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Investigation of influence of nano H-ZSM-5 and NH_4-ZSM-5 zeolites on membrane fouling in semi batch MBR

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Abstract. The objectives of this research were the reduction of membrane fouling and improvement of sludge properties by using synthesized H-ZSM-5 and NH_4-ZSM-5 zeolites. These two nano zeolites were synthesized and added to the membrane bioreactor (MBR). Three similar MBRs with the same operational condition were used in order to evaluate their effect on the mentioned matters. The evaluated parameters were trans-membrane pressure (TMP), Fourier-transform infrared spectroscopy (FTIR), particle size distribution (PSD), soluble microbial product (SMP), extracellular polymeric substances (EPS) and, excitation-emission matrix (EEM). The MBR_0 was without any additional zeolite while 0.4 g/L of H-ZSM-5 and NH_4-ZSM-5 were added to MBR_{HZSM-5} and $MBR_{NH4ZSM-5}$, respectively. The COD removal of the MBR_0, $MBR_{H-ZSM-5}$ and $MBR_{NH4-ZSM-5}$ were 87.5%, 93.3% and 94.6%, respectively. The TMP of the $MBR_{H-ZSM-5}$ was 45% less than MBR_0 whereas the reduction for $MBR_{NH4-ZSM-5}$ was 65.5%. Also results showed that both H-ZSM-5 and NH_4-ZSM-5 caused reduction in protein and polysaccharide related EPS but the NH_4-ZSM-5 had better performance toward the elimination of organic compounds.

Keywords: submerged membrane bioreactor; NH_4-ZSM-5; H-ZSM-5; membrane fouling

1. Introduction

Membrane bioreactor (MBR) technology is a new way for the treatment of active sludge wastewater by using the solid-liquid separation ability of the membranes. Using MBRs for treating and recycling of wastewater instead of conventional activated sludge process (CASP) is getting a lot of attention due to their advantages in comparison to other common methods in the last few years (Hai *et al*. 2013, Khan *et al*. 2012). The less required space (Stephenson *et al*. 2000), producing high quality effluent (Iorhemen *et al*. 2016), the ability for high organic shocks tolerance (Stephenson *et al*. 2000) and producing less sludge in comparison to the other common biological methods (Kraume and Drews 2010) are the main advantages of using MBRs. But the great disadvantage of using this method that influences its advantages is the membrane fouling. Membrane fouling leads to reduction in productivity and reduction in effluent stream as well. All these causes to increasing of costs of using the MBRs (Chang *et al*. 2002, Meng *et al*. 2009). The main parameters that influence the membrane fouling are sludge properties, membrane structure and its properties, wastewater properties, and operational conditions (Le-Clech *et al*. 2006).

Among these different parameters, the main influencing parameter on the membrane fouling is sludge properties (Cho *et al*. 2005). Different technologies and procedures were carried out by researchers in order to reduce the membrane fouling which each one had its own problems. For example, the airing and physical and chemical cleaning methods cause the reduction in the membrane lifetime and costs high. Recently, some researchers reported that some sludge properties like the size of the flocculation, soluble microbial product (SMP), extracellular polymeric substances (EPS) and, viscosity can be improved by adding some additives like organic coagulants (Hazrati *et al*. 2018, Koseoglu *et al*. 2008, Ngo and Guo 2009), biological carriers (Hazrati and Shayegan 2016), adsorbents (such as zeolites and activated carbon) (Du *et al*. 2017). Adding these compounds causes the increase of flocculation size whilst the soluble organic pollutants decrease (Ji *et al*. 2014). Yuniarto *et al* (2013) used activated carbon and zeolites in order to reduce the membrane fouling. In both cases, the critical flux was reduced but activated carbon showed better performance towards reducing critical flux. Despite the good performance of activated carbon, the complications and high costs of synthesizing activated carbon are the disadvantages of using it in reducing membrane fouling (Hazrati *et al*. 2018). Zeolites and other particles were used widely as adsorbents for separation and treatment processes in the last decades due to their ability for ion exchange and high selectivity (Safavi *et al*. 2017, Wang and Peng 2010). The properties of zeolites can be improved by using different methods like ion exchange and surfactant effect which leads to the higher adsorbing ability of the zeolites (Li *et al*. 2011).

As mentioned above, it can be concluded that with the improvement of the synthesized nano zeolites and adding it

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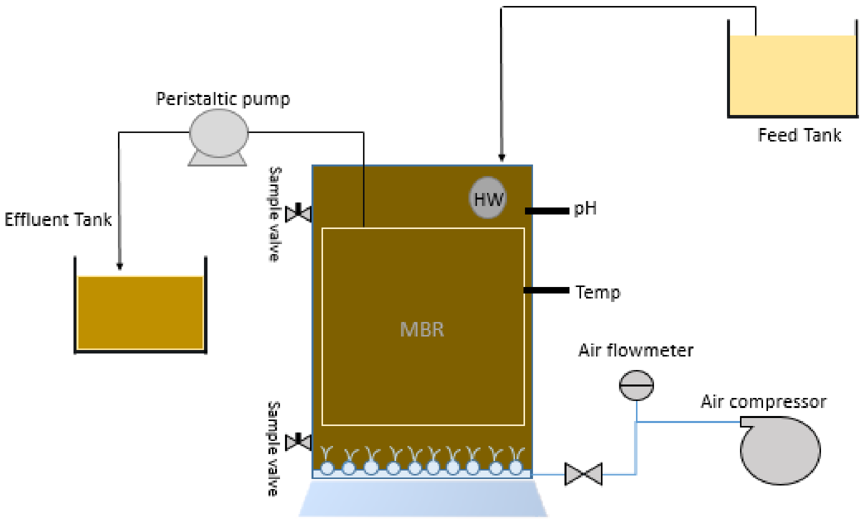


