J. Water Environ. Nanotechnol., 4(2): 88-96 Spring 2019

ORIGINAL RESEARCH PAPER

Adsorption of organic compounds on the Fe_3O_4 nanoparticles for forestalling fouling in membrane bioreactor

Sedigeh Sabalanvand*[1]*, Hossein Hazrati*[1,2,]***, Abbas Jafarizad*[1]*, Yoones Jafarzadeh*[1]**

[1] *Faculty of Chemical Engineering, Sahand University of Technology, Tabriz, Iran*
[2] *Environmental Engineering Research center, Sahand University of Technology, Tabriz, Iran*

Received: 2019-02-27 Accepted: 2019-04-02 Published: 2019-05-01

ABSTRACT

Many studies have been done to reduce the membrane fouling and to increase the quality of the effluent from a membrane bioreactor (MBR). One of the most important researches in this filed is the use of adsorbents and nanoparticles in the biological system. In this study, the effects of Fe_3O_4 nanoparticles were investigated using COD, extracellular polymeric substances (EPS), soluble microbial products (SMP), flux, particle size distribution (PSD) and FTIR analysis. The chemical oxygen demand (COD) test showed that the removal rate was 86.92% in MBR without Fe_3O_4 (R_1) and 98.17% in MBR with Fe_3O_4 (R_2). The amount of EPS and SMP in the reactor containing nanoparticles is lower than that of a non-nanoparticle reactor. Flux rate is higher in R_2, so it can be said that the presence of nanoparticles has a positive effect of reducing the membrane fouling. Also, FTIR analysis showed that the amount of protein in the biologic system R_2, which is the major membrane contaminant, is greater than R_1.

Keywords: *Extracellular Polymeric Substance; Fe_3O_4 Nanoparticles; MBR; Membrane Fouling; Soluble Microbial Products*

How to cite this article
Sabalanvand S, Hazrati H, Jafarizad A, Jafarzadeh Y.. Adsorption of organic compounds on the Fe_3O_4 nanoparticles for forestalling fouling in membrane bioreactor. J. Water Environ. Nanotechnol., 2019; 4(2): 88-96.
DOI: 10.22090/jwent.2019.02.001

INTRODUCTION

In recent years wastewater treatments have been performed as an activated sludge process. These systems required large tanks and produced a lot of sludge [1]. Nowadays, once of the most important processes used in municipal and industrial wastewater treatment is membrane bioreactor (MBR) technology [2-4]. First time, MBR technology was recommended in 1960 [5]. These system combines activated sludge and membrane filtration process, and do not require to sedimentation and disinfection process in usual activated sludge methods [6]. Some recent pollutants such as stable organic matter, heavy metals, and environmental nanoparticle pollutants can be removed by MBR [7]. MBR performance including; higher organic loading rate, high output fluid quality, less sludge production [8-11]. However, Membrane fouling is the main defect of the MBR system, that caused a high operation cost, increase the energy demand, and increase in hydraulic resistance, reduce system efficiency and permeate flux or trans-membrane increase, and frequency of cleaning [12-14]. Fouling occurred due to activated sludge components interaction with membrane structure and happened for the reason that blockage of membrane pores by sieving and adsorption of components on the membrane surface or in membrane pores [13, 15]. The activated sludge liquor include; substrate components, cell, soluble microbial products (SMP), extracellular polymeric substances (EPS), bacteria, protein, carbohydrate, humic and fulvic acids, and there are the main membrane foulants in MBR [1, 16-

---

* Corresponding Author Email: *h.hazrati@sut.ac.ir*

19]. For reduce and control the membrane fouling phenomenon, there are three methods: membrane structure modification, variation the operation condition, and improved biomass properties [5, 10, 20]. Many researchers have been studied the adsorbent and nanoparticles effect on improving the sludge properties and membrane fouling; using the non-reactive chemical addition such as: activated carbon, zeolite, biocarriers, metal salts, poly aluminium chloride, poly ferric chloride and etc can be improved sludge characteristics (such as: size of floc, SMP, EPS, and viscosity) [6, 14, 21] ; also the other matter such as ZnO, Fe_2O_3, Fe_3O_4 with pretreatment and also non-adsorbent materials such as ozone. Crystalline zeolite nano-adsorbents with large pores and functional group such as OH can reduce 66% TMP, and adsorbed organic compounds. They reported these nano-adsorbent decreased the cake formation rate and irreversible fouling [6]. Magdalene Tan and et al. (2015) showed both of EPS and SMP are the main causes of fouling, and an increasing amount of ZnO can reduce the EPS and SMP production rate, but did not have a significant effect on membrane fouling [8]. However, Fe_3O_4 nanoparticles were not used directly in the mixed liquor suspended solids (MLSS) for a comprehensive investigation of polyvinylidene fluoride (PVDF) membrane fouling. In the previous study, Fe_3O_4 nanoparticles were added as a pretreatment before the MBR system, for example, Yu et al. [16] studied the contribution of Fe_3O_4 nanoparticles to the fouling of ultrafiltration with coagulation pre-treatment. Using the obtained analysis, they concluded that increased levels of protein and polysaccharide increased the amount of TMP. The TMP system had a slowly increasing trend sever increase in TMP due to fouling of the membrane (22 kPa after 25 day). Also in another study, Fe_2O_3 nanoparticles were added on the membrane not mixed liquor in the MBR system. They concluded that at high mixing rate, the deposition of nanoparticles on the membrane would increase the fouling, and the presence of this nanoparticle reduces contamination and increases the membrane performance at moderate mixing rates [14].

