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**Regular Article** 

# **Reduction of fouling in the membrane bioreactor using the combination of electrochemical and adsorbention processees**

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#### ABSTRACT

The membrane bioreactor (MBR) is a combination of biological and membrane systems. It utilizes advanced technologies in the treatment of various types of wastewater, having unique advantages such as the highquality effluent and improved efficiency. The primary limiting factor for the utilization of this bioreactor is the membrane fouling phenomenon, which increases operational costs. In this study, four membrane bioreactors were used, with the first MBR (R1) serving as the control bioreactor. In the second MBR (R2), an adsorption process was employed, while in the third (R3) and fourth MBR (R4), in addition to the adsorption process, the electrochemical process was applied with voltages of two and one volts respectively. For the four bioreactors, the percentages of the Chemical Oxygen Demand (COD) were recorded as 86%, 91.2%, 90.7%, and 95.3% respectively. The levels of the total Extracellular Polymeric Substances (EPS) in R1, R2, R3, and R4 were about 260, 155, 177, and 98 mg/gVSS respectively. The R4 exhibited significantly lower EPS (98 mg/gVSS) compared to R1 (260 mg/gVSS), possibly due to the adsorption of EPS by nanoparticles and its subsequent removal during the electrochemical process. The role of voltage was evident in R3, where the higher voltage (2V) resulted in the less removal of EPS (155 mg/gVSS) compared to the same in R4 (98) mg/gVSS). The study found that the values of the Soluble Microbial Products (SMP) for R4, R3, R2, and R1 were about 15, 65, 55 and 139 mg/L respectively. Particularly in the most effective MBR, R4, where the addition of the zeolite adsorbent alongside metal ions demonstrated the best performance in the removal of SMP.

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# 1. Introduction

According to reports, the global water demand is projected to increase by 55 percent by the year 2050 due to a 400 percent increase in production of various material[1].Water resources around the world are declining due to various factors such as the population growth and agricultural and industrial activities[2]. Also, with the increasing growth of petrochemical industries in the country, the environmental problems being resulted from the wastewater produced by these industries have increased. Therefore, water recycling seems necessary in all industries, especially in petrochemical industries. Global water problems require the provision of new and more cost-effective methods of water and wastewater treatments, which have the capability of treating various types of effluents [3, 4]. Biological methods compared with other methods have a wide spectrum of advantages as they are compatible to the nature. Among the biological methods, the conventional activated sludge has been employed in many industries including the petrochemical industry [5]

Using the membrane Bioreactor (MBR) technology is a method in which the activated sludge and membrane separation are combined Using the MBR technology [6]. has advantages over the activated sludge method, including the high-quality water being produced, less sludge being produced, and retention time being reduced.[7]. The MBR method can be used for the treatment of various types of wastewater, such as the ones in textile[8, 9], tannery[10, 11], paper and pulp[12, 13], and petrochemical industries[14], landfills[15, 16], grey water[17, 18], Pharmaceutical industry[19-21] and so on...

Studies have shown that 3 to 3.5 cubic meters of petrochemical wastewater is produced per ton of petrochemical products [22]. The wastewater treatment in petrochemical industries can be challenging due to the factors such as the high molecular weight, strong molecular bonds, hydrophobicity, and low hydrocarbons solubility of in water. Additionally, the high Chemical Oxygen Demand (COD) and low biodegradability make their treatment difficult. Furthermore, the effluents generated in different stages have varying compositions and are often complex in terms of physical and chemical properties.[23] MBR systems, despite their high efficiency, also have limitations such as membrane fouling [24]. Membrane fouling is used to describe the blockage of pores caused by the deposition of particles and colloids on the membrane surface [25, 26]. The types of deposits formed on the surface of membranes include suspended solids such as small particles of sand or clay, organic materials such as lipids and carbohydrates, and microbial biomass due to the growth of bacterial and fungal populations and protozoa that aid in the degradation of organic matter [27].

