Journal of Environmental Health Science and Engineering (2021) 19:1015–1023
https://doi.org/10.1007/s40201-021-00666-1

RESEARCH ARTICLE

Magnetic MBR technology: from the fabrication of membrane to application in wastewater treatment

Mohammad Reza Mehrnia[1] · Targol Hashemi[1] · Aydin Marandi[1]

Received: 24 February 2021 / Accepted: 5 April 2021 / Published online: 16 April 2021

Abstract
The aim of this study is to synthesize a magnetic nanocomposite membrane using iron oxide and alumina nanoparticles and employing it in magnetic membrane bioreactors (MBRs) for oily wastewater treatment. Al_2O_3 and Fe_3O_4 nanoparticles with approximate sizes of 20 and 30 nm respectively, were settled into a polysulfone (PSf) membrane matrix via magnetic casting method. The concentration of alumina and iron oxide nanoparticles were 0–0.25 wt% and 0.03 wt%, respectively. Compared with the blank membrane, an increase in the concentration of Fe_3O_4 up to 0.2 wt%, led to the flux as much as 70% and mitigated total resistance by 70%. The presence of the magnetic field around the bioreactor increased the flux significantly and reduced the cake resistance by 93%. Moreover, by applying the static magnetic field to MBR, the Chemical Oxygen Demand (COD) removal rate was increased to 93%, while in the MBR without the magnetic field the COD removal rate was 80%. Our investigation illustrated that the magnetic casting is an effective method to improve the flux and mitigate the fouling of the magnetic nanocomposite membrane. The output of this research indicates that the magnetic casting method enhance the magnetic MBRs performance for wastewater treatment.

Keywords Fe_3O_4 nanoparticle · Al_2O_3 nanoparticle · Magnetic casting · Fouling · Magnetic membrane bioreactor

Introduction

A membrane bioreactor as a combination of bioreactor and membrane [1], has appeared as a wastewater treatment technology of choice over the activated sludge process (ASP). MBR as one of the most important novation [2–4], and powerful tools [5] has been used recently for the industrial and urban wastewaters treatment. Compared to the conventional processes, MBRs have many benefits such as small footprint, better effluent quality, and low sludge production [6]. Apart from advantages, the major impediment of MBR is membrane fouling [2]. Membrane fouling by dissolved organic matter is an inherent problem in the ultrafiltration (UF) treatment of various effluents [7]. Fouling effect is reduced the membrane performance and lifetime significantly, lead to an increase of its maintenance [8, 9], and significantly prevents the widespread application of MBRs [10]. In recent years, the mitigation of membrane fouling and investigation of the strategies for its reduction have been an objective of many studies [11]. The methods to mitigate fouling in the membrane bioreactors can categorize in two major groups: changing the operational conditions and altering the membrane structures [3, 12].

The application of hydrophilic particles in the membrane structure has been studied in recent years [13]. Metal oxide nanoparticles are the most suitable hydrophilic additives used to reduce the fouling within the membrane structure and improve the membrane performance [14–16]. By embedding the nanoparticles into a polymer structure, they offer their inherent properties in the membrane [17], and can influence on the structure, surface, and physicochemical properties, particularly hydrophilicity of the membrane [13]. Up to now, alumina nanoparticles, titanium oxide nanoparticles, silver and zinc nanoparticles, and iron oxide nanoparticles have been used in the structure of nanocomposite employed in MBR [15, 18–21]. Iron oxide nanoparticles have been used for the formation of magnetic nanocomposite membranes. The magnetic property has also been exploited by changing the hydrodynamic conditions to mitigate fouling in the membrane bioreactor [22].

✉ Mohammad Reza Mehrnia
mmehrnia@ut.ac.ir

[1] School of Chemical Engineering, University College of Engineering, University of Tehran, P.O. Box 11155-45, Tehran, Iran

In recent years, in some reported studies the external forces (such as electric or magnetic fields) have been used in the membrane casting process to promote the enrichment of inorganic particles and improve the membrane performance [23–27]. Daraei et al. [23] reported during membrane preparation, a magnetic field can make the magnetic Fe_3O_4 nanoparticles move along the magnetic field direction, subscribing the increase of water flux and rejection. Huang et al. [24] studied the effect of parallel magnetic fields on the performance of Polyvinylidene fluoride (PVDF)/Fe_3O_4 membranes during membrane formation and the results showed that the membrane performance (in terms of flux) is increased significantly. In other studies, [25, 26], Fe_3O_4/GO (Fe_3O_4/Graphene oxide) nanocomposite membranes was prepared under the magnetic casting condition. Compared to the pristine and other modified membranes, the higher hydrophilicity, water flux, and high flux recovery ratio was obtained.

Also, the combination of membrane fouling reduction strategies in magnetic MBR (by changing the membrane structure and operating conditions) has been an attractive idea. In this system, by using the magnetic nanoparticles in the presence of magnetic field, a magnetic membrane is created which is sensitive to the magnetic field. The applied magnetic field can affect the structure and porosity of the membrane and create some movements. By applying a magnetic field on the membrane sheets, a moving membrane module can reduce the amount of fouling with the magnetic field changing. This performance led to a reduction of the filtration resistance compared to the conventional MBRs. [22, 28, 29].

However, the polymeric membrane containing nanoparticles have better performance than the blank polymeric membranes. However, there are some limitations for using them, due to the accumulation of nanoparticles in high amounts. Therefore, relate to usual polymeric membranes, magnetic casting could be a new method to increase the membrane acceptance capacity of nanoparticles. Furthermore, applying a magnetic field to the membranes containing nanoparticles, can improve the morphology as well as the performance of the membrane in the magnetic MBR. This study investigates the magnetic casting and evaluates the performance of magnetic hydrophilic nanocomposite membrane with a high amount of Fe_3O_4 nanoparticle loading. Also, the efficiency of magnetic MBR for oily wastewater treatment is evaluated.