Therefore, in this study, we used this nanoparticle directly in the mixed liquor suspended solid and investigated their properties on the membrane fouling and adsorption organic and inorganic components. These particles are inert and biocompatible, and also adsorb compounds with high efficiency and low concentration. Furthermore, we used these nanoparticles in the presence of PVDF membrane and were discussed its effects with different analysis such as SMP, EPS, Fourier-transform infrared spectroscopy (FTIR) analysis for cake layer, particle size distribution (PSD) of mixed liquor.

MATERIALS AND METHODS

Material

The synthetic sewage is a model of petrochemical wastewater. Wastewater synthesized included: ethanol: 350; K_2HPO_4: 35; KH_2PO_4: 45; Urea: 560; $MgSO_4{\bullet}7H_2O$: 13; $CaCl_2{\bullet}2H_2O$: 7; $FeCl_3$: 5; $ZnSO_4$: 2; $NaHCO_3$: 500; EDTA: 7.

Set up

As shown in Fig. 1 two membrane bioreactors were with dimensions of 10*10*35 cm, and an operating volume of 1.5 liters have been used. From

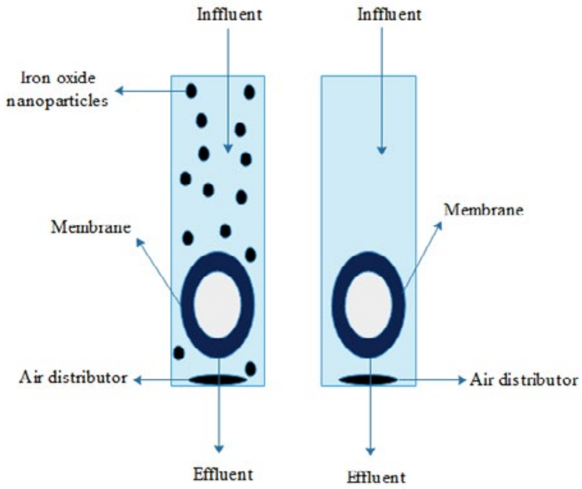


Fig.1. Schematic diagram of the MBR systems

Table 1. Operation condition of MBR system

Parameter	dimension	Value
T	°C	20
TMP	bar	0.12
pH	_	8.55
COD (mg/l)	mg/L	930
HRT	h	36
SRT	d	30
MLVSS	mg/L	R_1=3060
		R_2=2120

the PVDF membrane was used with an effective area, mean pore size and porosity $39*10^{-2}$ m^2, 0.9 µm and 73%, respectively. The synthetic wastewater of the petrochemical company is used as input to the system. In one of the bioreactors, at the first added the 0.9 g nanoparticles in the system and each time sampling 0.3 g Fe_3O_4 nanoparticles were added (R_2), and the other was used as control (R_1). The hydraulic retention time (HRT) and sludge retention time (SRT) for both bioreactors were 36 h and 30 days, respectively. The other operating conditions are given in Table 1. For evaluating the effect of Fe_3O_4 nanoparticles in MBR system, the amount of flux, COD, EPS, SMP, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS) was measured; also, FTIR analysis and PSD of the sludge were taken.

MLSS, MLVSS and membrane fouling analysis

MLSS and MLVSS were estimated according to the standard methods [22]. For membrane fouling, after operation of MBR, its flux after fouling was measured, J_1. Then the cake layer on the membrane was washed with distilled water, membrane flux after washing was called J_2. Finally, J_3 which is membrane flux after chemical washing was measured. As there is a direct relationship between fouling mechanism and reduction of flux, resistance in the serial model is the simplest method which uses Darcy law [21]. Total fouling, reversible, irreversible and recovery flux can be obtained by following equations relative to pure water flux from clean membrane module [23, 24].