Various methods have been developed to control or reduce fouling in MBRs. The most common approaches include employing the conventional physical and chemical methods, optimizing the operation of the MBR process, reducing hydraulic flux, increasing aeration, utilizing electric fields or ultrasound, etc.[28]. Electrochemical Membrane **Bioreactors** (EMBRs) work in conjunction with electrode configurations in a MBR to facilitate an electrochemical reaction and enhance the removal of pollutants and nutrients from wastewater[29]. In a study conducted by[30], it was found that the use of electrochemical coagulation in a MBR resulted in an increase in the efficiency of the removal of COD from 71.24% to 83.53% compared to using the control MBR. Another investigation by[31] revealed that the application of an electric field increased the membrane flux and reduced the thickness of the fouling layer formed on the membrane. In the study by[32], it was determined that the presence of an electric field inside the MBR led to a 16.3% reduction in irreversible membrane fouling [33]. Also it reported a 4% improvement in the efficiency of the removal of COD and a decrease in membrane fouling due to the use of electrocoagulation.

Another method for reducing fouling in MBRs is the use of absorbents.[34] Adsorbents particularly offer the potential to adsorb dissolved organic polymers, notably Soluble Microbial Products (SMP), hence reducing the propensity for membrane fouling [35]. The main substances used for adsorption in MBRs include activated carbon and zeolite as adsorbents.[35, 36]. In the present study, the zeolite adsorbent has been used, which has been identified in the investigation by [37]to improve the removal of COD and increase critical flux when. Additionally, the concentration of SMP decreased while the concentration of Extracellular Polymeric Substances (EPS) increased. In another study conducted by [38] two types of zeolite were synthesized and the results showed that adding zeolite reduced Transmembrane Pressure (TMP) by 47% and 67% for one of the synthesized wastewater. In another research by Damayanti et al., three different befouling mitigates, powdered activated carbon (PAC), zeolite (Ze), and Moringa oleifera (Mo), were used with the doses of 4, 8, and 12 grams per respectively. Short-term filtration liter experiments and critical flux experiments were conducted. The results showed that all adsorbents successfully removed soluble microbial products (SMP) with the removal percentages of 58%, 42%, and 48% for PAC, Ze, and Mo respectively [39].

The aim of this research was to investigate the effects of adsorption and electrocoagulation

processes simultaneously on the mitigation of fouling in a membrane bioreactor. In this study, the synthesized zeolite adsorbent and electrochemical processes were employed. Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile Suspended Solids (MLVSS)/MLSS ratios. Particle Size distributions (PSD), concentrations of SMP and EPS, and the FTIR analysis, were measured to evaluate the effects of adsorption and electrochemical processes. Furthermore, the synthetic wastewater was simulated as petrochemical wastewater in terms of COD which was about 900 mg/L.

# 2. Methods and materials 2.1. Synthesis of zeolite

After combining the raw materials and preparing the solution, according to [40], an autoclave equipped with electric temperature controller was employed for the hydrothermal synthesis of zeolite. The autoclave maintained constant temperature throughout a the synthesis process. Following a temperature reduction and adjusting the pH of the prepared powder to 7 to eliminate templating molecules, the materials were once again subjected to a temperature of 540 degrees Celsius for 24 hours inside a furnace under atmospheric pressure to produce the adsorbent. The BET analysis and Fourier Transform Infrared (FTIR) spectroscopy were utilized to determine characteristics of the the synthesized adsorbent (See supplementary data).

# 2.2. MBR

To carry out this project, four MBRs with dimensions of 10\*10\*35 centimeters were designed and constructed. The MBRs are made of plexiglass, and the effective volume within each MBR is 2 liters. In the third and fourth MBRs, an electric field is created by two baffles placed near the membrane module. The MBR is composed of several main parts, including an air diffuser placed at the bottom of the MBR, and two sampling valves embedded at distances of 2 and 15 centimeters from the bottom of the tank. A 200-watt heater is installed inside the MBRs to regulate the temperature. The schematic diagram of the system is shown in Figure 1. The used membrane is made of PVDF (Polyvinylidene fluoride) with a pore size of 0.1 micrometers. It has an effective surface area of 12.5 square centimeters and is placed inside the modul.



Figure 1. Schematic of the membrane bioreactor used in the investigation.