Materials and methods

Materials

Polysulfone (average MW 7500 Da) (purity 15 wt%) was purchased from Acros Organics and used as the main polymer for the membrane fabrication. N-Methylpyrrolidone (NMP) (purity 75 wt%) as the solvent, Polyethylene glycol (PEG) (average MW 2000 g/mol) (purity 10 wt%) as a pore former were obtained from Merck. Fe_3O_4 and γAl_2O_3 (average size 30 and 20 nm, respectively) were purchased from Neutrino. COD vial that for the membrane analysis was made by Merck (100–150 mg COD/Lit). Kerosene was used as a wastewater effluent in the MBR.

Preparation of Fe_3O_4-Al_2O_3 nanocomposite membrane

The nanoparticles were dispersed into the N-methylpyrrolidone in ultrasound bath. Polysulfone resins were gradually added to organosol at 70 °C and mixed for 10 h. The return distillation system was used to prevent solvent evaporation and remove solvent vapors from the media. Having ensured the homogeneity, a casting solution containing 15 wt% of the polymer was prepared. The desired membrane was cast on a glass plane using a casting knife with a thickness of 350 μm. A 500 mT static magnetic field under the glass was applied to the molded membrane and exposed to the magnetic field for 5 min in fresh air and room temperature. Next, it was immersed in a water coagulation bath at 25 °C for 24 h to form the membrane. According to the previous research [12], the ratio of alumina nanoparticles to polysulfone assumed 0.03 wt%, explained by details in "Cross-sectional structure" section.

The specification of the fabricated magnetic casting membrane reports in Table 1.

The filtration tests in a membrane bioreactor system

In order to investigate the performance of the synthesized magnetic nanocomposite membranes and the treatment of synthetic oil effluent, the prepared membranes were placed inside a membrane bioreactor with an active volume of 7 L. The bioreactor contained two submerged flat sheet modules and had an effective membrane area of 28.2 cm^2. One of the

Table 1 The concentration and specification of the magnetic casting nanocomposite and blank PSf membranes placed inside the magnetic membrane bioreactor

Membrane name	Fe_3O_4/PSf ratio	Al_2O_3/PSf ratio	Contact angle (°)
blank	0	0	81
0.03 Al_2O_3	0	0.03	50
0.03 Al_2O_3–0.03 Fe_3O_4	0.03	0.03	53
0.03 Al_2O_3–0.1 Fe_3O_4	0.1	0.03	54
0.03 Al_2O_3–0.15 Fe_3O_4	0.15	0.03	55
0.03 Al_2O_3–0.2 Fe_3O_4	0.2	0.03	46
0.03 Al_2O_3–0.25 Fe_3O_4	0.25	0.03	42

modules kept the magnetic nanocomposite membrane and exposed to.

the magnetic field with a frequency of 50 Hz and maximum intensity of 600 mT. The other modules act as a control, keeps the membrane devoid of nanoparticles at a long distance from the magnetic field.

Filtration was done at a constant TMP of 0.3 bar (300 kPa) using a vacuum pump and aeration was performed by sparger with tiny bubbles. A fixed discharge pump with a flow rate of 29.0 L/h was used to keep the hydraulic residual time constant. The contaminant in this study was kerosene. According to the previous reported studies the general formula of kerosene defines as $C_{11}H_{22}$ [30–32]. Kerosene is a non-polar compound and almost insoluble in water. The solubility of kerosene in water is 5 mg/L at 20 °C, while kerosene is soluble in organic solvents [33].

In this study, the synthetic wastewater model is an oil effluent. To prepare this effluent and dissolving the kerosene in water, we combined kerosene (700 mg/L) as an oil medium and about 5 wt% of kerosene from Archopal N10 (ethoxylated nonylphenol) as a surfactant, together. [34, 35]. According to the method described in the "Measurement of chemical oxygen demand (COD)" section, the amount of COD of synthetic effluent was measured equal to 2000 mg/L. By adding water to the effluent, the input COD level always remained constant. In this reactor, the pH was 7.45, sludge retention time (SRT days) was infinite, the MLSS (Mixed Liquor Suspended Solid) was 10 g/L, and the COD was 2000 mg/L.

Analysis of membrane fouling

The degree of membrane fouling was calculated quantitatively using the series resistance model [18]:

$$J = \frac{\Delta P_T}{\eta R_t} \quad (1)$$

Where, J is the output flux (m^3/m^2 s), ΔP_T is the transmembrane pressure (Pa), η is the viscosity of the output solution (Pa s), and R_t is the total resistance of the filtration (m^{-1}).

The total filtration resistance is the summation of the membrane's intrinsic resistance (R_m), the cake resistance caused by the cake layer formed on the membrane surface (R_c), and the fouling resistance developed in response to the closure of pores and irreversible absorption of contaminants against the walls of the pores and the membrane surface (R_f) [36]:

$$R_t = R_m + R_c + R_f \quad (2)$$

Where these resistances can be calculated by the experimental data and using the following equations:

$$R_m = \frac{\Delta P_T}{\eta J_w} \quad (3)$$

$$R_f = \frac{\Delta P_T}{\eta J'_w} - R_m \quad (4)$$

$$R_c = \frac{\Delta P_T}{\eta J_f} - R_m - R_f \quad (5)$$

In these relations, J_f is the flux in MBR, J_w is the initial flux of water, and J'_w is the final flux of water following the removal of the cake layer through physical washing.

Scanning electron microscopy (SEM) analysis

The morphology of membrane samples was investigated by the SEM device (Hitachi, Model: S4160, Japan). For cross-sectional observation, the membrane samples were broken using liquid nitrogen. All samples were dried at room temperature, coated by a thin layer of gold (to become conductive), and prepared for observation by SEM. Moreover, SEM images were combined with energy-dispersive. A scanning electron microscope performed X-ray analysis (Philips, XL30ESEM, Netherlands) operated at 30 kV.