COD Analysis

For the investigation, the effect of the Fe3O4 nanoparticles on the MBR systems, COD standard method was measured [22]. 2.5 ml of sample, 1.5 ml of potassium dichromate and 3.5 ml of sulfuric acid solution was poured into the vial, and placed in the termo-reactor for 2 h at 148 °C. Then, after cooling, the absorbance read at 600 nm. For calculating the COD removal, calibration curve used:

$$COD = 3171.4 * ABS - 17.934$$

SMP and EPS Extraction

To analyze the amount of protein and carbohydrates, SMP and EPS were extracted from the mixed liquor. SMP was attained via centrifuging 50 ml of sludge at 12000 rpm for 10 min. Then the EPS is extracted by the thermal method. In this way, the 0.9% NaCl solution is added to the remaining sludge, and heated in a water bath at 60 °C for 30 min [8]. Protein amount was measured with a modified Lowry method and carbohydrate analysis was performed by Anthron method [25].

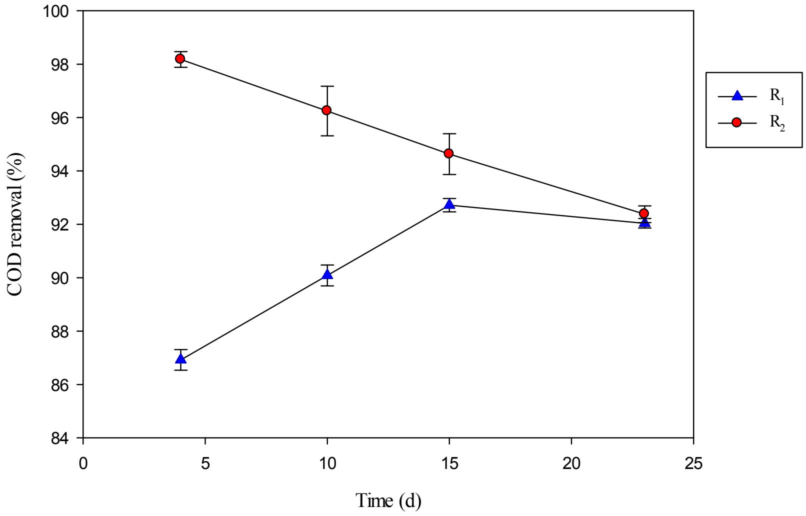


Fig. 2. Effect of Fe_3O_4 nanoparticles on COD removal (%) in the MBR

Particle Size Distribution (PSD)

PSD was determined by the Fritsch "analysette 22" with a detection range of 0.01-1000 µm.

Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

For FTIR analysis, 50 ml of the mixed liquor was centrifuged for 10 min at 9000 rpm and placed in an incubator at 55 °C for 48 h to dry.

RESULTS AND DISCUSSION

COD removal efficiency

Fig. 2 showed COD removal efficiency in both membrane bioreactors. The results obtained from the first COD removal measurement indicate that the removal efficiency in R_1 and R_2 were 86.92 and 98.17%, respectively. Fig. 2 shows that the presence of Fe_3O_4 nanoparticles improved the COD removal efficiencies, but over time the removal efficiency reduced due to saturation of the adsorption capacity (92.38% in day 23) and removal efficiency decreased. In R_1, the number of COD removal increases due to the growth of microorganisms and an increase in MLSS; the increasing of MLSS caused more utilization from organic matter and COD removal increased. The use of additives such as SiO_2, ZnO and Ag nanoparticles caused the COD removal efficiency to be no significant effect, more than 95% and around 95%, respectively [26, 27].

MLSS Variations

According to the prior studies, the amount of MLSS in aerobic MBR is usually reported to be between 3000-31000 mg/L [1]. Of course, this range is not fixed in various studies. It seems that the membrane fouling decrease in lower MLSS concentration, but in MLSS concentration above 15000 mg/L, membrane fouling increases. Although the high MLSS concentration plays an effective role in increasing the removal percentage, it reduces the MBR performance [5]. According to Fig. 3 shown in the MLSS concentration in both MBR, during the operation period, MLSS is less than 5000 mg/L, and there is no significant effect on membrane fouling. Also, the growth of the sludge in the system containing Fe_3O_4 nanoparticles is low compared to the without nanoparticles. It can be concluded that the presence of the nanoparticles reduces the growth rate. This nanoparticle is toxic and the presence of it near sludge cause to spoil the cell structure and also change the amount of nutrition.

