

**TREATMENT OF COAL MINE ACID WATER USING NF270 MEMBRANE AS ENVIRONMENTALLY FRIENDLY TECHNOLOGY****Kiswanto^{*1}, H. Susanto², Sudarno³**¹Doctoral Program of Environmental Science, Undip, Indonesia²Chemical Engineering Study Program, Undip, Indonesia³Environmental Science Program Undip, Indonesia**DOI: 10.15294/jpii.v9i3.23310**Accepted: February 5th 2020. Approved: September 28th 2020. Published: September 30th 2020**ABSTRACT**

Ex-mining pond water is widely used for the daily needs of the people these days, such as bathing, washing, and even drinking. Over time, it turns out that coal mine acid water has polluted the environment. The use of membrane technology to produce water that meets drinking water quality standards by the Minister of Health Regulation No. 492 of 2010 can be a solution to this problem. The NF270 membrane is a membrane process between reverse osmosis and ultrafiltration, which has a lower flux and operating pressure below 0.2-1.53 Mpa compared to reverse osmosis. Membrane NF270 is used for the reclamation of wastewater, water purification and softening, seawater desalination, and others. Its high rejection of organic molecules with a molecular weight of 200-2000 Da ions and multivalent can remove suspended solids, natural organic matter, bacteria, viruses, salts, and divalent ions contained in water, including coal mine acid water. The purpose of treating acid mine drainage with the NF270 membrane is to remove COD, TSS, TDS, and Fe metals. The NF270 membrane was used in this study to treat the coal mine acid water of PT. Bukit Asam. The performance of the NF270 process was assessed from the effect of pressure (4, 5, and 6 bar) on the flux and rejection rate of each parameter in a single solution, mixed and aqueous coal mine acid solution. The optimum pressure of the NF270 membrane for all parameters was 6 bar. This optimum pressure was then used to compare the phenomenon of flux that occurred and the level of rejection produced in the original sample of coal mine acid water. In the original coal mine acid water, there was a significant decrease in flux due to fouling deposition on the membrane surface. This phenomenon of decreasing flux was caused by fouling and polarization concentration. The rejection rates produced for the parameters of COD, TSS, TDS, and Fe with NF270 membranes were 56.4-93.1%; 78.5-100%; 43-69.3%; 67-100% respectively. Treated coal mine acid water using NF270 membrane technology can be used as drinking water that meets the standards of the Indonesian Ministry of Health Regulation. Thus, NF270 membrane technology can be used to process coal mine acid water into environmentally friendly drinking water.

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Keywords: rejection; flux; coal mine acid water; NF270 membrane

INTRODUCTION

Indonesia has abundant natural resources, especially coal. One of the coal mining areas in South Sumatra Province is located in Tanjung Enim District, Muara Enim Regency. The mining process changes due to exposure to rock layers

that affects the pH of the soil and water, thereby increasing the solubility of microelements. Therefore, the water in the former coal mine ponds becomes acidic water. The mine acid water is the result of the oxidation reaction of pyrite minerals known as the common reaction, which produces mine acid water (Gautama, 2014).

Surface mine water has chemical properties and compositions that change in seasons and

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after the rainy season. One of the environmental problems in coal mining activities is related to the mine acid water or Acid Mine Drainage (AMD) (Nasir et al., 2014; Afrianty et al., 2012; Ashari et al., 2015). In general, coal mine acid water contains high amounts of organic contaminants, ammonia, heavy metals, suspended solids (SS), and organic matter (Afrianty et al., 2012; Susanto, 2018; Ashari et al., 2015; Said, 2014).

There have been many alternative technologies for acid mine drainage treatment ranging from conventional, biological, and physical/chemical treatment so far (Dandautiya, 2012; Sun et al., 2015). However, this processing technology still has many shortcomings such as processing that does not meet quality standards, requires a large area of land, long residence time, expensive operational costs and maintenance, high energy requirements, and produces a lot of sludge (Zaman, 2013; Zamani et al., 2015; Sun et al., 2015).

Based on the acid water treatment problems, it is necessary to have an alternative mine water treatment that is environmentally friendly and prevents negative impacts on the environment. Membrane-based technology is fundamental in water management and environmental engineering because of its superiority from a technical, economic, and ecological perspective (Peters, 2010; Susanto, 2011; Wenten, 2015). Therefore, the nanofiltration 270 membrane is the best solution for quality water treatment and also environmentally-friendly (Wenten et al., 2010; Dewi, 2015).

