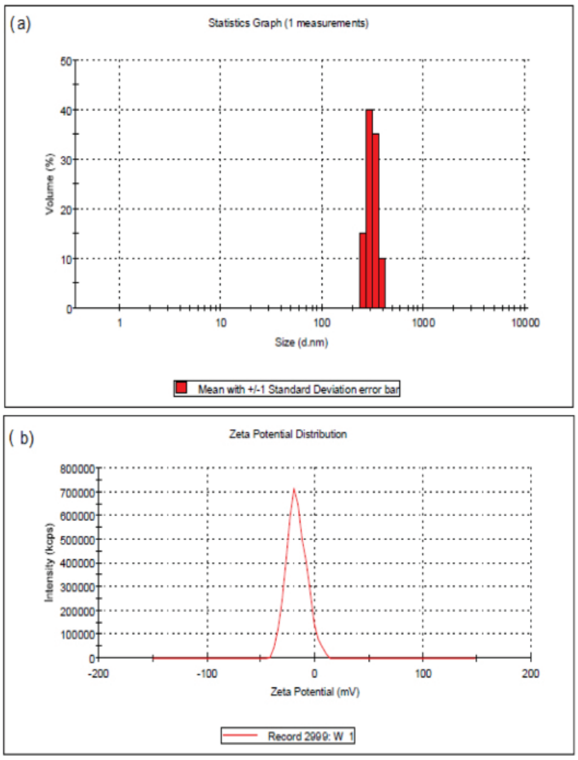

Fig. 2 Wastewater type 1 (a) particle size distribution (b) zeta potential.

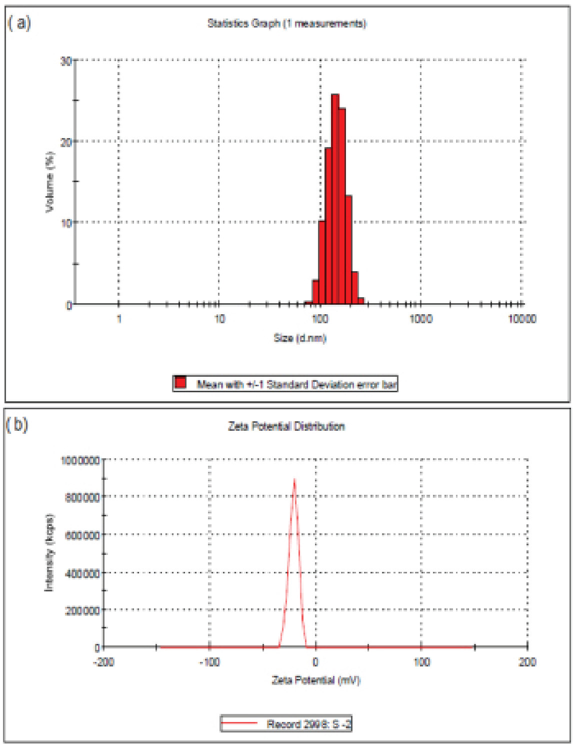

Fig. 3 Activated sludge (a) particle size distribution (b) zeta potential

Membrane specifications and filtration test procedure

Two Polyvinylidene fluoride (PVDF) ultrafiltration membranes, prepared via phase inversion method as a collaborative research work by Mohsenpour et al. [28-30], were fixed on flat Plexiglas sheets modules and submerged in bioreactors, as illustrated in Figure 4. The membrane fabrication steps briefly include (1) drying polymers and additives in a vacuum oven, (2) preparing a homogeneous solution dope of polymer, solvent, and additives, (3) degassing the dope solution in the vacuum oven, (4) casting the solution on polyester support with the thickness of 220 µm and (5) finally completing the coagulation by immersing the films in a water bath. The specification of the membranes was summarized in Table 2. As can be seen, the incorporation of TiO_2 nanoparticles improved the hydrophilicity and the permeability of the PVDF membranes, to some extent, which was discussed in detail in the previous article [28]. Also, permeate was extracted through nuzzles on the top of the membrane modules by suction provided by the peristaltic pumps.

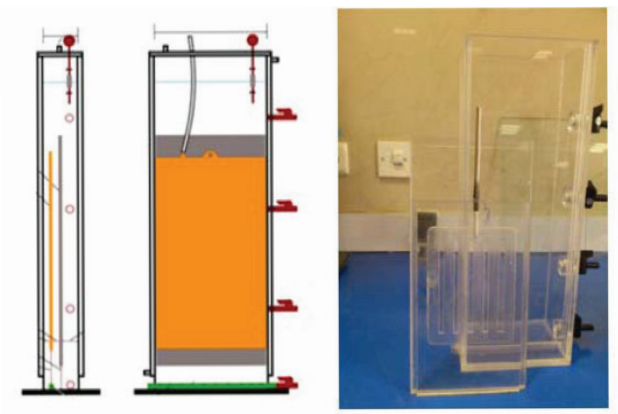

Fig. 4 Membrane module submerged in the bioreactor.