SMP and EPS Changes

EPS and SMP are two main types of membrane foulants and include the sum of proteins and polysaccharides material [12,28,29]. Figs 4 and 5 show the variation of EPS and SMP in both membrane bioreactor system; the EPS and SMP concentration of R_2 are less than R_1. On average, EPS in R_1 and R_2 is respectively 231.38 and 199.7 mg/L, and also, the SMP amount is 110.8 and 69.96 mg/L. The difference in both cases can be attributed to adsorption by Fe_3O_4 nanoparticles, as well as the shock to bacteria by these nanoparticles, which reduces their production and growth of the sludge and microorganisms [6, 30]. It seems the toxicity of nanoparticle causes the destruction of

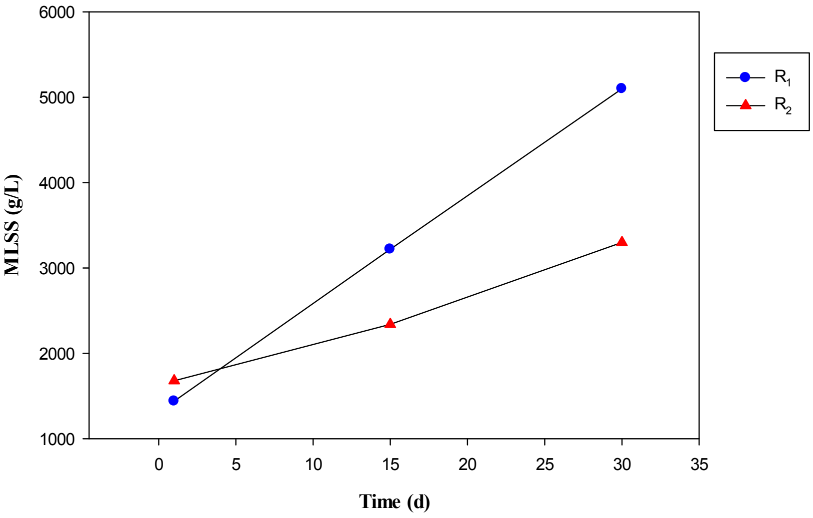


Fig. 3. MLSS concentration in MBR systems

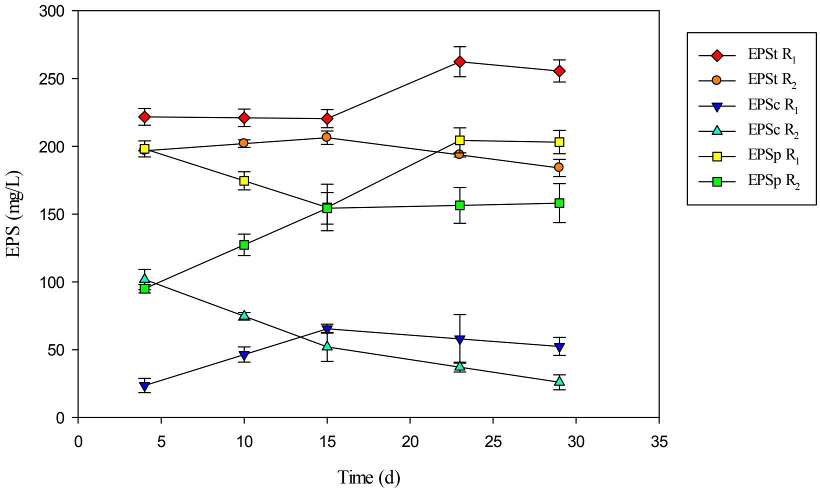


Fig. 4. EPS of mixed liquor in MBRs

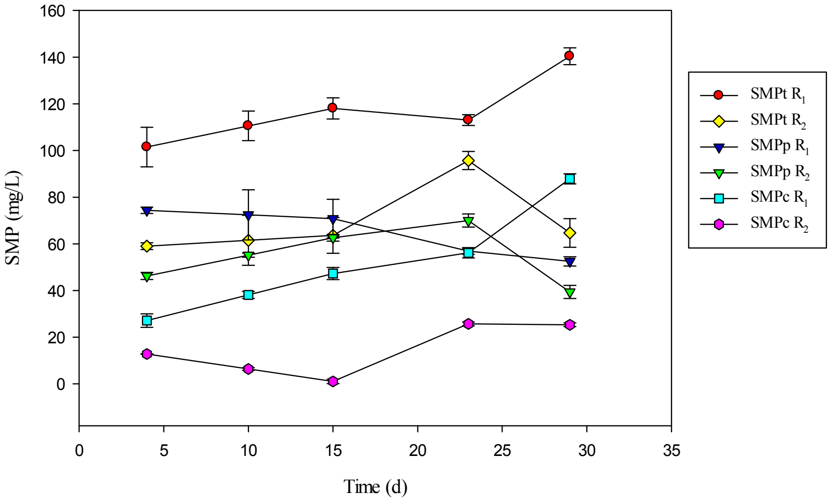


Fig. 5: SMP of mixed liquor in MBRs

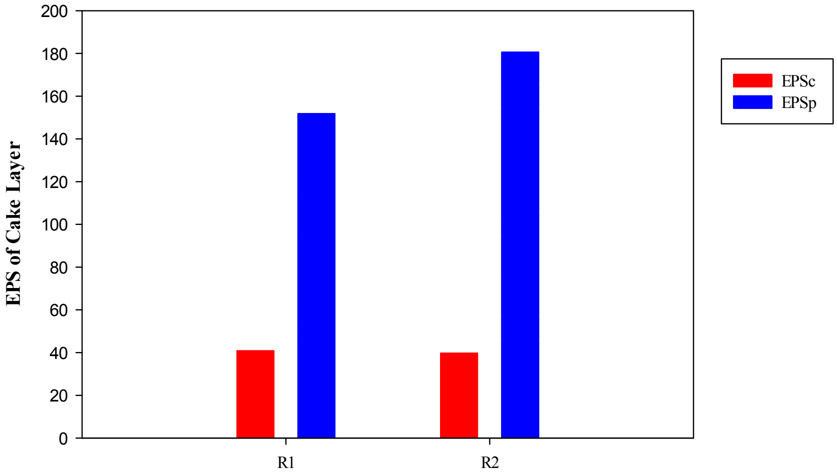


Fig. 6: EPS of cake layer in MBRs

some bacteria. Also, due to the reduced adsorption capacity of nanoparticles, the production of EPS and SMP are slowly increasing trend gradually.

According to the data shown, it can be concluded that in both MBR, the protein content of EPS and SMP is greater than that of polysaccharide, and protein is identified as the main contaminant of the membrane as the system. Also, the EPS measured the cake confirmed the presence of protein in the cake layer, which Fig. 6 shows the level of EPS_p in the cake layer. The amount of EPS_c in the cake layer in the two membranes is not significantly different (40.75 and 39.70 mg/L in R_1 and R_2, respectively). But the EPS_p level of cake layer in R_1 is 151.87 and R_2 is 180.625 mg/L). Increasing the activity of bacteria in the presence of Fe_3O_4 nanoparticles increases the amount of protein in the biological system. The presence of Fe_3O_4 nanoparticles resulted in accumulation of $Fe(OH)_3$ as an electron