NF270 membranes have been applied in various industrial sectors, like dye removal, wastewater treatment, pharmaceutical and biotechnology processes, and food engineering (Kedang, 2019). NF 270 is also known as "loose RO" because of the larger gap size and the lower pressure requirements of RO (Fane et al., 2011). For hospital wastewater treatment, the NF 270 process can reduce COD, $\text{NH}_3\text{-N}$, and $\text{PO}_4\text{-P}$ to 92%, 88%, and 68%, respectively (Kootenaei & Rad, 2013).

The NF270 membrane is a polyamide composite membrane consisting of an active polyamide layer of piperazine and trimesoyl chloride (TMC), a polysulfone support layer, and a polyester non-woven layer. The resulting polyamide is insoluble in all solvents, including concentrated sulfuric acid. Some of the chloride product does not react with amines but is hydrolyzed from the carboxylic group, which causes a thin layer of anionic-charged polyamide at neutral pH (Ore-amuno, 2011). It has an isoelectric point at pH 3.2 (Dalwani, 2011).

NF 270 membranes are often used with water with small amounts of Total Dissolved Solids (TDS) for softening purposes (removal of polyvalent cations) and removal of disinfectant byproducts as natural organic matter, bacteria, viruses, salts and divalent ions contained in water and synthetics (Wenten, 2010; Mulder, 2012; Dewi, 2015). Nano-filtration is a membrane that uses pressure as a driving force as its working principle (Shon et al., 2013; Hilal et al., 2015).

The NF 270 membrane has a pore size of about 1-5 nm operated below 0.2-1.53 MPa. NF 270 membrane properties can control which components will flow, and which will be maintained based on the particular properties of molar mass or particle size (Hilal et al., 2015; Salehi, 2014). NF270 membranes improve membrane performance, including fluxes and rejection, mechanical and thermal stability, and anti-fouling and anti-bacterial properties (Ji et al., 2017).

Several studies mention that NF 270 membranes can be used in water treatment (Al-Zoubi et al., 2010; Galanakis et al., 2012; Hidalgo et al., 2013; Madsen & Sogaard, 2014; Teixeira et al., 2011) but research on the use of 270 nanofiltration membranes in treating mine acid water has not been conducted.

NF270 membrane technology has been applied for the treatment of waste leachate, batik liquid waste and domestic waste with the results of COD, TSS, TDS, and Fe and Mn metal ions are 90-100%; 100%; 40-63%; 93-100% and 100% (Christy et al., 2015; Kiswanto et al., 2019; Gomes et al., 2010). Therefore, the research topic of acid mine drainage treatment using an environmentally friendly NF 270 membrane is a challenging research topic to be carried out so that it can be a choice for acid mine drainage treatment in the future.

The objective of this study is to treat coal mine acid water using NF270 membrane technology for drinking water per the Minister of Health Regulation no. 492 of 2010.

METHODS

Materials

The NF270 membrane is a polyamide composite membrane consisting of an active polyamide layer of piperazine and trimesoyl chloride (TMC), a polysulfone support layer, and a non-woven polyester layer. The resulting polyamide is insoluble in all solvents, including concentrated sulfuric acid. The membrane used was NF270 produced by DOW Filmtec, which characteristics can be seen in table 1.

Table 1. Characteristics of NF270 Membrane

Characteristic	NF270
Material	PolyamideComposite
P maximum (bar)	41
T maximum (°C)	45
pH range	2-11
Rejection of MgSO ₄ (%)	>97% (2000 ppm MgSO ₄ T = 25°C)

Open mining in coal mines can cause the release of certain chemical elements such as Fe and Sulfide from pyrite compounds (Fe₂S), which produce acidic wastewater (Acid mine water). For the characteristics of coal mine acidic water, many studies have been carried out that the highest concentration of heavy metals is iron ions (Susanto, 2018; Said, 2014; Nasir et al., 2014; As-hari et al., 2015). The coal mine acid water was obtained from PT. Bukit Asam (PTBA), Muara Enim, Indonesia. The characteristics of the acid water are according to Table 2.

Table 2. Coal Mine Acid Water Characteristics

Parameter	Value (mg/L)	Standard Value (mg/L)	Standard Value (mg/L)
COD	99,3	100*	50**
TSS	522	400*	200**
TDS	200		500**
Fe	7,6	7*	0,3**

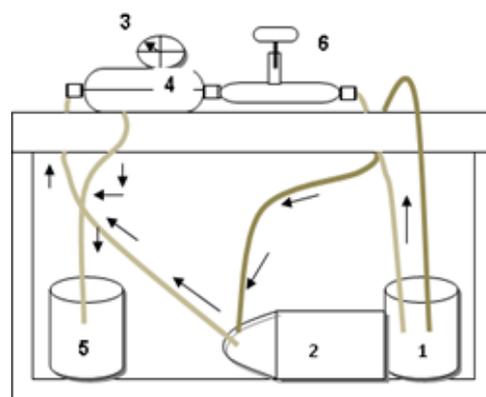
* Decree of the Minister of Environment No. 113 of 2003 concerning Coal Waste water Quality Standards.