Contact angle analysis (CA)

The membrane surface hydrophilicity and the presence of iron oxide nanoparticles were evaluated by water contact angle measurement. To this aim, firstly the surface of membranes was washed and then dried. After that, a drop of distilled water was instilled on the clean and dry membrane surface at 25 °C. Using the contact angle device (Camera Model SJA-833, PAL), the membrane surface was filmed. With the aim of minimizing the experimental error, the contact angle was measured for two times and averaged for each sample.

Measurement of chemical oxygen demand (COD)

The source of activated sludge used in the MBR was taken from the wastewater treatment plant of Ekbatan Co., for adapting the sludge, 60 days before the trials. For this purpose, a special COD vial (made by Merck) and a spectrophotometer device (made by Multy) were used. Due to the low measurable COD range, the samples were diluted 20 times with deionized water.

Opening pore size and distribution

The porosity of the fabricated membranes was investigated by SEM analysis of the membrane microphotography, prepared from pristine membrane surfaces [37].

Results and discussion

The performance of the synthesized nanocomposite membranes (described in Table 1), was evaluated in a magnetic MBR by altering the concentration of nanoparticles and the presence of the magnetic field.

The effect of the concentration of nanoparticles on the nanocomposite membranes structures and MBR performance

The effect of the concentration of nanoparticles was investigated on the membrane structure and performance of the membrane bioreactor. The structure, flux, and fouling resistances in the studied magnetic MBR was studied to evaluate the membrane behavior in the presence of nanoparticles.

Cross-sectional structure

SEM images reveal the effect of the presence of alumina nanoparticles on the membrane morphology. Figure 1 provides a comparison of membrane structure in the presence and absence of alumina nanoparticles. In part A, in the presence of alumina nanoparticles, the length of the finger pores is increased, and the membrane pores align with each other. In contrast, in part B, in the absence of alumina nanoparticles, the finger pores are narrower and irregular orientations are seen between the pores. In this case, the flux through the membrane expects to decrease. Other researchers also have investigated the effect of the presence of Al_2O_3 nanoparticles on the membrane structure. The results of our previous studies [12, 38, 39] show that the length of finger pores increases due to the presence of alumina nanoparticles.

Alumina nanoparticles are a good choice for hydrophilizing the membrane surface due to their special hydrophilic properties [38]. Based on the previous study [12], in the presence of 0.03 wt% of Al_2O_3 nanoparticles on the substrate of PSf polymer, we saw the optimal conditions on the MBR morphology and membrane performance. In this regard, the pure water flux in 0.03 wt% of alumina increased up to 4 times compared to the membrane without nanoparticles. Therefore, according to our previous study [12], the composition of alumina nanoparticles was considered constant at 0.03 wt%. Moreover, due to the inertia of the magnetic field on these nanoparticles and their placement on the membrane surface, they were used as hydrophilic agents to increase the hydrophilicity of the synthesized membrane surfaces.

Figure 2 also shows that the increase of nanoparticles amounts and weight percentage, cause the accumulation of nanoparticles as well as decreases the size of pores. A study by Homayoonfal et al. [39] also points out that increasing nanoparticles lead to reduce the amount of porosity and membrane flux. In fact, nanoparticles act as coagulation accelerators, and effect on the viscosity of the casting solution by increasing the concentrations. Also, they reduce the coagulation as well as membrane porosity. Decreased porosity of the nanocomposite membrane in presence of nanoparticles has also been observed in other reports [40, 41]. Initially, in the presence of a limited amount of nanoparticles the porosity estimates about 40% which improved compared to the blank membrane. As mentioned above, in the case of further increase of nanoparticles, the porosity will reduce to 20–25% due to the agglomeration.

Flux and resistance

The flux of nanocomposite membranes in the MBR has been presented in Fig. 3. As can be observed in this Fig by enhancing the amount of nanoparticles up to 0.2 wt% for Fe_3O_4 and 0.03 wt% for Al_2O_3, the flux has an increasing trend due to the high hydrophilicity and considerable length of the finger pores. By adding more nanoparticles, the flux will reduce because of the accumulation of Fe_3O_4 in the lower layers of the membrane. In another study [22], the results showed that increasing up to 0.07 wt% of iron oxide nanoparticles, membrane flux was improved by 30%. While in the present study, the highest percentage of Fe_3O_4 nanoparticles is 0.2 wt%. Therefore, it can be said that the magnetic casting method

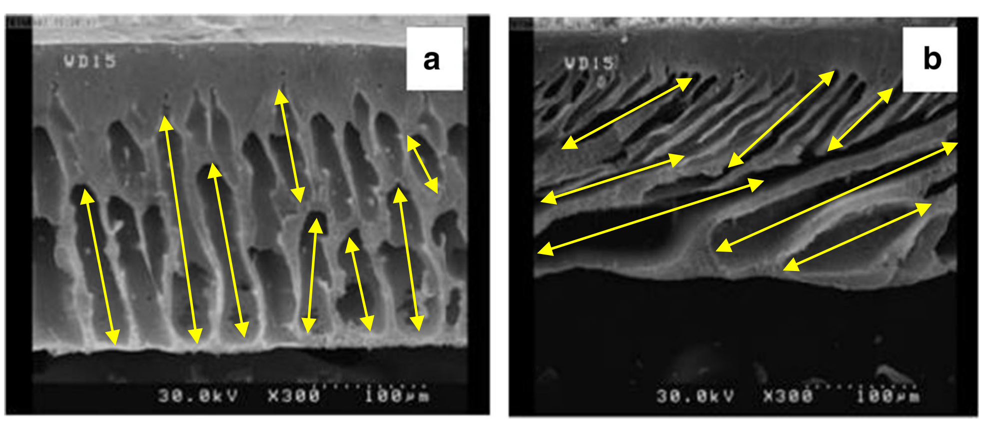

Fig. 1 SEM images of the effect of presence and absence of alumina nanoparticles on the cross-section of the membranes A: 0.03 Al_2O_3–0.15 Fe_3O_4, B: 0.15 Fe_3O_4