receptor for aeration of bacteria in the cake layer, which leads to an increase in the protein [16]. With regard to the above, it is expected that the membrane fouling in the R_2 system is greater than R_1, the results showed in the opposite of this (Fig. 7) and the flux rate in R_2 is higher (on average 211 ml/m^2 h and 154.87 ml/m^2 h in R_2 and R_1, respectively). According to a study by Yu et al. (2015), due to the high density of the Fe_3O_4 nanoparticles in the floc, the flocs in the bioreactor are easily removed and settled; and the presence of lower floc, decreasing the thickness of the cake layer formed in the R_2 membrane relative to R_1 membrane [16]. Hence, the rate of flux increased in R_2. Table 2 also shows that the reversible fouling induced the formation of the cake layer on the membrane surface is less in R_2; in general, the rate of fouling in R_1 is higher due to the blockage of the pores and presence of cake layer.

PSD in MBRs

The distribution of the sludge particle size of the two MBR is shown in Fig. 8. The particle size in R_2 is more than R_1, but this difference is negligible and the distribution of particle size in both MBR is inappropriate. The particle size in a maximum of points is 21.8 and 24.4 μm in R_1 and R_2, respectively. Yu et al. (2015) concluded that the presence of the Fe_3O_4 nanoparticles does not change the properties of the sludge significantly and they reported that the high density of this nanoparticles improved the separation and settling of flocs [16]. In the other studies, they reported that particle sizes smaller than 50 μm increase the membrane fouling and, by placing it on the membrane surface, reduced the permeability [2]. It can be considered that due to the small size of the particle in R_1, the rate of fouling is greater than R2. Also, SEM images (Fig. 9) show that membrane fouling for R2 is lower than R1. For R_1 all pores of the membrane were blocked but for R_2 there are pores of the membrane.