The sludge used in the membrane bioreactors obtained from Tabriz Petrochemical is Company with concentration of а approximately 2200 mg/L of MLSS. It was fed with synthetic wastewater according to Table 1 for one month to become compatible with the MBR environment. Sampling was conducted from the membrane effluent and the mixed liquid inside the MBR every three days for the relevant analysis. The operational conditions, as mentioned in Table 2, were considered. The filtration process performed was discontinuously. Daily feeding was followed by a sufficient retention time, and a constant suction was applied to maintain the TMP (Transmembrane Pressure). The suction duration was 10 minutes, followed by a 2minute rest. The filtration process was repeated three times per day.

# 2.3. Operational conditions

Operational conditions were the same in all MBRs except for the use of adsorbent and/or establishment of an electric field. The control MBR (R1) was considered as the simple MBR and no adsorbent or electric field was used. In the second MBR (R2), the zeolite adsorbent was added. In the third (R3) and fourth MBRs (R4), an adsorbent was used alongside an electric field. The only difference in these two MBRs was the applied voltage. Aluminum anode and cathode plates were placed in these

two MBRs. Other conditions were the same for all MBRs. The operational conditions are listed in Table 2. In this study, the temperature was kept constant. For this purpose, a thermocouple was used to regulate the temperature at 30 degrees with an error of around 2 degrees. Additionally, the daily pH was measured.

#### Table1

Characteristics of the synthetic wastewater

materials	concentration (mg/l)		
C <sub>2</sub> H <sub>5</sub> OH	350		
$K_2HPO_4$	35		
$KH_2PO_4$	45		
Urea	560		
MgSO <sub>4</sub> .7H <sub>2</sub> O	13		
CaCl <sub>2.</sub> 2H <sub>2</sub> O	7		
FeCl <sub>3</sub>	5		
NaHCO <sub>3</sub>	500		

#### Table2

Operating conditions of reactors

adsorbent	Electric field(volte)	MLSS(mg/L)	HRT(hr)	рН	aeration rate
					(L/min)
-	-	3000-5000	8	6-7.5	8
Zeolite	-	3000-5000	8	6-7.5	8
Zeolite	2V	3000-5000	8	6-7.5	8
Zeolite	1V	3000-5000	8	6-7.5	8
	adsorbent - Zeolite Zeolite Zeolite	adsorbentElectric field(volte)Zeolite-Zeolite2VZeolite1V	adsorbent         Electric field(volte)         MLSS(mg/L)           -         -         3000-5000           Zeolite         -         3000-5000           Zeolite         2V         3000-5000           Zeolite         1V         3000-5000	adsorbent         Electric field(volte)         MLSS(mg/L)         HRT(hr)           -         -         3000-5000         8           Zeolite         -         3000-5000         8           Zeolite         2V         3000-5000         8           Zeolite         1V         3000-5000         8	adsorbent         Electric field(volte)         MLSS(mg/L)         HRT(hr)         pH           -         -         3000-5000         8         6-7.5           Zeolite         -         3000-5000         8         6-7.5           Zeolite         2V         3000-5000         8         6-7.5           Zeolite         1V         3000-5000         8         6-7.5

# **2.4.** Measurement of the net water flux and resistance

To measure the net water flux, a membrane was placed inside the module and the MBR was filled with distilled water. Water is sucked from the membrane under a pressure of 0.12 bar, the amount of water passed through the membrane was measured. This flux was called J0. Then, the liquid mixture was poured into the MBR and the module was placed inside the MBR system. After a filtration process in the MBR to determine the pure water flux, the module was removed from the MBR and placed back into the MBR containing water to measure its flux after fouling (J1). After physical cleaning, the flux passing through the membrane in the presence of water was measured (J2). Finally, after chemical cleaning, the flux passing through the membrane, referred to as (J3), was measured. Since there is a direct relationship between fouling and the decrease in flux through the membrane, the simple series resistance model is the easiest method to determine the flux. The following formula is used to measure the resistances:

$$R_t = R_m + R_f + R_c + R_p \tag{1}$$

In this equation, Rt represents the total resistance of the membrane, Rm represents the intrinsic resistance of the membrane, Rf represents the fouling resistance, RC represents the cake layer resistance, and RP represents the pore resistance with a unit of 1/m. The following equations were used to measure each of these resistances:

$$R_t = \frac{TMP}{\mu J_1} \tag{2}$$

$$R_m = \frac{TMP}{\mu J_0} \tag{3}$$

$$R_c = R_T - \frac{TMP}{\mu J_2} \tag{4}$$

$$R_f = \frac{TMP}{\mu J_3} - R_m \tag{5}$$

$$R_p = R_T - (R_m + R_C + R_F) \tag{6}$$

In these equations, TMP represents the

transmembrane pressure (0.12 bar) with a unit of Pascal.