Fig. 1 A lab scale MBR

to a MBR, the membrane fouling be delayed; yet there is not any research toward this subject by modification the crystallinity, the pore structure and adding functional groups on the synthesized zeolites (Hazrati *et al.* 2018). Therefore, two modified ZSM-5 zeolites with functional groups were used in this research (Rostamizadeh *et al.* 2018). Results were evaluated with trans-membrane pressure (TMP), chemical oxygen demand (COD), EPS, SMP, particle size distribution (PSD) and excitation-emission matrix (EEM) in the MBR.

2. Materials and methods

2.1 Nano adsorbents preparation and procedures

For synthesizing the zeolites, Tetra propyl ammonium bromide (TPABr, $C_{12}H_{28}BrN$, > 99 wt.%), Silicic acid ($SiO_2.xH_2O$, > 99 wt.%), sodium aluminate ($NaAlO_2$, Al_2O_3 wt. % = 55), (NH_4NO_3, 99 wt.%), sodium hydroxide (NaOH, 99.6 wt.%) and sulfuric acid (H_2SO_4, 98 wt.%) were used. All the chemicals were purchased from Merck Company.

The solution of NaOH, sodium aluminate and deionized water was stirred for 30 min. TPABr was then added and stirred for 1 h (solution A). Simultaneously, silicic acid was dissolved in 100 mL of deionized water (solution B). The solution A was added to the solution B drop by drop under continues agitation and stirred for 2 h. Appropriate amount of sulfuric acid adjusted the pH of solution. The final solution included the molar composition of 1.5SiO_2: 0.0037Al_2O_3: 0.075TPABr: 0.112Na_2O.

Crystallization process was done using a stainless steel autoclave with Teflon veneer and under the pressure of the solution itself for 48 h inside oven at 180°C. The oven was temperature programmed for providing a fixed temperature during the process. The resulting powder was washed with distilled water for several times and filtered by using a vacuum filtration. The powder then dried in the oven at 110°C for 12 h. Calcination process was done afterwards in order to remove the template molecules from the structure of the zeolite at 540°C for 24 h with 3°C/min in the atmospheric pressure. After calcination process, the powder was ion exchanged with 1 molar ammonium nitrate for four times. Each ion exchange process was done at 90°C for 10 h. At the end, the final powder which is NH_4-ZSM-5 was dried at 110° for 12 h. By the calcination of this powder at 540°C for 12 h with 3°C/min under the atmospheric pressure the H-ZSM-5 was achieved then was modified with silver.

2.2 Experimental set-up and operation condition

The semi batch membrane bioreactor was 60 cm × 7 cm × 22 cm and showed in Fig. 1. The reactor was made from Plexiglas and the volume of it was 7 liters. The membrane that used in this research was a flat one made from polyethylene with the pore size of 0.4 µm, 0.1 m^2 as the surface area and the dimension of 22 cm × 30 cm. The using initial sludge was from the CASP of the Tabriz petrochemical company with mixed liquid suspended solid (MLSS) of 2500 mg/L and was fed with synthesized wastewater for one month. The synthetic wastewater was simulated to petrochemical wastewater in terms of COD which were about 1200 mg/L. The synthetic wastewater had the following composition (mg/L): C_2H_5OH: 450; K_2HPO_4: 35; KH_2PO_4: 45; Urea: 560; $NaHCO_3$: 500.

The experiment was conducted by operating the MBR without nano particle (called MBR_0), and then followed by two different nano adsorbent, called $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$. For all MBRs, air flow rate was 8-9 L/min and the hydraulic retention time (HRT) and solid retention time (SRT) were 8 hours and 15 days, respectively. The amount of dissolved oxygen (DO) in the reactors was fluctuant between 3 to 6 mg/L. The initial nano particles of H-ZSM-5 and NH_4-ZSM-5 were 0.4 g/L. It was necessary to bring out 0.46 liters of sludge each day in order to maintain the SRT 15 days for the recovery of the zeolites that exits with the sludge each day, 0.2 g of zeolite was added to the reactor. The operational conditions for three

Table 1 Operational condition for three MBRs

Operational conditions	Quantity
HRT(h)	8
Flux ($m^3/m^2.s$)	1.25×10^{-6}
DO (mg/L)	3-6
MLSS (mg/L)	3000-5000
Air rate (L/min)	8
pH	6-7

MBRs are presented in Table 1.

2.3 Analytical methods

2.3.1 EPS and SMP analyses

For determination the amount of protein (SMP_p and EPS_p) Bradford method was used and polysaccharide determination (SMP_c and EPS_c) was done using phenol–sulfuric acid method (Association *et al*. 1915, Zuriaga-Agustí *et al*. 2013).

2.3.2 FTIR analysis

The FTIR analysis reveals information about the functional groups of the EPS in the cake formed on the membrane (Ding *et al*. 2015, Saha *et al*. 2007). To prepare sample for this analysis, the formed cake was collected and dissolve in 500 ml of distilled water. Then 50 ml of the solution was centrifuged at 9000 rpm for minutes. Eventually, the remaining solid was dried at 50°C in oven for 48 h (Hazrati and Shayegan 2016). Analysis was done using a TENSOR 27, BRUKER.