Table 2 PVDF Membrane specifications.

Membrane	PVDF (wt.%)	PVP (wt.%)	TiO_2 (wt.%)	Flux (LMH)	Contact Angle°	Pore size	Porosity	Reference
M1	15	1	0	230	81.4	49.8	0.79	[28]
M2	15	1	0.5	250	76.4	48.6	0.81	

The pore size of the prepared membranes was adjusted not larger than the size of the smallest particles of the activated sludge and the wastewater. Zeta potential of the prepared membranes was measured using streaming potential measurements performed with electrokinetic analyzer (Anton Paar, Austria) [31]. For all the membranes, the zeta potential was determined at sodium chloride concentrations of 0.001 M and a pH of 7.4.

To determine the critical flux of each membrane, the flux stepping method, as explained by Tiranuntakul et al. [27], was used. While using the flux stepping method, it is assumed that by increasing the flux, fouling the membrane occurs, so the TMP increases, and it decreases again when the flux reduction begins. Hence, the amount of TMP is measured in each flux period in two cycles of upwards and downwards until it reaches a TMP amount, which exceeds 10 percent difference in each cycle, and the mean value of the corresponding fluxes can be taken as the critical flux [27].

Results and Discussion

SMP-EPS measurement

To investigate the effect of TiO_2 of the PVDF membrane on bioreactor activated sludge microorganism, total SMP and EPS were measured during the MBR operation, and the results are illustrated in Figure 5. As can be seen in the figure, TiO_2 had no significant effect on the microorganism destruction or growth, since the amounts of SMP and EPS remained almost stable during MBR operation for both membranes.

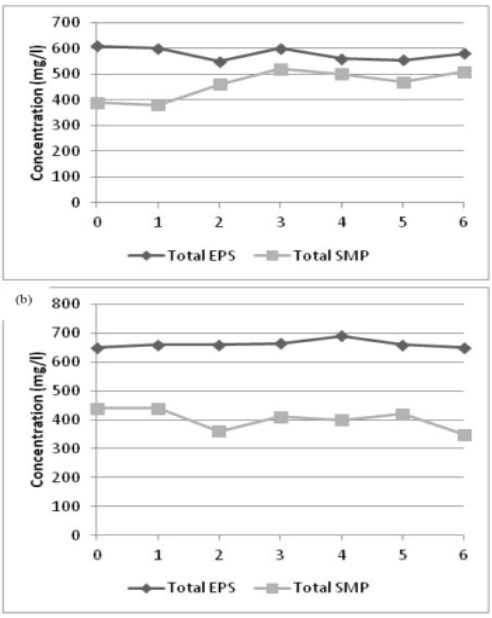

Fig. 5 Total SMP and total EPS variation with time for bioreactor with (a): M1 and (b) M2 membrane.

Phenol and COD Removal

In Figures 6 and 7, the membrane influence on phenol and COD removal efficiency in the MBR, for each type of wastewater is shown respectively. The role of the PVDF/TiO_2 membrane is more significant in phenol removal than COD. This phenomenon can be interpreted by the presence of TiO_2 in the membrane matrix. Furthermore, the effect of radiation sources on the TiO_2 photocatalytic degradation of phenol was studied by Shawabkeh et al., and their study demonstrated that such photocatalytic degradation is possible under visible light (e.g. the sun) and even in darkness with less degradation percentage.

Hydroxyl radicals are responsible for phenol photocatalytic degradation on the PVDF/TiO_2 membrane surface [32]:

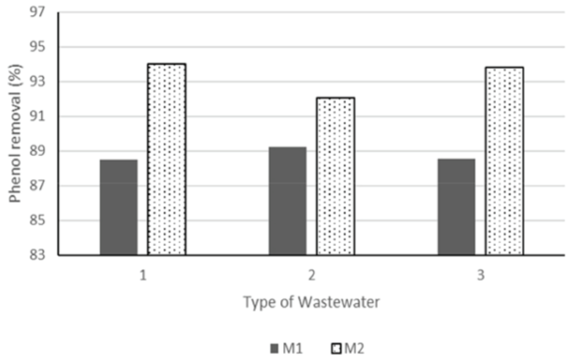

Fig. 6 Phenol removal efficiency.