# 2.5. Physical cleaning and chemical cleaning:

For the physical cleaning of the membrane, after separating the membrane from the module, the surface of the membrane was washed with distilled water for 5 minutes. For chemical cleaning, the membrane was placed in a 1% volume hypochlorite solution for 15 to 30 minutes.

#### 2.6. Analysis methods

In this project, the thermal method was used to extract EPS. The analysis of protein and carbohydrate was carried out to measure the amount of EPS and SMP in the sample. The Lowry method was used to measure the protein content, and the Anthrone method was used for the analysis of the carbohydrate. The standard wastewater treatment method was used for the analysis of COD [41]. The FTIR analysis provides information about the functional groups present in the EPS cake formed on the surface of the membrane. Each experiment was repeated three times.

The adsorption isotherms were determined using the NOVA2000 (USA) Quantachrom device, and the surface area and pore volume were calculated based on the experimental data. The particle size analysis PSD was used to determine the size of the sludge particles and the cake formed on the membrane. The mixed liquor suspended solid (MLSS) and mixed liquor volatile suspended solid (MLVSS) were estimated according to the standard methods.

#### 3. Results and discussion

The permeate flux through the membrane was evaluated in all four MBRs, and it was observed that the permeate flux in the fourth MBR (R4) was significantly higher than that in the other MBRs. After 30 days, the nonabsorbent membrane (R1) was completely fouled, and the permeate flux reached zero. Figure 2 shows the flux decline in the four MBRs, with a steeper slope in the first MBR (R1).



Figure 2. Permit flux through the membrane in each of the four bioreactors.

In addition, in the third and fourth MBRs (R3 and R4), the electric field fusion with voltages of 2V and 1V, respectively, were used alongside the adsorbent. Initially, the flux passing through the membrane in the R3 was higher than the same in the R4 but gradually decreased, and membrane fouling increased. The reason for this phenomenon can be interpreted as the rapid corrosion of the anodic membrane with the application of a high voltage in the MBR, and an increase in metallic particles that are separated from the surface of the anode during electrolytic dissolution and reach the membrane surface, leading to an increase in fouling. Therefore, by the application of the high voltage the flux initially increased, but after a while, it completely clogged the membrane pores, and even after chemical cleaning, the flux passing through R2's membrane was lower, indicating the irreversible fouling in the R3. In general, comparing the four MBRs, it can be concluded

that in the first MBR, due to the absence of an electric field and adsorbent, the permeate flux through the membrane decreased significantly over time, a phenomenon that is always observed in membrane filtration processes due to the presence of activated sludge particles fouling the membrane. However, in the R2, the adsorbent with its characteristics was able to improve the membrane performance to a satisfactory extent. In the R3 and R4, it was observed that the voltage of 2V adversely affected the EMBR performance.

**3.1. Examining the type of membrane fouling** As mentioned in Figure 2, it was determined that the permeate flux through the membrane would decrease over time, indicating the fouling of the membrane and the blockage of its pores. By comparing the permeate flux, it is observed that the highest flux is related to the R4, and the lowest flux is related to R1. Approximately 35% and 25% improvements in the amount of flux are observed in the R2 & R3

respectively, while around 50% improvement in the amount of flux is observed in R4. Considering the operational conditions in the R4, the improvement in the properties of the sludge and its characteristics can be attributed to the use of an alternating electric field and the presence of the zeolite adsorbent. To determine the resistance of the membrane fouling in MBR, the flux after the physical and chemical cleaning of the membrane was measured using the specified equations, and the results are presented in Table 3. Based on the results, it can be understood that the highest resistance to fouling is in R1, while the lowest resistance is in R4. Additionally, in R4, the cake layer resistance is zero and does not affect the flux reduction. The fouling created through physical cleaning is not removable and requires chemical cleaning. Furthermore, these results show that the cake layer resistance in the R4 decreases about 51% compare to that in the R1. In another study conducted by [32] to investigate the effect of the zeolite adsorbent, it was determined that the cake resistance decreased by only 16.3%. In the present study, this amount increased further (about 51%) due to the simultaneous use of electrocoagulation and adsorption, leading to a 50% increase in membrane flux after cleaning.