2.3.3 EEM analysis

EEM analysis was done at the end of the process on the EPS of the formed cake. The cake layer was collected from the membrane and dissolved in 500 ml of distilled water. 100 ml of the solution was then centrifuged at 9000 rpm for 10 minutes. The EPS was extracted from the remaining solid by using the thermal method and used in EEM analysis. Analysis was done by using a fluorescence spectrophotometer (LS 55; PerkinElmer, USA). In the measurements of fluorescence, EEM spectra was obtained by collecting the wavelength of both excitation over a range of 200–450 nm and emission of 200–600 nm in stepwise by 10 nm. The scanning speed was set at 1200 nm/min for all the measurements.

2.3.4 PSD

Particle size distribution was measured by the Fritsch “analysette 22” with a detection range of 0.01–1000 µm.

2.3.5 Other analysis

MLSS, MLVSS and COD analyses was done using the standard methods (Clesceri *et al*. 1998).

3. Results and discussion

3.1 COD removal and MLSS Change

Fig. 2 shows the COD removal for each three reactors.

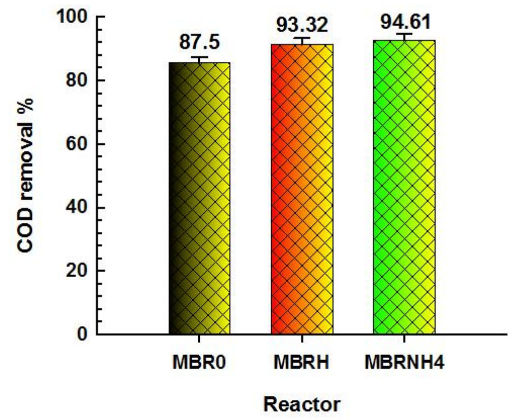


Fig. 2 COD removal three MBRs

Results showed that the average of COD removal for MBR_0, $MBR_{H-ZSM-5}$ and $MBR_{NH4-ZSM-5}$ reactors was 87.5, 93.32 and 94.61%, respectively. According to the results, most of the COD was removed in all three reactors. The amount of MLSS was stable for all three reactors during the process (3000 mg/L to 4500 mg/L). The COD removal and the amount of MLSS show that the inherent specifications of the zeolites are in good compatibility with the nutrients and it does not have any toxic effect and even improve the performance of the microorganisms as well. Also, it can be concluded that the higher COD removal in reactors with zeolite is due to the adsorption of organic compounds on the zeolite surface (Yang *et al*. 2010).

3.2 Evaluation of MLVSS/MLSS

The MLVSS to MLSS ratio is one the key parameters in the determining the increased amount of inorganic compounds inside the reactor which can also indicate the microbial activity as well. As can be seen from Fig. 3, in all three reactors the MLVSS/MLSS had decreased slightly during the process. The average amount for the MBR_0, $MBR_{H-ZSM-5}$ and $MBR_{NH4-ZSM-5}$ was 0.879, 0.761 and 0.830, respectively. This ratio had a more decreasing amount in both $MBR_{H-ZSM-5}$ and $MBR_{NH4-ZSM-5}$ in comparison to MBR_0, this could be a result of the accumulation of inorganic compounds in MBRs with zeolite (Yang *et al*.

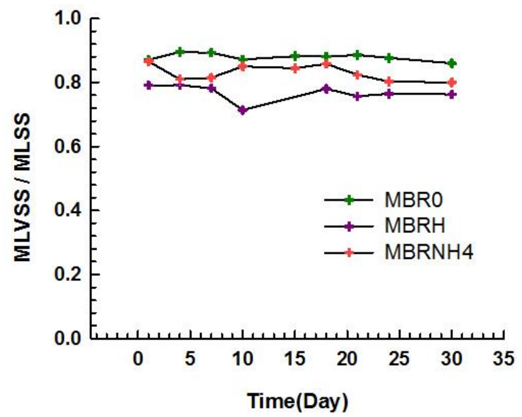


Fig. 3 MLVSS/MLSS for three MBRs

(2010). As a matter of fact, because zeolite is inorganic matter and adsorbed the inorganic compounds as well, this ratio decreased.

3.3 Transmembrane pressure

The process in all three reactors was done at steady fixed flux and regarding this the TMP was measured (Iorhemen *et al*. 2016). Fig. 4 shows the TMP changes in the reactors. After 30 days, in all three reactors the TMP increased but the increasing in the MBR0 is more considerable in comparison to the other reactors. At the day 30, the TMP for MBR_0, $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ was 4, 2.2 kPa and 1.5 kPa, respectively. In MBR_0 a dramatic increase in TMP was observed in the first days whereas in $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ the trend is different and it shows a slight rise in the first days and a jump in the final days of the process which is due to the decrease in organic compounds like SMP and EPS by the presence of zeolite. Also, the SMPs filled the vacant molecular space in the cake layer is another reason for this different in trends (Arabi and Nakhla 2008), More adsorption of SMPs by the zeolite results in porosity of the cake layer and decrease in the extension of biomass as well which leads to the fouling reduction in the reactors. Also, zeolites can increase the size of particles and this way prevent the fouling of the pores and improve the returning the particles from the surface of the membrane to the reactor. The reason for the jump in the TMP is due to the capability of zeolite for adsorption in the final days of the process is decreased. The TMP rise in $MBR_{NH4\text{-}ZSM\text{-}5}$ is less than $MBR_{H\text{-}ZSM\text{-}5}$ which is related to the functional groups of the mentioned zeolite and its structure as well because the NH_4-ZSM-5 has better performance in adsorbing the organic compounds in comparison to the H-ZSM-5.