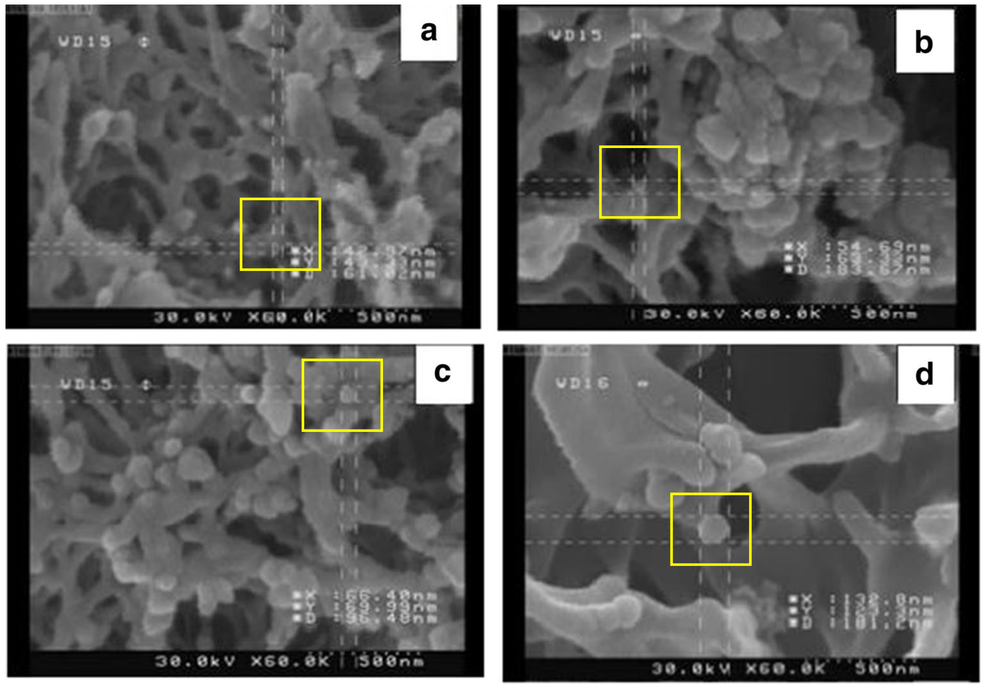

Fig. 2 SEM images of the cross-section of the membranes containing different concentrations of nanoparticles A: 0.03 Al_2O_3–0.1 Fe_3O_4, B: 0.03 Al_2O_3–0.15 Fe_3O_4, C: 0.03 Al_2O_3–0.2 Fe_3O_4, and D: 0.03 Al_2O_3–0.25 Fe_3O_4

increases the flux up to 70% compared to the blank membrane. In other studies [23, 42], the highest flux amount was observed in the presence of 0.1 wt% of Fe_3O_4 on the polymer substrate. The results showed that an increasing amount of nanoparticles leads to particle aggregation and reduces the flux. Our results illustrated that the presence of a magnetic field during casting of the membrane would significantly affect the filtration performance.

The roughness of the membrane surface, the reduction of flux, and the porosity of the membrane (due to the adhesion of nanoparticles in high percentages) are the most important disadvantages of adding nanoparticles to the membrane structure at high amount concentrations [23–27]. This drawback has been noticed as one of the problems of adding nanoparticles.

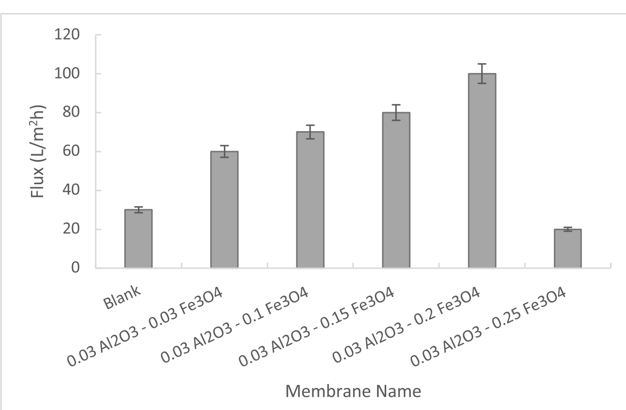

Fig. 3 The effect of concentration of nanoparticles on the membrane flux in the MBR

In this study by using magnetic casting as a novel method, we tried to increase the acceptance capacity of nanoparticles by membrane without causing side effects on the morphology and performance. Figure 3 reveals that magnetic casting has an increasing effect on the flux of the nanocomposite membrane. This upward trend can be observed up to 0.2 wt% of Fe_3O_4 nanoparticles, and then we will have a significant decrease due to the agglomeration of nanoparticles and the reduction of membrane porosity. The amount of 0.25 wt% of Fe_3O_4 nanoparticles is so much that magnetic casting is not able to withstand. In this condition nanoparticles in the magnetic MBR hurt the structure and function of the membrane.

Figure 4 presents the filtration resistance of blank PSf and nanocomposite membranes in the MBR. According to Fig. 4, the cake layer's resistance on the membrane is the main mechanism of membrane fouling in the MBR. As a result, by increasing the nanoparticles up to 0.2 wt%, the total membrane resistance is decreased, and the lowest extent of total resistance is related to the 0.03 Al_2O_3–0.2 Fe_3O_4 membrane. As mentioned in Table 1 the contact angle of this membrane was about (46°), so the 0.03 Al_2O_3–0.2 Fe_3O_4 membrane is more hydrophilic than the blank membrane and also other nanocomposite membranes. As our group reported [22], among the investigated membranes the highest total resistance of filtration is related to the conventional polymer membrane devoid of nanoparticles. The lowest filtration resistance was related to the nanocomposite membranes, and the fouling mitigation was 48%. To compare, in this study we can reach 0.2 wt% of iron oxide nanoparticles and observe the fouling mitigates as much as 70%.