The reason for the decrease in the cake layer resistance in the R4 can be explained as follows:

the zeolite absorbent and metal particles detached from the anode electrode adsorb the soluble microbial products (SMP) and reduce their concentration in the bulk liquid. The SMPs can fill the empty spaces between particles in the cake layer, increasing the porosity and reducing its compaction factor upon removing the SMPs. Additionally, the thickness of the cake layer decreases. Furthermore, in the R4, the particle size distribution increases due to the presence of the absorbent and the application of the electric flocculation process. Consequently, the size of the sludge flocs increases, and due to their inability to penetrate the pores, they remain on the surface of the membrane, increasing the possibility of the backflow of particle from the surface of the membrane to the liquid phase and reducing the cake layer resistance to nearly zero. Moreover, by examining the results, it can be understood that the main fouling is caused by pore blockage and is irreversible, but can be removed by chemical cleaning. The adsorption of proteins and smaller particles inside the air pockets of the membrane pores creates irreversible fouling. The membrane resistance includes intrinsic membrane resistance (Rm), cake layer resistance (Rc), fouling resistance (Rf), and pore resistance (Rp). In this study, these resistances were measured at the end of the process for all four MBRs.

#### Table3

Membrane resistances for each of the reactors

MBR	<b>R</b> <sub>t</sub> *10 <sup>12</sup>	<b>R</b> <sub>m</sub> *10 <sup>12</sup>	$R_c*10^{12}(m^{-1})$	R <sub>f</sub> *10 <sup>12</sup>	R <sub>p</sub> *10 <sup>12</sup>
	( <b>m</b> <sup>-1</sup> )	( <b>m</b> <sup>-1</sup> )		( <b>m</b> <sup>-1</sup> )	( <b>m</b> <sup>-1</sup> )
R1	6.03	0.35	0.96	1.77	2.87
R2	2.96	0.35	0.18	0.56	1.87
R3	3.16	0.35	0.21	0.63	1.97
R4	1.83	0.35	0	0.08	1.4

# 3.2. Removal of COD and MLSS

The MBR is fed daily with COD with the concentration of 1000 mg/L. Figure 3 illustrates the efficiency of the removal of COD for four MBRs. The MBR without zeolite (R1) shows an efficiency of 86% of the removal of COD, while the MBR with zeolite (R2) demonstrates a higher efficiency of 91.2%. This indicates that the zeolite adsorbs organic substances on its surface, leading to an increase in the removal of COD and growth of MLSS suggest that the zeolite adsorbent is compatible with microorganisms and has no adverse effects.

The R3, which operates with an adsorbent and a voltage of 2V, initially exhibits a rapid removal of COD, but its concentration gradually decreases over time, following a constant and then descending trend. The efficiency of the removal of COD is 90.7%. However, the R4, which is set at a voltage of 1V, achieves better results with an efficiency of 95.3% of the removal of COD. This is due to the strong electric field increasing the anodic reaction rate, resulting in faster separation of ions from the anode. However, applying higher voltages initially increases the permeate flux, but after a while, it causes complete pore blocking and irreversible fouling. Additionally, it affects the adsorbent and interferes with its performance. The concentrations of MLSS remain constant across all four MBRs throughout the process. According to a study

conducted by Hou et al. [30], for the comparison of using electrocoagulation alone in a membrane bioreactor, the efficiency of the removal of COD increased from 71.24% to 83.5% compared to the same in the control reactor. However, in the current study, this removal rate increased from 86% to 95.3% compared to that in the control reactor. Also, other researchers show that the efficiency of the removal of COD reached 92% by adding the zeolite adsorbent, indicating a lower amount compared to the obtained results in the present research [32].