FTIR pattern

To confirm the EPS in the mixed liquor, the sludge analyzed by FTIR. According to Fig. 10, the wavelengths of polysaccharides and

Table 2. Membrane fouling measurement

MBR	Total fouling	reversible fouling	irreversible fouling	recovery ratio
R1	0.992381	0.062857	0.929524	0.285714
R2	0.949	0.009	0.94	0.15

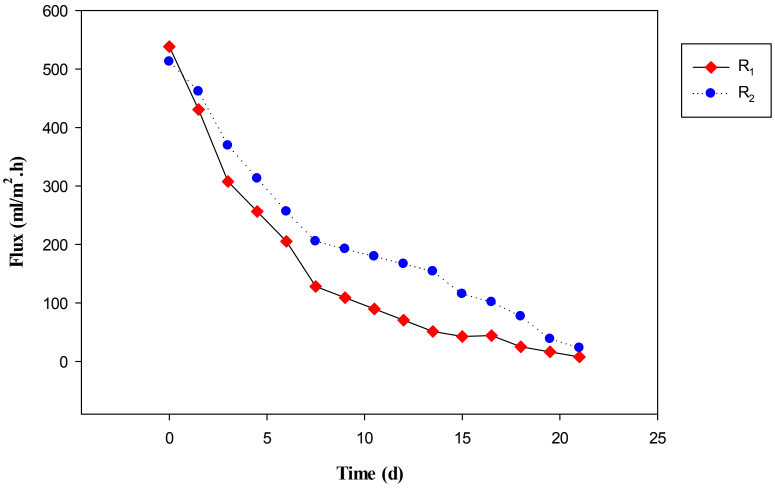


Fig. 7. Flux variation during the MBR operation

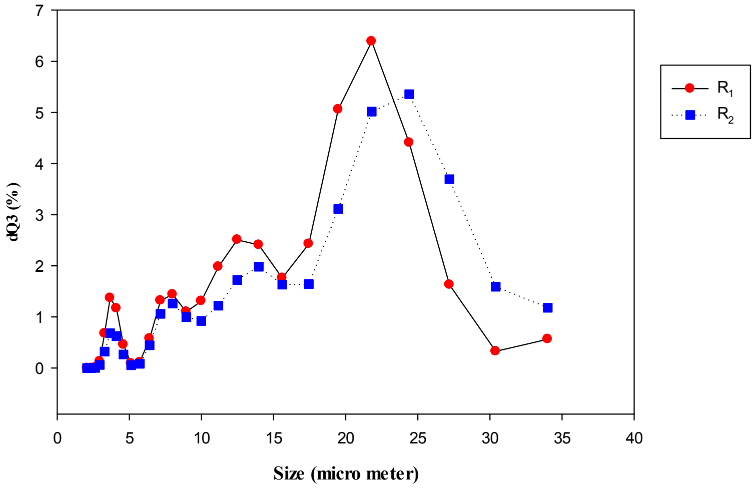
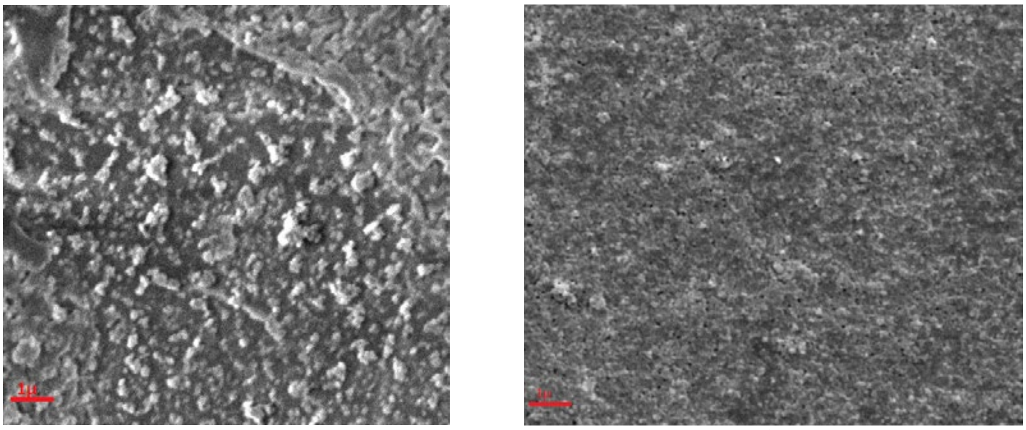


Fig. 8. Particle size distribution (PSD) analysis



(a)

(b)