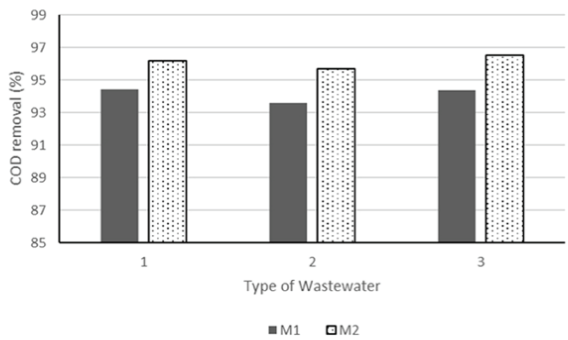

Fig. 7 COD removal efficiency.

The MBR effluent specifications for each membrane were shown in Table 3. For COD and phenol concentration in the range of 343-451 and 292-424 mg/L respectively, the removal percent is about 88-96%. For both containments, the membrane containing TiO_2 nanoparticles showed better removal percentages, which were more effective in the case of phenol. However, as can be seen, no clear relation between contaminant content (COD and phenol) and membrane operation was found with these data, and further investigation will be required to obtain a definite conclusion about this issue, which will be the subject of our future research.

Critical Flux Determination

The critical flux is an important factor in MBR operation, and any improvement of it has a positive effect on the MBR performance. In this section, by using the flux stepping method and the deviation of the flux curve versus pressure from linearity, the influence of incorporated TiO_2 on the critical flux of the PVDF membrane was studied. First, flux has been increased with 4 $L.m^{-2}.h^{-1}$ steps until a considerable TMP increment with a sharp slope is seen. Such flux stepping procedures for M1 and M2 membranes are illustrated in Figures 8 and 9, respectively.

Table 3 MBR effluent specifications.

Wastewater type	Membrane type	Turbidity (NTU)	TSS ($mg.L^{-1}$)	TOC($mg.L^{-1}$)	Oil and Greece($mg.L^{-1}$)	Phenols ($mg.L^{-1}$)	COD ($mg.L^{-1}$)
1	M1	0.25	Trace	7.5	0.3	33.58	19.67
	M2	0.18	Trace	6.2	0.2	17.52	13.54
2	M1	0.55	Trace	25.4	0.3	45.62	21.93
	M2	0.38	Trace	20.67	0.17	25.45	14.70
3	M1	0.27	Trace	10.05	0.45	36.75	25.42
	M2	0.15	Trace	8.36	0.32	19.85	15.62

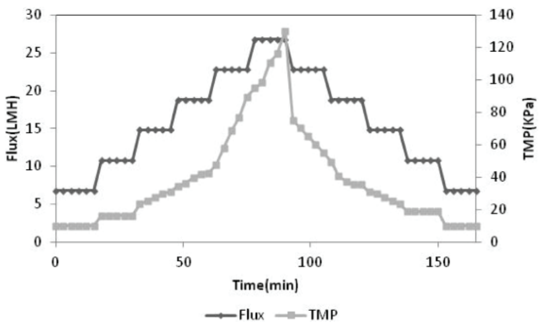

Fig. 8 M1 membrane Flux and TMP variation trend.

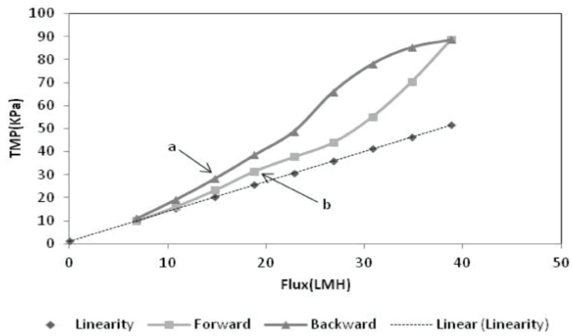

Fig. 10 M1 membrane fouling reversibility trend.

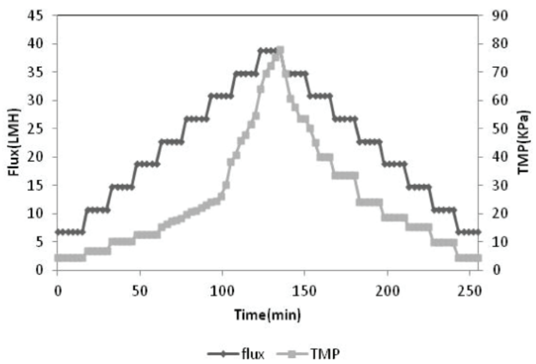

Fig. 9 M2 membrane Flux and TMP variation trend.