In the R4, the high efficiency of the removal of COD in MBR can be attributed to the electrical condensation, encompassing the electrochemical oxidation and electrochemical adsorption. The applied electric field promotes the oxidation of organic matter, leading to an increase in the biological decomposition and enhanced removal of COD and other pollutants. The cationic monomers and polymers of Al(OH)3 and Al3+ act as adsorbents, absorbing organic substances on their surface, thus accelerating the removal rate of organic loads. These cationic monomers and polymers are compatible with microorganisms and non-toxic and improve the performance and activity of microorganisms in removing the organic load. Moreover, the use of nano zeolite as an adsorbent in this system enhances the removal of COD due to its ability to adsorb organic matter onto its surface.



Figure 3. Percentages of the removal of COD for MBRs.

Figure 4 shows the levels of the concentration of the sludge in all four MBRs. As it is evident in the figure, the concentration of MLSS is approximately the same for all four MBRs and fluctuates between 3500 to 5000 milligrams per liter. Therefore, it can be concluded that the zeolite and electric field have not caused any disruption in the growth of microorganisms. The concentration of the biomass increases over time in all four MBRs. The high percentage of the removal of COD in all MBRs indicates an increase in the biological growth and demonstrates its activity.



Figure 4. Changes in MLSS during the operation of the MBRs.

#### 3.3. Analysis of the MLSS/MLVSS ratio

In all MBRs, the ratio of volatile solids to total solids in the mixed liquor showed an increasing trend throughout the experimental period. In all MBRs, this ratio was initially around 0.75 grams per liter, as all MBRs were supplied by the same activated sludge source. As observed in Figure 5, all MBRs followed a similar trend until the fifteenth day, but from that day onward, an increase in the concentration of MLVSS was more noticeable in the second and fourth MBRs (R2 and R4). For example, on day 30, in comparison to the R1, the concentration of MLVSS in the R4 was 21% higher, and in the R2, it was 17% higher. The growth of MLVSS after 15 days can be attributed to two factors. First, due to the presence of nano zeolite in these two MBRs compared to the R1, there is a higher consumption of the medium due to the ammonium adsorption, leading to an increase in cation exchange between the adsorbent and activated sludge. The increased consumption of

ammonium leads to more assimilation of the medium. This enhanced assimilation not only results in the removal of nutrients but also promotes the growth of microorganisms. Second, due to the presence of the adsorbent and increased ammonium assimilation in the mixed liquor, the population of nitrifying bacteria increases [42]. The steady growth of nitrate reducers after the fifteenth day leads to the formation of biofilm on the adsorbent particles, promoting the growth of MLVSS. In the R4, due to the establishment of an electric field and the presence of metallic particles alongside the adsorbent, the growth of MLVSS is higher compared to the same in the R2. the Additionally, in R3, due the to establishment of a strong electric field, the concentration of MLVSS is lower compared to that in the R2 and R4. In other research, it has been shown that by creating a strong electric field, it is possible to reduce the biological activity and MLVSS/MLSS ratio [43, 44]



Figure 5. MLSS/MLVSS ratio during the operation of the MBRs.

#### 3.4. SMP and EPS analysis

The total levels of EPSt in R1, R2, R3, and R4 are about 260, 155, 177, and 98 mg/gVSS respectively. Comparing the R1 &R2, it was observed that EPS in R2 was significantly lower than in R1. This decrease could be due to EPS being absorbed by the surface of nanoparticles and subsequently being removed from the system during sludge settling. In the R3 compared to the R4, due to the higher voltage (2V), there was less removal of EPS. R4 was observed to have the highest level of the removal of EPS compared to other MBRs. The decrease in EPS in R4 could be attributed to the role of the adsorbent and metal particles, which separate from the anode surface during the electrochemical dissolution and precipitate by absorbing organic compounds and colloids. compared to the R1, Therefore, more adsorption occurs, and on the other hand, with adsorption, the content of EPS in the planktonic EPS decreases, resulting in a less compact layer formed on the membrane. Thus, it can be said that the presence of the zeolite adsorbent, alongside metal ions, improves the removal of EPS from the solution. It was also observed that the levels of  $EPS_c$  and  $EPS_p$  in the R4, were lower than the same in the other MBRs. The values of EPSc for R1, R2, and R3 and R4 were 31.95, 24.10, 27.12, 7.75 mg/gVSS respectively, and the values of EPS<sub>p</sub> for the mentioned four **MBRs** were 228.04,130,89,149.87 and 90.24 mg/gvss. The SMPt values for R1, R2, R3 and R4 were 139,55,65 and 15 mg/L respectively. The SMP<sub>c</sub> values for the four MBRs were 46.53, 17.35 ,21.32 and 3 mg/L, and the SMP<sub>p</sub> values for the four MBRs mentioned were 92.46, 37.64, 43.67 and 12 mg/L. As it's observed, the role of the