In another research, the results were different. For instance, Wu *et al*. (2009) claimed the addition of PAC with the dosage less than 50 mg/liter and more than 700 mg/liter is not efficient for the fouling reduction because in the low concentrations of PAC, the limited surface of the adsorbent results in low capability of adsorbing organic compounds while in high concentration of PAC the diffusion of fine particles into the membrane pores causes membrane fouling (Wu *et al*. 2009). Another research by Guo *et al*. (2008) was done towards reduction of membrane fouling by adding MPE50 to the MBR and observed that MPE50 had no significant effect on the membrane fouling (Hazrati *et al*. 2016). However, Lee *et al*. (2007) found out that the addition of 50 mg/liter of MPE50 to a submerged MBR results in an increase of filtration and reduction in membrane fouling (Lee *et al*. 2007). These results indicate that the capability of a cationic polymer like MPE50 is strongly dependent to the design of the MBR system, the specifications of the feed as well as operational conditions (Guo *et al*. 2008, Hazrati *et al*. 2018).

3.4 PSD and its effect on the membrane fouling

Particle size distribution is one of the important factors toward membrane fouling in the membrane reactors. Because the formed cake layer of the flocculation is a reversible one, the concentration will be on the sub-micron particles which cause irreversible fouling (Geilvoet 2010, van den Brink *et al*. 2011). Fig. 5 presents the PSD of the three reactors. The average PSD values are 13.70, 14.80 and 19.17 µm for MBR0, $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ reactors, respectively. The increases in the PSD of the reactors with zeolites is due to the presence of adsorbents by their ability to adsorb solved organic compounds, fine colloidal particles and floating bacteria and turning them to flocculation. In another words, the adsorbent plays the role of an intermediate for connectivity of the biomass and the extension of the flocculation (Akram and Stuckey 2008). The rise in the PSD results in the formation of porous cake layer which can delay the membrane fouling and as mentioned before this type of fouling is totally reversible (Yang *et al*. 2010). Lee *et al* claimed that the increase in the size of the particles can increase the possibility of the crossing the of the particles from the membrane as well as the returning the of the particles on the surface of the membrane to the reactor (Lee *et al*. 2001). On a research done by Yang *et al*. (2010), it was concluded that the size of the particles is related to the TMP. They claimed that the increase of the PSD leads to reduction in membrane fouling so the fine particles can penetrate inside the membrane and foul the pores (Yang *et al*. 2010).