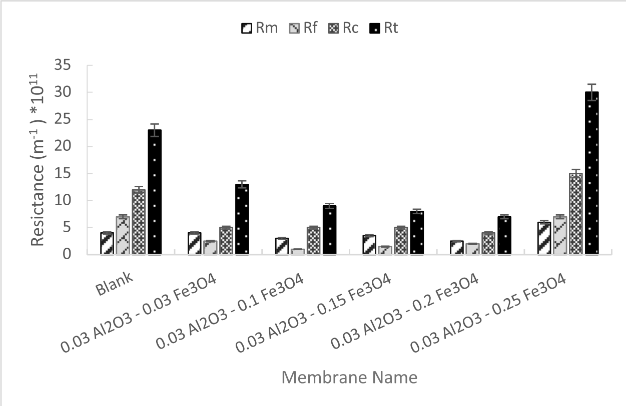

Fig. 4 The membrane (R_m), cake (R_c), pore (R_f), and total (R_t) filtration resistances of blank PSf and nanocomposite membranes in the MBR

The effect of the magnetic field on the nanocomposite membranes structures and MBR performance

The effect of the magnetic field was investigated on the structure and performance of the membrane bioreactor. The membrane behavior evaluates in response to a magnetic field's presence in terms of the structure, flux and fouling resistances in the studied MBR.

Cross-sectional structure

Figure 5 represents the effect of a magnetic field on the structure of the membrane. Generally, by increasing the number of nanoparticles and applying a magnetic field, the structure of the finger pores of the membrane is changed. Also, the presence of a magnetic field causes moving the nanoparticles to the lower layers of the membrane, and in contrast, it will increase the thickness of the membrane shell. On the other hand, the magnetic field can align the nanoparticles with each other and create a better uniform structure for the membrane.

In part A, in 0.1 wt% of Fe_3O_4 and 0.03 wt% of Al_2O_3 nanoparticles, the pores are almost aligned, and the lower layers have high porosity while the thickness of the membrane shell is small. In part B, with increasing the number of iron oxide nanoparticles, the thickness of the membrane shell is increased, and the length of finger pores is changed. In part C, the orientation of the pores at the amount of 0.2 wt% of Fe_3O_4 nanoparticles is the best condition. Furthermore, the thickness of the membrane shell, which is due to the presence of hydrophilic alumina nanoparticles, is acceptable. With further increase of iron oxide nanoparticles in part D, the loss of porous structure can observe; in this case, due to the roughness and agglomeration of nanoparticles in high percentages, the membrane performance in the bioreactor is decreased.

In the previous study of this group [22], the magnetic field effect on the membrane structure investigations. The results show that the length of the finger pores and the direction of the pores are affected by the magnetic field. Also, the direction of the magnetic field affects the orientation of the pores. In another study [43], Fe_3O_4 magnetic nanoparticles mention factors, increased the membrane porosity and permeability. The results also show that iron oxide nanoparticles place along the magnetic force line by applying a magnetic field. The dimensional size will change their magnetic striction; thus, they may bring the skin layer and pore structure deformation.

Flux and resistance

To evaluate the efficiency of the synthesized membranes in MBR, we placed the synthesized nanocomposites in the MBR and compared this situation related to the blank situation.

Figure 6 shows the effect of applying a magnetic field with 600 mT on the MBR flux. The results revealed that in the presence and absence of the magnetic field, the flux is increased. As described in "Cross-sectional structure" section, with an increase of iron oxide nanoparticles up to 0.2 wt% and a constant amount of 0.03 wt% of alumina nanoparticles, the length of the finger pores is changed, and the porosity is improved. Under this condition, the membrane hydrophobicity and flux in the MBR is increased. As mentioned in our previous study, although the percentage of nanoparticles was low and the casting method was different, it increased flux and decreased the fouling observe. Besides, in the presence of a magnetic field the alignment of magnetic nanoparticles in the membrane affects the flux rate; Fig. 6 shows a significant difference between the presence and absence of a magnetic field on flux. Jian et al. [43] investigated the effect of a magnetic field with an intensity of 500 mT on the Fe_3O_4/PSf membrane. The results showed that the magnetic field had low effect on the flux rate. Therefore, our research results show that by increasing the intensity of the magnetic field, as much as 100 mT, the flux can significantly increase. In this regard, the previous research of this group [22] shows an increase about 80% in flux using magnetic field in the range of 40 to 100 mT.

On the other hand, the vibration of the membrane under the magnetic field may increase the flux rate, following reduce the intrinsic resistance of the membrane [28].

Figure 7 shows the effect of a magnetic field on the filtration resistance. Besides the ratio of cake resistance to the total resistance which decreases from 0.5 to 0.13, the results confirmed in 0.03 Al_2O_3–0.2 Fe_3O_4 membrane (the main mechanism of fouling), the cake resistance reduce significantly due to the reduction in sedimentation of sludge particles onto the membrane surface. Noormohamadi et al. [29] also indicated by applying the magnetic field, the removal efficiency of the cake resistance is increased. So, in the presence of the magnetic field the fouling of the membranes and cake resistance is greatly reduced. As proven in the previous research [22], the flux also increased in the MBR magnetic system by using low percentages of iron oxide