Fig 9. SEM images from the fouling: (a) for R$_1$ (b) for R$_2$

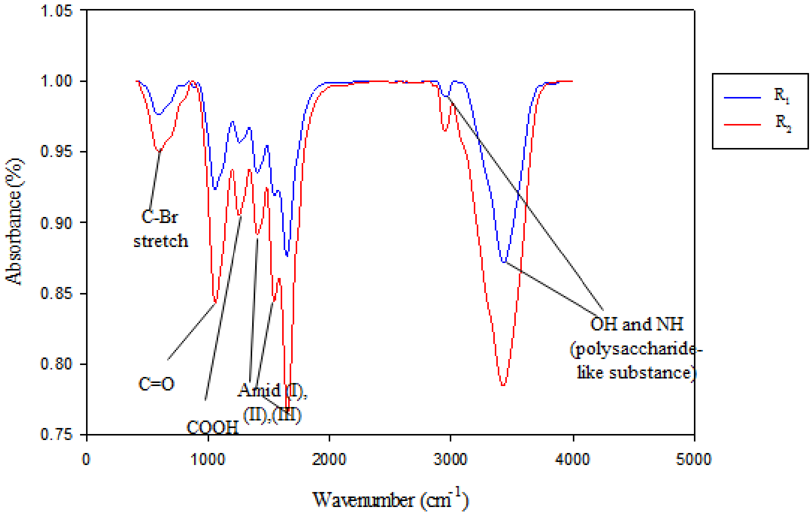


Fig. 10. The peaks obtained the FTIR analysis of the sludge

polysaccharide-like substance, protein, and protein-like substance, humic acid were observed. The peak at the wavelength of 1053.69 cm^{-1} corresponded to the presence of C=O bonds (polysaccharides or polysaccharide-like substance), the wavelength of 1252.05 cm^{-1} related to COOH bonds (humic acid), and the wavelengths of 1404.28, 1542.70 and 1652.53 indicated the presence of Amide (I), (II) and (III) (protein or protein-like substance), respectively [31, 32]. Also, the wavelengths of 2947.84 and 3428.03 cm^{-1} related to O-H and N-H bounds (polysaccharides or polysaccharide-like substance). The peak intensity of R_2 is lower than R_1, that shows all of the organic and inorganic component reduced.

CONCLUSION

According to the analysis done in this work, it can be concluded that:

1. In R_2, the amount of COD removal compared to R_1 is higher, due to the adsorption of organic matter by the nanoparticle with biological treatment.
2. The presence of Fe_3O_4 nanoparticles in a biological environment causes shock to bacteria and reduces the amount of sludge production, EPS and SMP.
3. The positive effect of the presence of nanoparticles is to increase the amount of flux, although the amount of protein measured in R_2 cake layer is greater than R_1, the thickness of the formed cake layer is less.
4. The main reason for the fouling of the membrane is blockage of membrane pores and is irreversible. The protein is a major source of contamination and has been confirmed by FTIR analysis.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Chang I-S, Le Clech P, Jefferson B, Judd S. Membrane Fouling in Membrane Bioreactors for Wastewater Treatment. Journal of Environmental Engineering. 2002;128(11):1018-29.
2. Mashayekhi F, Hazrati H, Shayegan J. Fouling control mechanism by optimum ozone addition in submerged membrane bioreactors treating synthetic wastewater. Journal of Environmental Chemical Engineering. 2018;6(6):7294-301.
3. Dong Z, Shang W, Dong W, Zhao L, Li M, Wang R, et al. Suppression of membrane fouling in the ceramic membrane bioreactor (CMBR) by minute electric field. Bioresource Technology. 2018;270:113-9.
4. Di Trapani D, Mannina G, Viviani G. Membrane Bioreactors for wastewater reuse: Respirometric assessment of biomass activity during a two year survey. Journal of Cleaner Production. 2018;202:311-20.
5. Le-Clech P, Chen V, Fane TAG. Fouling in membrane bioreactors used in wastewater treatment. Journal of Membrane Science. 2006;284(1-2):17-53.
6. Hazrati H, Jahanbakhshi N, Rostamizadeh M. Fouling reduction in the membrane bioreactor using synthesized zeolite nano-adsorbents. Journal of Membrane Science. 2018;555:455-62.
7. Mei X, Wang Z, Zheng X, Huang F, Ma J, Tang J, et al. Soluble microbial products in membrane bioreactors in the presence of ZnO nanoparticles. Journal of Membrane Science. 2014;451:169-76.
8. Tan M, Qiu G, Ting Y-P. Effects of ZnO nanoparticles on wastewater treatment and their removal behavior in a membrane bioreactor. Bioresource Technology. 2015;185:125-33.
9. Wang Z, Huang F, Mei X, Wang Q, Song H, Zhu C, et al. Long-term operation of an MBR in the presence of zinc oxide nanoparticles reveals no significant adverse effects on its performance. Journal of Membrane Science. 2014;471:258-64.
10. Abdelrasoul A, Doan H, Lohi A. Fouling in Membrane Filtration and Remediation Methods. Mass Transfer - Advances in Sustainable Energy and Environment Oriented Numerical Modeling: InTech; 2013.
11. Nam A, Kweon J, Ryu J, Lade H, Lee C. Reduction of biofouling using vanillin as a quorum sensing inhibitory agent in membrane bioreactors for wastewater treatment. Membrane Water Treatment. 2015;6(3):189-203.
12. Lin H, Zhang M, Wang F, Meng F, Liao B-Q, Hong H, et al. A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: Characteristics, roles in membrane fouling and control strategies. Journal of Membrane Science. 2014;460:110-25.
13. Bagheri M, Mirbagheri SA. Critical review of fouling mitigation strategies in membrane bioreactors treating water and wastewater. Bioresource Technology. 2018;258:318-34.
14. Tampubolon SDR, Semblante GU, You S-J, Lin Y-F. Application of magnetic γ-Fe2O3 to reduce membrane fouling. Journal of the Taiwan Institute of Chemical Engineers. 2014;45(2):317-24.
15. Chen J, Zhang M, Li F, Qian L, Lin H, Yang L, et al. Membrane fouling in a membrane bioreactor: High filtration resistance of gel layer and its underlying mechanism. Water Research. 2016;102:82-9.
16. Yu W, Xu L, Graham N, Qu J. Contribution of Fe3O4 nanoparticles to the fouling of ultrafiltration with coagulation pre-treatment. Scientific Reports. 2015;5(1).
17. Liu Y, Zhang X, Hao Ngo H, Guo W, Wen H, Deng L, et al. Specific approach for membrane fouling control and better treatment performance of an anaerobic submerged membrane bioreactor. Bioresource Technology. 2018;268:658-64.
18. Teng J, Shen L, He Y, Liao B-Q, Wu G, Lin H. Novel insights into membrane fouling in a membrane bioreactor: Elucidating interfacial interactions with real membrane surface. Chemosphere. 2018;210:769-78.
19. Mirzavandi A, Hazrati H, Ebrahimi S Investigation of influence of temperature and solid retention time on membrane fouling in MBR. MEMBRANE WATER TREATMENT. 2019; 10(2):179-189.