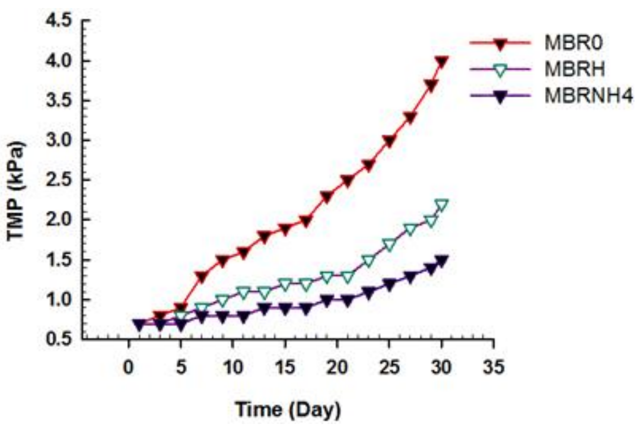


Fig. 4 Increase of TMP in duration process

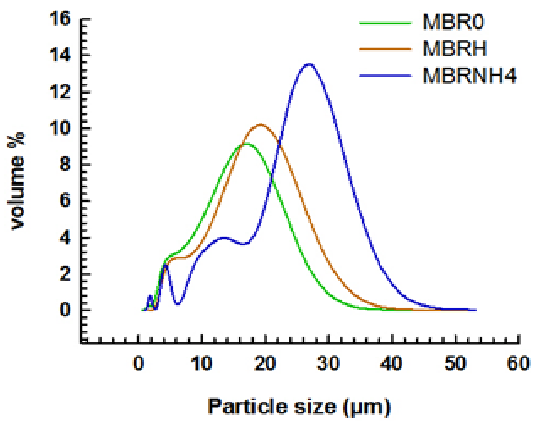


Fig. 5 PSD of cake layer for three MBRs

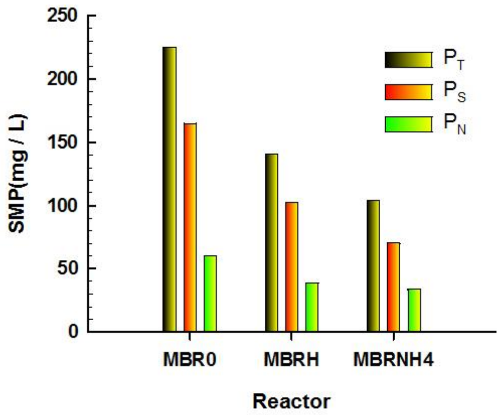


Fig. 6 SMP of three MBRs

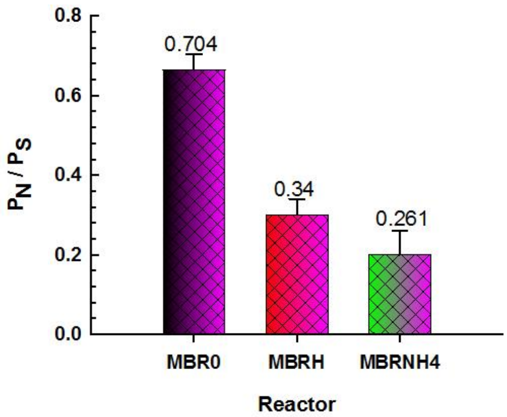


Fig. 7 Ratio protein to polysaccharide

3.5 SMP and EPS inside the mixed liquid

According to a previous research, SMP and EPS have significant effect on fouling rate of membranes. In general, SMP and EPS are considered as a total of protein and polysaccharides. The effect of Nano particles on EPS is different due to the complexity of the bio systems as well as the nature of the adsorbents (Lin *et al*. 2014, Rezaei and Mehrnia 2014). Fig. 6 shows the SMP and EPS of MBR0, $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$. Overall and component average of SMP and EPS decreased in $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ in comparison to MBR_0. It can be related to the role of SMP in the reactor. SMP is considered as a part of the solution cellular which releases during the decomposition of the cells during the process. Adding the adsorbents to the mixed liquids causes the adsorption of SMP molecules and formation of flocculation that attached to the adsorbents; over time; the whole process results in decrease in SMP (Yuniarto *et al*. 2013). On the other side, the existence of adsorbents in the mixed liquid prevents the bacterial shock which leads to the less formation of EPS. The less amount of EPS means the less SMP as well (Meng *et al*. 2009). In this research, the existence of nano particles in the reactors caused the decrease in the protein and polysaccharide with more decrease in polysaccharides. It can be concluded that the growth of sludge flocculation is because of the growth of biofilm on the adsorbents which in overall caused this decrease in protein and polysaccharide (Rezaei and Mehrnia 2014). In another research, Rezaei *et al* (Rezaei and Mehrnia 2014), used Clinoptilolite for reducing fouling while Damayanti *et al*. (2011), used three different adsorbents (PAC, Zeolite and Moringaoleifera) and all reported that the effect of adsorbent is more on the protein than polysaccharide, however, in another research by Rezaei it was concluded that the overall decrease of SMP, especially the polysaccharide SMP, caused the decrease in TMP which leads to reducing in membrane fouling (Rezaei and Mehrnia 2014). Khan used PAC and Polymer for reducing membrane fouling and reported that both did not any effect on EPS_P while the EPS_P was decreased 66 and 55%, respectively (Khan *et al*. 2012). Yuniarto *et al* reported that the properties and concentration of additives is the main factor in low growth trend of TMP in which that the adsorption colloids and organic compounds like SMPs by this additives result in the reducing the membrane fouling.

3.6 The ratio of protein to polysaccharide

Fig. 7 shows the protein to polysaccharide ratio in MBR_0, $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ reactors which are 0.704, 0.340 and 0.261, respectively. The results clearly show that in all three reactors the concentration of polysaccharide in EPS is more than the protein. Some of the researchers have indicated that protein and humic acid exist in EPS while some of them are saying that the amount of polysaccharides is more in EPS. Costerton *et al*. reported that the polysaccharide is the dominant compound in EPS (Costerton *et al*. 1981). The results in this research showed that the protein to carbohydrate ratio decreased in $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ in comparison to MBR0; this result is in good accordance with Mishima results (Mishima and Nakajima 2009). Since proteins have a good effect on the hydrophobicity of the microbial flocculation, it can be concluded that protein of EPS tends to adsorb on the zeolite and exit with the extra sludge from the reactor. One of the reasons for the increase of protein to olefin ratio in the reactors is the improper operational condition which leads to death and decomposition of the cells resulting that protein and polysaccharide attached to the sludge. Considering the hydrophobicity of the proteins, they attach to the sludge more than the polysaccharide while polysaccharides decompose easier. Because the operational compositions of all three catalysts were similar, it can be concluded that zeolite improved the conditions.

3.7 FTIR analysis

FTIR analysis was used to identify the functional groups on the cake layer formed on the surface of the membrane and can improve the understanding of the fouling mechanism of the membrane during the filtration process. Fig. 8 shows the FTIR spectrum related to MBR_0, $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$, respectively. As it can be seen from the figure, in all three reactors most of the fouling is caused by the protein and polysaccharide but they are not the only compounds and aromatic hydrocarbons and the intermediate