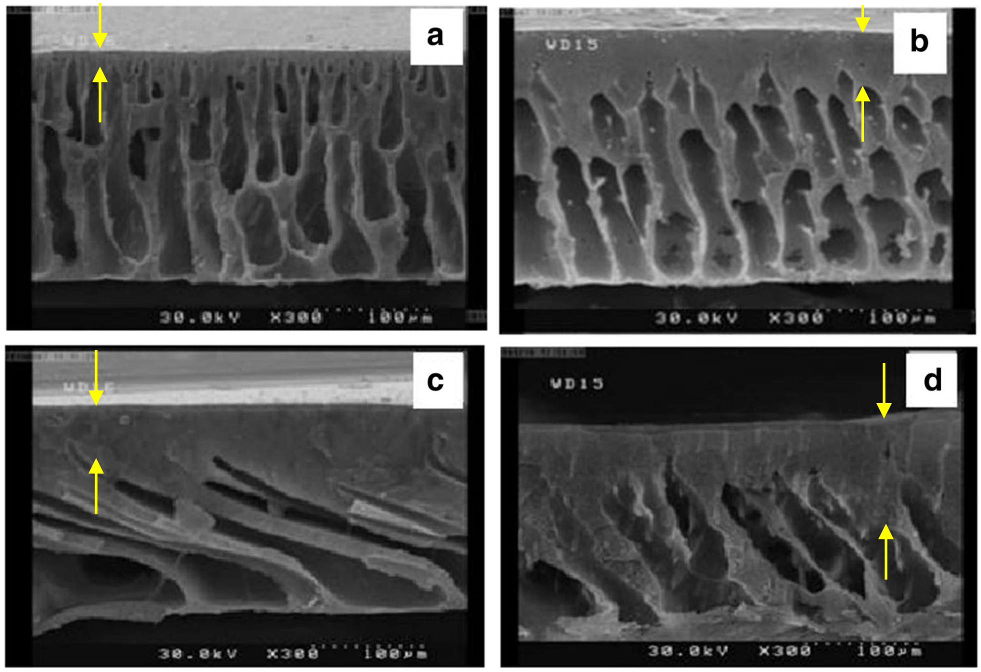

Fig. 5 SEM images of the cross-section of the membranes containing different concentrations of nanoparticles in presence of the magnetic field A: 0.03 Al_2O_3–0.1 Fe_3O_4, B: 0.03 Al_2O_3–0.15 Fe_3O_4, C: 0.03 Al_2O_3–0.2 Fe_3O_4, D: 0.03 Al_2O_3–0.25 Fe_3O_4

nanoparticles. In the current study, because of the usage of the magnetic casting method, the fouling mitigates significantly. Therefore, increasing nanoparticles with the magnetic casting is a considerable method to enhance the efficiency and development of the magnetic MBR performance.

COD removal

Table 2 represents the effect of different magnetic field states on the COD removal rate in a membrane bioreactor. As can be seen (Table 2), the magnetic field application leads to increase the COD removal. Other researchers [44–47] have shown that using a magnetic field increases the removal efficiency of the contaminants in activated sludge. These results showed that the COD removal rate for the static magnetic field is higher than the other states because the applied magnetics flux for the activated sludge is increased in the static magnetic field state.

Conclusion

In this research, nanocomposite membranes were synthesized by iron oxide and alumina nanoparticles via the magnetic casting method. The prepared membrane was applied to examine the MBR for oily wastewater treatment. The structure and performance of the nanocomposite membranes was evaluated, and the best membrane was selected according to the tow factors of minimum fouling and highest filtration efficiency in the MBR. The parameters including the concentration of Al_2O_3 and Fe_3O_4 nanoparticles, magnetic fields on the

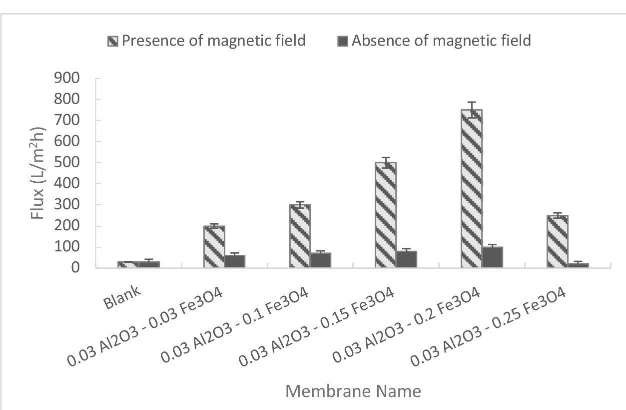

Fig. 6 Comparison of the flux of the magnetic nanocomposite membrane in the presence and absence of the magnetic field in the MBR

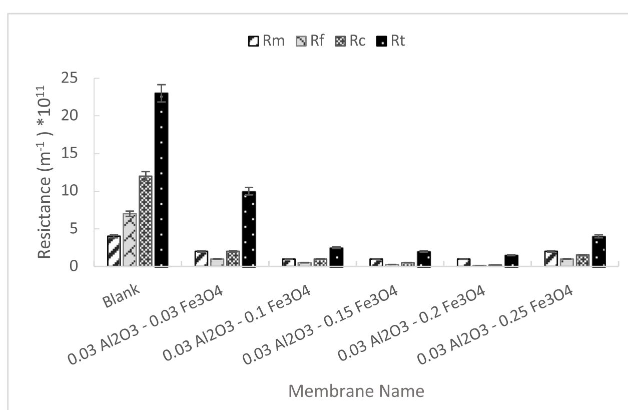

Fig. 7 The membrane (R_m), cake (R_c), pore (R_f), and total (R_t) filtration resistances of blank PSf and nanocomposite membranes in the presence of a magnetic field in the MBR