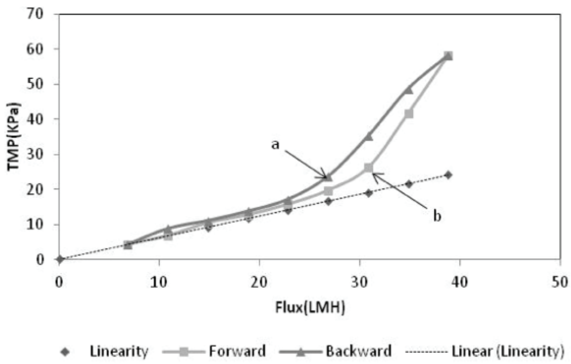

Fig. 11 M2 membrane fouling reversibility trend.

As shown in the figure, for the M1 membrane flux increment from 15 L.m-2.h^{-1} resulted in increasing the slope of the TMP curve, and the fouling trend accelerated. The TMP value at the flux of about 30 L.m-2.h^{-1} reaches its maximum value, which shows the flux increment should be terminated, and the flux decreasing trend should be started. In the case of M2 membrane flux, an increment from 23 $L.m^{-2}.h^{-1}$ resulted in increasing the slope of the TMP curve, and the fouling trend accelerated. The TMP value at the flux of about 40 $L.m^{-2}.h^{-1}$ reaches its maximum value.

The results of the fouling reversibility method, which is illustrated in Figure 10, show that the critical flux is laid between two fluxes of 14.8 L.m-2.h-1 and 18.8 $L.m^{-2}.h^{-1}$ since the difference between TMP in the upward and backward in point “b” is more than 10 percent of the TMP in this point. While such amount in point “a” is less than 10 percent. Hence, the critical flux of M1 is 16.8 $L.m^{-2}.h^{-1}$.

The results of the fouling reversibility method, which is illustrated in Figure 11 show that the critical flux is laid between two fluxes of 26.8 $L.m^{-2}$.h-1 and 30.8 $L.m^{-2}.h^{-1}$. The mean value of these two fluxes equals 28.8 $L.m^{-2}.h^{-1}$, which is the critical flux of M2. The presence of TiO_2 nanoparticles in the PVDF membrane improved the critical flux of about 70%.

While the impact of TiO_2 nanoparticles on the flux and hydrophilicity enhancement of the PVDF membrane (as shown in Table 2) was not so impressive, but its role in fouling reduction was more significant. This phenomenon could be interpreted based on Zhang et al. findings, which concluded that membrane surface zeta potential showed a more significant impact on interactions between particle foulants and membranes compared to hydrophilicity [33]. The measured zeta potential values of the prepared membranes in this study are -19.75 and -31.6 (mv) for the neat PVDF and PVDF/TiO_2 membranes, respectively. As illustrated in Figure 2, both the activated sludge and wastewater in this study have negative charges, and by increasing membrane surface charge as a result of the incorporation of TiO_2 nanoparticles, the created repulsive force prevents foulant from adhesion to the membrane surface. The results confirmed previous research that the surface charge of the membrane plays a much more important role than other surface modification strategies such as hydrophilicity enhancement in fouling mitigation of MBRs [33-35].

Conclusions

In this study, the effect of TiO_2 nanoparticles on PVDF membrane filterability of mixed liquor in MBRs for treating oil refinery wastewater was studied. It was found that the fouling of the TiO_2/PVDF membrane was reduced compared to the neat PVDF membranes, and it showed a higher critical flux while TiO_2 nanoparticles embedding in the membrane matrix did not affect the growth or destruction of the microorganism of the bioreactor. Furthermore, the results showed that the presence of TiO_2 nanoparticles improved phenol removal, but it was less effective for COD removal in the MBRs. Ultimately, it can be concluded that the effect of TiO_2 incorporation in the membrane matrix was more significant in fouling reduction than permeability improvement and the surface charge of the membrane played a much more important role than other surface modification strategies such as hydrophilicity enhancement, in fouling mitigation of MBRs.

Nomenclatures

DAF: Dissolved air floatation
HRT: Hydraulic retention time
MBR: Membrane bioreactor
MLSS: Mixed liquid suspended solids
NP: Nanoparticles
PVDF: Polyvinylidene fluoride
SRT: Sludge retention time
TMP: Transmembrane pressure

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