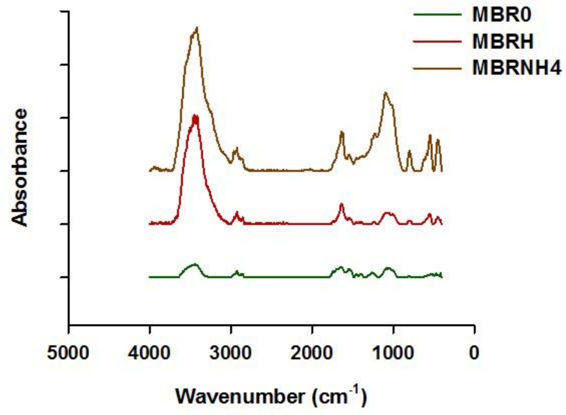


Fig. 8 FTIR spectrum of MBRs

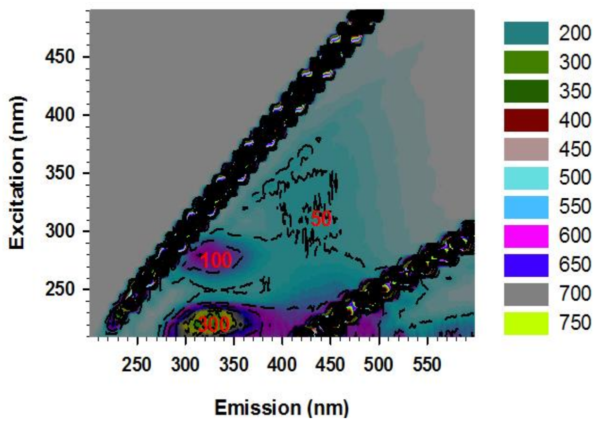
compounds of their decomposition also caused the membrane fouling as well. The polysaccharide related peaks at 800, 1039 and 1080 cm^{-1} decreased in $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ in comparison to MBR0. Also peaks at 1650 and 1652 cm^{-1} which are related to the protein were observed in all three reactors but the decrease of these peaks is less in $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ in comparison to MBR0. This result is in good accordance with the EPS of the cake layer in all three catalysts.

3.8 EEM analysis

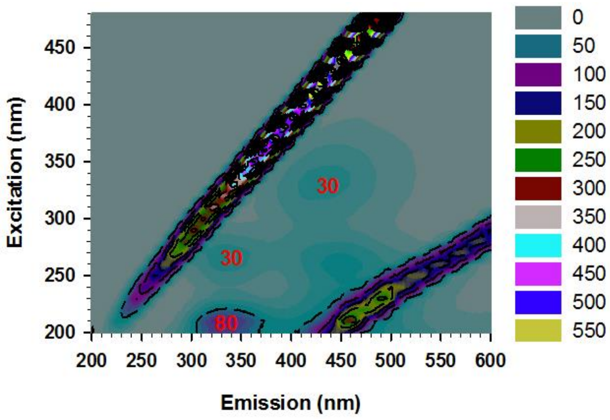
The EEM analysis was done for all three reactors and the results are presented in Fig. 9. In MBR_0 (Fig. 9(a)), the first reactor was observed at E_x/E_m = 270-285/310-340 which shows the protein peak with fluorescence related to aromatic amino acid (tryptophan) and has the intensity of 100. This peak was observed in $MBR_{H\text{-}ZSM\text{-}5}$ (Fig. 9(b)) and $MBR_{NH4\text{-}ZSM\text{-}5}$ (Fig. 9(c)) at intensities of 30 and 25, respectively. The second peak was observed in E_x/E_m = 200-220/310-340 which is related to the protein with the intensities of 30, 80 and 70 for MBR_0, $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$, respectively. As it can be observed, the intensity of the peaks decreased in reactors with zeolite indicating the absorbance of protein compounds by zeolite. Also, a peak at E_x/E_m = 320/440 was observed in MBR_0, $MBR_{H\text{-}ZSM\text{-}5}$ which is related to humic acid. The intensity of this peak was much less in $MBR_{NH4\text{-}ZSM\text{-}5}$ reactor sowing the better performance of $MBR_{NH4\text{-}ZSM\text{-}5}$ in comparison to MBR_0.

4. Conclusions

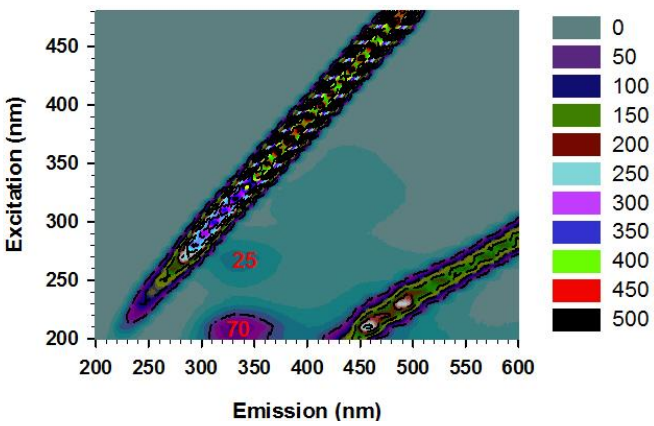
In this research the effect of H-ZSM-5 and NH_4-ZSM-5 nano particles on the membrane fouling was evaluated:



(a) MBR_0



(b) MBR_H



(c) MBR_{NH4}

Fig. 9 EEM of the particles precipitated on the membrane

- The results showed that adding zeolite nano particle enhanced the performance of microorganisms.
- The decrease in TMP in $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ were 45% and 62.5%, respectively due to the existence of zeolite nano particles in the reactors.
- Zeolites caused increase in the size of the particles which leads to the returning of particles from the membrane to the bulk.
- SMP and EPS of the reactors with added zeolites decreased significantly where the SMP decreased 37.5% and 53.9% for $MBR_{H\text{-}ZSM\text{-}5}$ and $MBR_{NH4\text{-}ZSM\text{-}5}$ respectively. EPS decreases were 37.1% and 41.4% in the same order as well.
- FTIR results showed the zeolite nano particles decreased the amount of EPS related to protein and polysaccharide.
- EEM results indicated that zeolites decreased the humic acid and protein on the surface of the membrane.

References

Akram, A. and Stuckey, D.C. (2008), "Flux and performance improvement in a submerged anaerobic membrane bioreactor (SAMBR) using powdered activated carbon (PAC)", *Process Biochem.*, **43**(1), 93-102. https://doi.org/10.1016/j.procbio.2007.10.020

Arabi, S. and Nakhla, G. (2008), "Impact of protein/carbohydrate ratio in the feed wastewater on the membrane fouling in membrane bioreactors", *J. Membr. Sci.*, **324**(1-2), 142-150. https://doi.org/10.1016/j.memsci.2008.07.026

Association, A.P.H., Association, A.W.W., Federation, W.P.C. and Federation, W.E. (1915), Standard methods for the examination of water and wastewater; American Public Health Association.