Table 2 COD removal rate in different magnetic field modes

Field type	Input COD (mg/L)	Output COD (mg/L)	COD removal (%)
Without field	2000	400	80
Dynamic field	2000	340	83
Static field	2000	140	93

membrane flux, filtration resistance and COD removal rate were examined in a magnetic membrane bioreactor. The highest percentages of Fe_3O_4 and Al_2O_3 nanoparticles in magnetic casting conditions are 0.2 wt% and 0.03 wt%, respectively, which cause increasing of membrane hydrophilicity and fouling mitigate in MBR. The magnetic casting method provide higher percentages loading nanoparticles, increase the effect of the magnetic field on the MBR performance, and improve the filtration process in MBR. However, in higher percentages of nanoparticles, the fouling increased due to the accumulation of nanoparticles in the membrane pores. In a magnetic field zone, the porosity of the nanocomposite membrane, the flux and also the resistance would be improved. Among the synthesized nanocomposite membranes, the 0.03 Al_2O_3–0.2 Fe_3O_4 membrane was the optimal membrane in the cases of flux and fouling. The results indicated that in COD removal, the type of membrane is ineffective, also the main mechanism of COD removal rate in MBR is biological effluent removal. The static magnetic field removed COD more than the dynamic magnetic field, and in general, the magnetic field improved the sludge performance in COD removal rate. Overall, the results indicated that it is possible to profit from the induced magnetic field in MBRs for the membrane fabrication and filtration process of oily wastewater.

Acknowledgements Authors thank Dr. Maryam Homayoonfal for her kind advice.

Code availability 'Not applicable'.

Data availability 'All the results and data are available and can be provided'.

Declarations

Conflicts of interest/competing interests 'The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.'

References

1. Côté P, Mourato D, Güngerich C, Russell J, Houghton E. Immersed membrane filtration for the production of drinking water: case studies. Desalination. 1998;117:181–8.
2. Drews A. Membrane fouling in membrane bioreactors—characterisation, contradictions, cause and cures. J Membr Sci. 2010;363(1):1–28.
3. Le-Clech P, Chen V, Fane TAG. Fouling in membrane bioreactors used in wastewater treatment. J Membr Sci. 2006;284(1):17–53.
4. Meng F, Chae SR, Drews A, Kraume M, Shin HS, Yang F. Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. Water Res. 2009;43(6):1489–512.
5. Chapter 1 - Introduction, in The MBR Book (Second Edition), S. Judd and C. Judd, Editors. 2011, Butterworth-Heinemann: Oxford. p. 1–54.
6. Kimura K, Hara H, Watanabe Y. Removal of pharmaceutical compounds by submerged membrane bioreactors (MBRs). Desalination. 2005;178(1):135–40.
7. Amy G. Fundamental understanding of organic matter fouling of membranes. Desalination. 2008;231(1):44–51.
8. Chang I-S, le Clech P, Jefferson B, Judd S. Membrane fouling in membrane bioreactors for wastewater treatment. J Environ Eng. 2002;128(11):1018–29.
9. Wei Y, Li G, Wang B. Application of granular sludge membrane bioreactor in the treatment of wastewater. Procedia Environ Sci. 2011;10:108–11.
10. Chen C-H, Fu Y, Gao D-W. Membrane biofouling process correlated to the microbial community succession in an a/O MBR. Bioresour Technol. 2015;197:185–92.
11. Guo Y-F, Sun P-C, Wei J-F. New insight into the fouling behavior of hydrophobic and hydrophilic polypropylene membranes in integrated membrane bioreactors. Environ Technol. 2018;39(24): 3159–68.
12. Homayoonfal M, Mehrnia MR, Rahmani S, Mohades Mojtahedi Y. Fabrication of alumina/polysulfone nanocomposite membranes with biofouling mitigation approach in membrane bioreactors. J Ind Eng Chem. 2015;22:357–67.
13. Yin J, Deng B. Polymer-matrix nanocomposite membranes for water treatment. J Membr Sci. 2015;479:256–75.
14. Homayoonfal M, Mehrnia MR, Shariaty-Niassar M, Akbari A, Ismail AF, Matsuura T. A comparison between blending and surface deposition methods for the preparation of iron oxide/ polysulfone nanocomposite membranes. Desalination. 2014;354: 125–42.
15. Homayoonfal M, Mehrnia MR, Mojtahedi YM, Ismail AF. Effect of metal and metal oxide nanoparticle impregnation route on structure and liquid filtration performance of polymeric nanocomposite membranes: a comprehensive review. Desalin Water Treat. 2013;51(16–18):3295–316.
16. Akbari A, Homayoonfal M. Sulfonation and mixing with TiO2 nanoparticles as two simultaneous solutions for reducing fouling of polysulfone loose nanofiltration membrane. Korean J Chem Eng. 2016;33(8):2439–52.
17. Yang Y, Zhang H, Wang P, Zheng Q, Li J. The influence of nano-sized TiO2 fillers on the morphologies and properties of PSF UF membrane. J Membr Sci. 2007;288(1):231–8.
18. Bae T-H, Tak T-M. Effect of TiO2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration. J Membr Sci. 2005;249(1):1–8.
19. Maximous N, Nakhla G, Wan W, Wong K. Performance of a novel ZrO2/PES membrane for wastewater filtration. J Membr Sci. 2010;352(1):222–30.
20. Bae T-H, Kim I-C, Tak T-M. Preparation and characterization of fouling-resistant TiO2 self-assembled nanocomposite membranes. J Membr Sci. 2006;275(1):1–5.
21. Maximous N, Nakhla G, Wan W, Wong K. Preparation, characterization and performance of Al2O3/PES membrane for wastewater filtration. J Membr Sci. 2009;341(1):67–75.
22. Mehrnia MR, Homayoonfal M. Fouling mitigation behavior of magnetic responsive nanocomposite membranes in a magnetic membrane bioreactor. J Membr Sci. 2016;520:881–94.