adsorbent and electric field is quite noticeable. The reason for this is the adsorption of proteins and polysaccharides onto nanoparticles and separate metal ions from the anode, which ultimately leads to a decrease in SMP in the system. The decrease in SMP can be explained as follows: SMP in the bulk solution is recognized as soluble cellular tissue components that are released into the solution during cell lysis. The presence of metal particles as absorbents in the mixed liquid causes the adsorption of SMP molecules with high molecular weight, resulting in the formation of large biomass flocs attached to the absorbent. Over time, it leads to the removal of organic matter such as SMP in the EMBR. Considering the results, the best performance is observed in the R4. This is because, in addition to the metal ions deposited from the anode, the zeolite adsorbent has also been added, which has also been observed in the removal of EPS. Figures 6 and 7 show the overall changes in EPS and SMP in MBR systems respectively. Based on these two figures, it can be concluded that the R4 had the most suitable performance. The EPS values in the R1, R2, and R3 and R4 were about 250 mg/gVSS, and in the end, they reached about 260, 155, 177, and 98 mg/gVSS respectively. The SMP values at the beginning of the process were about 100 mg/L and in the end, they reached about 139, 55, 65 and 15 mg/L. Based on these results, the EPS and SMP values increased in the R1, remained constant in the R2 & R3, and decreased in the R4, which was due to the adsorption by the adsorbent alongside the electrochemical field. In all MBRs, the amount of protein was higher than the amount of carbohydrates, suggesting that protein is the influential substance in membrane fouling.



Figure 6. Concentration of EPS during the operation of the MBRs.

In this study, the contents of protein and polysaccharide in EPS and SMP in the activated sludge were measured once every five days in each experiment. According to Figures 7 and 8, EPS and SMP showed an increasing trend in the R1, while they exhibited a decreasing trend in the other MBRs. These results are consistent with the results of other researchers who have separately used adsorbents and electrochemical processes to reduce membrane fouling in MBR. [38, 40].



Figure 7. Concentration of EPS during the operation of the MBRs.

#### 3.5. PSD analysis

The particle size and distribution of sludge in a system have significant impacts on the fouling and clogging of membrane pores. The measurement of the particle size of the activated sludge typically falls within the micrometer range. Since the cake layer formed by flocs is reversible, more focus is placed on fine micronsized particles, which create irreversible fouling. Figure 8 shows the distribution of the particle size of the sludge in four MBRs. According to the obtained results, the average particle size of the sludge in the R4 is larger than those in the other MBRs. In R4, where an electric field was used alongside an adsorbent, the largest particle size of the sludge was observed. This can be attributed to the presence of metallic particles and the adsorbent. The metallic particles, detached from the surface of the anode, along with the adsorbent, can adsorb dissolved organic compounds, colloidal matter, and floating bacteria, forming flocs. As a result, the average particle size in the R4 (about 75 micrometer) is higher than those in the other MBRs. The presence of the adsorbent and metallic particles leads to the formation of larger flocs, which in turn form a cake layer with higher porosity on the membrane surface, thereby increasing the permeate flux. In another study [40], the presence of zeolite nanoparticles increased the size of sludge particles. They reported that the average particle size under the same conditions was about 65 micrometers. While in this research, due to the simultaneous of absorbent and presence the the electrocoagulation process, the size of the particles has increased.



Figure 8. Particle size distribution on the cake in the membranes inside MBRs.

#### 3.6. FTIR analysis

To better understand the presence of proteinaceous and polysaccharide materials, as well as functional groups within the sludge, the FTIR analysis was conducted. Additionally, FTIR enables the identification of the functional groups present in the cake layer formed on the surface of the membrane, providing a better understanding of the fouling mechanism using different wavelengths. The compounds present in the sludge include proteinaceous materials, polysaccharides, aliphatic and aromatic hydrocarbons, as well as humic acids.