Chang, I.-S., Le Clech, P., Jefferson, B. and Judd, S. (2002), "Membrane fouling in membrane bioreactors for wastewater treatment", *J. Environ. Eng.*, **128**(11), 1018-1029. https://doi.org/10.1061/(ASCE)0733-9372(2002)128:11(1018)

Cho, J., Song, K.-G. and Ahn, K.-H. (2005), "The activated sludge and microbial substances influences on membrane fouling in submerged membrane bioreactor: unstirred batch cell test", *Desalination*, **183**(1-3), 425-429.

Clesceri, L., Greenberg, A. and Eaton, A. (1998), "Standard Methods for the Examination of Water and Wastewater, APHA, Washington, DC", In: *Standard Methods for the Examination of Water and Wastewater*, *(*20th Ed.), APHA, Washington, DC., USA.

Costerton, J., Irvin, R. and Cheng, K. (1981), "The bacterial glycocalyx in nature and disease", *Annual Rev. Microbiol.*, **35**(1), 299-324.

Damayanti, A., Ujang, Z. and Salim, M. (2011), "The influenced of PAC, zeolite, and Moringa oleifera as biofouling reducer (BFR) on hybrid membrane bioreactor of palm oil mill effluent (POME)", *Bioresource Technol.*, **102**(6), 4341-4346. https://doi.org/10.1016/j.biortech.2010.12.061

Ding, Y., Tian, Y., Li, Z., Zuo, W. and Zhang, J. (2015), "A comprehensive study into fouling properties of extracellular polymeric substance (EPS) extracted from bulk sludge and cake sludge in a mesophilic anaerobic membrane bioreactor", *Bioresource Technol.*, **192**, 105-114. https://doi.org/10.1016/j.biortech.2015.05.067

Du, X., Liu, G., Qu, F., Li, K., Shao, S., Li, G. and Liang, H. (2017), "Removal of iron, manganese and ammonia from groundwater using a PAC-MBR system: the anti-pollution ability, microbial population and membrane fouling", *Desalination*, **403**, 97-106. https://doi.org/10.1016/j.desal.2016.03.002

Geilvoet, S.P. (2010), *The Delft Filtration Characterisation method*: *Assessing membrane bioreactor activated sludge filterability*.

Guo, W., Vigneswaran, S., Ngo, H., Kandasamy, J. and Yoon, S. (2008), "The role of a membrane performance enhancer in a membrane bioreactor: a comparison with other submerged membrane hybrid systems", *Desalination*, **231**(1-3), 305-313. https://doi.org/10.1016/j.desal.2007.10.034

Hai, F.I., Yamamoto, K. and Lee, C.-H. (2013), *Membrane Biological Reactors*, Iwa Publishing.

Hazrati, H. and Shayegan, J. (2016), "Influence of suspended carrier on membrane fouling and biological removal of styrene and ethylbenzene in MBR", *J. Taiwan Inst. Chem. Engr.*, **64**, 59-68. https://doi.org/10.1016/j.jtice.2015.12.002

Hazrati, H., Shayegan, J. and Mojtaba Seyedi, S. (2016), "The effect of HRT and carriers on the sludge specifications in MBR to remove VOCs from petrochemical wastewater", *Desal. Water Treat.*, **57**(46), 21730-21742. https://doi.org/10.1080/19443994.2015.1125800

Hazrati, H., Jahanbakhshi, N. and Rostamizadeh, M. (2018), "Fouling reduction in the membrane bioreactor using synthesized zeolite nano-adsorbents", *J. Membr. Sci.*, **555**, 455-462. https://doi.org/10.1016/j.memsci.2018.03.076

Iorhemen, O.T., Hamza, R.A. and Tay, J.H. (2016), "Membrane bioreactor (MBR) technology for wastewater treatment and reclamation: membrane fouling", *Membranes*, **6**(2), 33. https://doi.org/10.3390/membranes6020033

Ji, J., Li, J., Qiu, J. and Li, X. (2014), "Polyacrylamide–starch composite flocculant as a membrane fouling reducer: key factors of fouling reduction", *Separ. Purif. Technol.*, **131**, 1-7. https://doi.org/10.1016/j.seppur.2014.04.013

Khan, S.J., Visvanathan, C. and Jegatheesan, V. (2012), "Effect of powdered activated carbon (PAC) and cationic polymer on biofouling mitigation in hybrid MBRs", *Bioresource Technolo.*, **113**, 165-168. https://doi.org/10.1016/j.biortech.2011.12.107

Koseoglu, H., Yigit, N., Iversen, V., Drews, A., Kitis, M., Lesjean, B. and Kraume, M. (2008), "Effects of several different flux enhancing chemicals on filterability and fouling reduction of membrane bioreactor (MBR) mixed liquors", *J. Membr. Sci.*, **320**(1-2), 57-64. https://doi.org/10.1016/j.memsci.2008.03.053

Kraume, M. and Drews, A. (2010), "Membrane bioreactors in waste water treatment–status and trends", *Chem. Eng. Technol.*, **33**(8), 1251-1259. https://doi.org/10.1002/ceat.201000104