20. Hazrati H, Shayegan J, Mojtaba Seyedi S. The effect of HRT and carriers on the sludge specifications in MBR to remove VOCs from petrochemical wastewater. Desalination and Water Treatment. 2015;57(46):21730-42.
21. Hazrati H, Shayegan J. Influence of suspended carrier on membrane fouling and biological removal of styrene and ethylbenzene in MBR. Journal of the Taiwan Institute of Chemical Engineers. 2016;64:59-68.
22. Federation WE, Association APH Standard methods for the examination of water and wastewater. American Public Health Association (APHA): Washington, DC, USA. 2005.
23. Behboudi A, Jafarzadeh Y, Yegani R. Polyvinyl chloride/polycarbonate blend ultrafiltration membranes for water treatment. Journal of Membrane Science. 2017;534:18-24.
24. Seyfollahi M, Etemadi H, Yegani R, Rabeii M, Shokri E The effect of polyethylene glycol grafted nanodiamond on antifouling properties of cellulose acetate membrane for Removal of BSA from Contaminated Water. Journal of Water and Environmental Nanotechnology. 2019; 4(1):1-16.
25. Zuriaga-Agustí E, Bes-Piá A, Mendoza-Roca JA, Alonso-Molina JL. Influence of extraction methods on proteins and carbohydrates analysis from MBR activated sludge flocs in view of improving EPS determination. Separation and Purification Technology. 2013;112:1-10.
26. Qiu G, Wirianto K, Sun Y, Ting Y-P. Effect of silver nanoparticles on system performance and microbial community dynamics in a sequencing batch reactor. Journal of Cleaner Production. 2016;130:137-42.
27. Sibag M, Lee S, Kim H, Cho J. Retention of Silica Nanoparticles in a Lab-Scale Membrane Bioreactor: Implications for Process Performance and Membrane Fouling. Water. 2016;8(7):277.
28. Zhang D, Zhou Y, Bugge TV, Mayanti B, Yang A, Poh LS, et al. Soluble microbial products (SMPs) in a sequencing batch reactor with novel cake filtration system. Chemosphere. 2017;184:1286-97.
29. Krzeminski P, Leverette L, Malamis S, Katsou E. Membrane bioreactors – A review on recent developments in energy reduction, fouling control, novel configurations, LCA and market prospects. Journal of Membrane Science. 2017;527:207-27.
30. Durán N, Marcato PD, Conti RD, Alves OL, Costa FTM, Brocchi M. Potential use of silver nanoparticles on pathogenic bacteria, their toxicity and possible mechanisms of action. Journal of the Brazilian Chemical Society. 2010;21(6):949-59.
31. Jin L, Ong SL, Ng HY. Fouling control mechanism by suspended biofilm carriers addition in submerged ceramic membrane bioreactors. Journal of Membrane Science. 2013;427:250-8.
32. Alresheedi MT, Basu OD. Support media impacts on humic acid, cellulose, and kaolin clay in reducing fouling in a submerged hollow fiber membrane system. Journal of Membrane Science. 2014;450:282-90.