23. Daraei P, Madaeni SS, Ghaemi N, Khadivi MA, Astinchap B, Moradian R. Fouling resistant mixed matrix polyethersulfone membranes blended with magnetic nanoparticles: study of magnetic field induced casting. Sep Purif Technol. 2013;109:111–21.
24. Huang Y, Xiao CF, Huang QL, Liu HL, Hao JQ, Song L. Magnetic field induced orderly arrangement of Fe3O4/GO composite particles for preparation of Fe3O4/GO/PVDF membrane. J Membr Sci. 2018;548:184–93.
25. Zinadini S, Zinatizadeh AAL, Rahimi M, Vatanpour V. Magnetic field-augmented coagulation bath during phase inversion for preparation of ZnFe2O4/SiO2/PES nanofiltration membrane: a novel method for flux enhancement and fouling resistance. J Ind Eng Chem. 2017;46:9–18.
26. Xu Z, Wu T, Shi J, Wang W, Teng K, Qian X, et al. Manipulating migration behavior of magnetic Graphene oxide via magnetic field induced casting and phase separation toward high-performance hybrid ultrafiltration membranes. ACS Appl Mater Interfaces. 2016;8(28):18418–29.
27. Huang Z-Q, Zheng F, Zhang Z, Xu HT, Zhou KM. The performance of the PVDF-Fe3O4 ultrafiltration membrane and the effect of a parallel magnetic field used during the membrane formation. Desalination. 2012;292:64–72.
28. Qin L, Fan Z, Xu L, Zhang G, Wang G, Wu D, et al. A submerged membrane bioreactor with pendulum type oscillation (PTO) for oily wastewater treatment: membrane permeability and fouling control. Bioresour Technol. 2015;183:33–41.
29. Noormohamadi A, Homayoonfal M, Mehrnia MR, Davar F. Employing magnetism of Fe3O4 and hydrophilicity of ZrO2 to mitigate biofouling in magnetic MBR by Fe3O4-coated ZrO2/PAN nanocomposite membrane. Environ Technol. 2020;41(20):2683–704.
30. Edwards T, Maurice L. Surrogate mixtures to represent complex aviation and rocket fuels. Journal of Propulsion and Power - J PROPUL POWER. 2001;17:461–6.
31. Nguyen H, Ying SJ (1990) Critical evaluation of Jet-A spray combustion using propane chemical kinetics in gas turbine combustion simulated by KIVA-II
32. Martel C (1988) Molecular weight and average composition of JP-4, JP-5, JP-8, and Jet A. AFWAL/POSF Report
33. Guibet JC, Faure-Birchem E (1999) Fuels and engines: technology, energy, environment. Atlasbooks Dist Serv.
34. Mehrnia MR, Towfighi J, Bonakdarpour B, Akbarnejad MM. Gas hold-up and oxygen transfer in a draft-tube airlift bioreactor with petroleum-based liquids. Biochem Eng J. 2005;22(2):105–10.
35. Mehrnia MR, Towfighi J, Bonakdarpour B, Akbarnegad MM. Influence of top-section design and draft-tube height on the performance of airlift bioreactors containing water-in-oil microemulsion. J Chem Technol Biotechnol. 2004;79(3):260–7.
36. Ahmad AL, Abdulkarim AA, Ismail S, Ooi BS. Preparation and characterisation of PES-ZnO mixed matrix membranes for humic acid removal. Desalin Water Treat. 2015;54(12):3257–68.
37. Mafirad S, Mehrnia M, Sarrafzadeh M. Effect of membrane characteristics on the performance of membrane bioreactors for oily wastewater treatment. Water science and technology : a journal of the International Association on Water Pollution Research. 2011;64:1154–60.
38. Ghezelgheshlaghi S, Mehrnia MR, Homayoonfal M, Montazer-Rahmati MM. Al2O3/poly acrylonitrile nanocomposite membrane: from engineering design of pores to efficient biological macromolecules separation. J Porous Mater. 2018;25(4):1161–81.
39. Mehrnia MR, Mojtahedi YM, Homayoonfal M. What is the concentration threshold of nanoparticles within the membrane structure? A case study of Al2O3/PSf nanocomposite membrane. Desalination. 2015;372:75–88.
40. Oh SJ, Kim N, Lee YT. Preparation and characterization of PVDF/TiO2 organic–inorganic composite membranes for fouling resistance improvement. J Membr Sci. 2009;345(1):13–20.
41. Soroko I, Livingston A. Impact of TiO2 nanoparticles on morphology and performance of crosslinked polyimide organic solvent nanofiltration (OSN) membranes. J Membr Sci. 2009;343(1):189–98.
42. Gholami A, Moghadassi AR, Hosseini SM, Shabani S, Gholami F. Preparation and characterization of polyvinyl chloride based nanocomposite nanofiltration-membrane modified by iron oxide nanoparticles for lead removal from water. J Ind Eng Chem. 2014;20(4):1517–22.
43. Jian P, Yahui H, Yang W, Linlin L. Preparation of polysulfone–Fe3O4 composite ultrafiltration membrane and its behavior in magnetic field. J Membr Sci. 2006;284(1):9–16.
44. Mohammed RR, M.R.K., and G. McKay (2014) Combined magnetic field and adsorption process for treatment of biologically treated palm oil mill effluent (POME). Chem Eng J. 243: p. 31–42.
45. Wang X-H, M.-H.D.Y.Y., Y.-J. Shi, M.-M. Gao, and S.-G. Wang (2012) Enhanced aerobic nitrifying granulation by static magnetic field. Bioresour Technol,. 110: 105–110.
46. Wang J, Yang J, Zhang H, Guo W, Ngo HH. Feasibility study on magnetic enhanced flocculation for mitigating membrane fouling. J Ind Eng Chem. 2015;26:37–45.
47. Niu C, Geng J, Ren H, Ding L, Xu K, Liang W. The strengthening effect of a static magnetic field on activated sludge activity at low temperature. Bioresour Technol. 2013;150:156–62.