Le-Clech, P., Chen, V. and Fane, T.A. (2006), "Fouling in membrane bioreactors used in wastewater treatment", *J. Membr. Sci.*, **284**(1-2), 17-53. https://doi.org/10.1016/j.memsci.2006.08.019

Lee, J., Kim, J., Kang, I., Cho, M., Park, P. and Lee, C. (2001), "Potential and limitations of alum or zeolite addition to improve the performance of a submerged membrane bioreactor", *Water Sci. Technol.*, **43**(11), 59-66. https://doi.org/10.2166/wst.2001.0667

Lee, W.-N., Chang, I.-S., Hwang, B.-K., Park, P.-K., Lee, C.-H. and Huang, X. (2007), "Changes in biofilm architecture with addition of membrane fouling reducer in a membrane bioreactor", *Process Biochem.*, **42**(4), 655-661. https://doi.org/10.1016/j.procbio.2006.12.003

Li, C., Dong, Y., Wu, D., Peng, L. and Kong, H. (2011), "Surfactant modified zeolite as adsorbent for removal of humic acid from water", *Appl. Clay Sci.*, **52**(4), 353-357. https://doi.org/10.1016/j.clay.2011.03.015

Lin, H., Zhang, M., Wang, F., Meng, F., Liao, B.-Q., Hong, H., Chen, J. and Gao, W. (2014), "A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: characteristics, roles in membrane fouling and control strategies", *J. Membr. Sci.*, **460**, 110-125.

https://doi.org/10.1016/j.memsci.2014.02.034

Meng, F., Chae, S.-R., Drews, A., Kraume, M., Shin, H.-S. and Yang, F. (2009), "Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material", *Water Res.*, **43**(6), 1489-1512. https://doi.org/10.1016/j.watres.2008.12.044

Mishima, I. and Nakajima, J. (2009), "Control of membrane fouling in membrane bioreactor process by coagulant addition", *Water Sci. Technol.*, **59**(7), 1255-1262. https://doi.org/10.2166/wst.2009.090

Ngo, H.-H. and Guo, W. (2009), "Membrane fouling control and enhanced phosphorus removal in an aerated submerged membrane bioreactor using modified green bioflocculant", *Bioresource Technol.*, **100**(18), 4289-4291. https://doi.org/10.1016/j.biortech.2009.03.057

Rezaei, M. and Mehrnia, M. (2014), "The influence of zeolite (clinoptilolite) on the performance of a hybrid membrane bioreactor", *Bioresource Technol.*, **158**, 25-31. https://doi.org/10.1016/j.biortech.2014.01.138

Rostamizadeh, M., Yaripour, F. and Hazrati, H. (2018), "Ni-doped high silica HZSM-5 zeolite (Si/Al=200) nanocatalyst for the selective production of olefins from methanol", *J. Anal. Appl. Pyrol.*, **132**, 1-10. https://doi.org/10.1016/j.jaap.2018.04.003

Safavi, B., Asadollahfardi, G. and khodadadi Darban, A. (2017), "Cyanide removal simulation from wastewater in the presence of titanium dioxide nanoparticles", *Adv. Nano. Res., Int. J.*, **5**(1), 27-34. https://doi.org/10.12989/anr.2017.5.1.027

Saha, N., Balakrishnan, M. and Ulbricht, M. (2007), "Sugarcane juice ultrafiltration: FTIR and SEM analysis of polysaccharide fouling", *J. Membr. Sci.*, **306**(1-2), 287-297. https://doi.org/10.1016/j.memsci.2007.09.006

Stephenson, T., Brindle, K., Judd, S. and Jefferson, B. (2000), *Membrane Bioreactors for Wastewater Treatment*, IWA Publishing.

van den Brink, P., Satpradit, O.A., van Bentem, A., Zwijnenburg, A., Temmink, H. and van Loosdrecht, M. (2011), "Effect of temperature shocks on membrane fouling in membrane bioreactors", *Water Res.*, **45**(15), 4491-4500. https://doi.org/10.1016/j.watres.2011.05.046

Wang, S. and Peng, Y. (2010), "Natural zeolites as effective adsorbents in water and wastewater treatment", *Chem. Eng. J.*, **156**(1), 11-24. https://doi.org/10.1016/j.cej.2009.10.029

Wu, B., An, Y., Li, Y. and Wong, F.S. (2009), "Effect of adsorption/coagulation on membrane fouling in microfiltration process post-treating anaerobic digestion effluent", *Desalination*, **242**(1-3), 183-192. https://doi.org/10.1016/j.desal.2008.04.005

Yang, X.-L., Song, H.-L., Lu, J.-L., Fu, D.-F. and Cheng, B. (2010), "Influence of diatomite addition on membrane fouling and performance in a submerged membrane bioreactor", *Bioresource Technol.*, **101**(23), 9178-9184. https://doi.org/10.1016/j.biortech.2010.07.037

Yuniarto, A., Noor, Z.Z., Ujang, Z., Olsson, G., Aris, A. and Hadibarata, T. (2013), "Bio-fouling reducers for improving the performance of an aerobic submerged membrane bioreactor treating palm oil mill effluent", *Desalination*, **316**, 146-153. https://doi.org/10.1016/j.desal.2013.02.002

Zuriaga-Agustí, E., Bes-Piá, A., Mendoza-Roca, J.A. and Alonso-Molina, J.L. (2013), "Influence of extraction methods on proteins and carbohydrates analysis from MBR activated sludge flocs in view of improving EPS determination", *Separ. Purif. Technol.*, **112**, 1-10. https://doi.org/10.1016/j.seppur.2013.03.048

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