#### Table 4

Specifications of and functional groups in bioreactor membrane cakes

<u> </u>		Eurotional		Abaambad Abaambad		Abasybod Abasybod		
	Wavelength	Functional	Result	Absorbed	Absorbed	Absorbed	Absorbed	
		group		IOF KI	IOF K2	IOF K5	IOF K4	
1	3100-3500	N-H stretching	Polysaccharide	0.49	0.45	0.43	0.51	
		Hydroxyl in						
		polysaccharides						
2	2850-3000	Characteristics	Polysaccharide	0.24	0.08	0.12	0.045	
		of	5					
		polysaccharides.						
		Aliphatic CH2						
		or C-H						
		stretching						
		alkana						
3	1652 1650		Protein	0.27	0.06	0.125	0.025	
5	1052-1050	C-IN Amid(I)	aomnounda	0.27	0.00	0.125	0.025	
4	1550 1540	$\operatorname{Amid}(\mathbf{I})$	Drotain	0.11	0.05	0.1	0.02	
4	1550-1540	Amu(II)		0.11	0.05	0.1	0.02	
			compounds					
5	1235-1385	Amid(III)	Protein	0.2	0.12	0.115	0.01	
5	1255 1505	/ mind(III)	compounds	0.2	0.12	0.115	0.01	
6	1/1/	Stretching and	A mino acid or	0.11	0.06	0.055	0.01	
0	1414	summetrie	aromatic	0.11	0.00	0.055	0.01	
		symmetric	aiomatic					
		COO with	compounds					
		COO- with						
		amino acid						
_	1000	amide bonds	<b>N</b> 1 1 1 1	0.4 7				
7	1200	Symmetrical	Polysaccharide	0.15	0.23	0.23	0.045	
		and stretching						
		C-0						
8	800-1414	Calcium	Polysaccharide	0.38		0.27	0.045	
		carbonate						

As shown in Table 4, membrane fouling primarily occurred due to the presence of proteins and polysaccharides in the R1. Additionally, compounds such as aliphatic and hydrocarbons aromatic or intermediate compounds also played a role in fouling. The concentration of polysaccharides decreased in the second MBR during the wavelengths of 1030-1080. Similarly, the amount of protein was lower at the wavelength of 1650. The EPS results also showed a decrease in the concentration of protein in the R2. In the R3, the amounts of protein and polysaccharide were less compared to the same the R1, but higher compared to that in the MBR where only the zeolite adsorbent was used. Favorable results were observed in the R4, where protein peaks and some polysaccharide peaks were significantly reduced.

# 4. Conclusion

The comprehensive evaluation of four MBRs in this study provides valuable insights into the performance and fouling mechanisms of membrene associated with different operational conditions. The findings indicate that the R4 exhibited superior permeate flux compared to

the other MBRs, which is attributed to the synergistic effects of an alternating electric field, applied voltages, and the presence of the zeolite adsorbent. However, it is crucial to note that the application of the high voltage in the R3 initially increased flux but led to irreversible fouling over time. Examining the type of membrane fouling revealed that the pore blockage was the primary cause, and while chemical cleaning was effective, some irreversible fouling persisted. The resistance to fouling was notably lower in the R4, where the adsorbent and electric field contributed to the enhanced sludge properties and reduced cake layer resistance. The role of EPS in fouling was evident, with the adsorbent and electric field being proved effective in reducing the level of EPS, particularly in R4. The analysis of the particle size distribution demonstrated that the R4 with the electric field and adsorbent had the sludge with bigger particle sizes, contributing to higher permeate flux. The FTIR analysis further highlighted the presence of proteins and polysaccharides as key contributors to membrane fouling, with the R4 exhibiting significant reductions in the amount of these compounds. Overall, the study underscores the importance of optimizing operational conditions, utilizing adsorbents, and carefully managing applied voltages to enhance the performance of MBR. The R4 emerged as the most effective configuration, showcasing an improved permeate flux, reduced fouling resistance, and enhanced removal of foulingsubstances. contributing These findings contribute to advancing our understanding of MBR processes and offer valuable insights for optimizing their performance in wastewater treatment applications.

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