** Minister of Health Regulation No. 492 of 2010 concerning Drinking Water Quality Requirements

Humic acid was chosen as a synthetic COD 99.3 mg/L, and 90% High-Grade Humic Acid was used. NaCl was chosen as synthetic TDS was NaCl of 256 mg/L. The material for making synthetic TSS was kaolin. As for Fe, FeCl₃.6H₂O from Merck was used.

Equipment

Membrane filtration equipment was used supported by Micron Purifier RO Pressure Buster Pump (voltage specifications 220-240 VAC, current 0.22 AMPS, open flow 0.31 GPM, and pressure 100 Psi) with the crossflow flow type. The membrane filtration equipment scheme can be seen in Figure 1.

**Figure 1.** Cross Flow Membrane Filtration Scheme (1) Feed tank, 2) Pump, 3) Pressure gauge, 4) Membrane compartment, 5) Permeate tank, 6) Valve)

Feed Water Preparation

The feed solution made was some single feed solutions of COD solution, TDS solution, TSS solution, Fe solution, and a mixture of all materials. The mixed solution was prepared by mixing 522 mg of kaolin, 99.3 mg of humic acid, 200 mg of NaCl, and 7.6 ml of Fe 1000 ppm dissolved in 1000 ml volumetric flask.

Membrane Filtration Preparation

The membrane was cut with a diameter of 4.22 cm and then immersed in distilled water for approximately 30 minutes before use. Afterward, it was compacted by flowing distilled water for 30 minutes with a pressure above the operating pressure used (NF270 = 4, 5, 6 bar). After that, the initial distilled water flux (J_0) measurements were taken by accommodating the permeate and weighing it in the first 15 minutes.

Filtration Process

Filtration of all solutions with the NF270 membrane was carried out for 120 minutes at each pressure. Flux measurements were carried out by storing and weighing permeate every 15 minutes with a holding time of 5 minutes. The formula calculated flux (J):

$$J = \frac{V}{A \cdot t} \quad (1)$$

Where J is the flux (L/m².hour), V is the permeate volume (L), A is the membrane surface area (m²), and t is time (hour). Then, the flux profile was displayed in a graph of the normalized (J/J_0) relation to time. Then, the COD, TSS, TDS, and Fe parameter rejection rates were calculated using:

$$R = 1 - \frac{C_p}{C_f} \times 100\% \quad (2)$$

C_p is the concentration of solute in permeate, and C_f is the concentration of solute in the feed. After the rate of rejection was obtained, the optimal operating pressure used was determined to compare the flux phenomena that occurred and the rate of rejection generated from the feed of coal mine acid water.

Analysis Methods

COD parameter was tested based on SNI 06-6989.3-2004 using the HACH COD reactor from USA and spectrophotometer (Genesys 10S UV-Vis Thermo Scientific USA) at the wavelength of 420 nm (COD <90 mg / L) and 600 nm (COD 100-1000 mg / L). TSS parameter was tested gravimetrically based on SNI 06-6989.3-2004 and by the graph of kaolin vs. turbidity using turbidimeter (Micro TPW Field Portable by HF Scientific USA). TDS parameter was tested with a TDS meter (HM Digital USA). Fe and Mn parameters were tested according to SNI 06-6989.4-2004 with AAS (210 VGP model of Buck Scientific USA) at a wavelength of 248 nm. Membrane morphology before and after use was characterized by SEM (Scanning Electron Microscopy) (Shimadzu Japan).

RESULTS AND DISCUSSION

At present, much research has been done and is even being carried out relating to surface water and wastewater treatment using nanofiltration membranes. The NF 270 membrane process to produce clean water (especially drinking water, sanitation water, and industrial process water) has already been carried out. The use of the NF 270 membrane is still new in its use for treating surface water and wastewater. Many studies have tested the performance of 270 nano-filtration membranes with rejection rates for COD, TSS, TDS, and Fe parameters respectively (90%-100%); (100%); (42-61%); (81.25-100%) (Yildirim et al., 2019; Kiswanto et al., 2019; Christy et al., 2015; Amalia et al., 2016).

NF270 Membrane Characterization

270 Nanofiltration membranes are used extensively on an industrial scale for the separation of charged or non-charged particles in aqueous solutions (Wenten, 2015; Susanto, 2011).

NF270 membrane for softening (removal of polyvalent cation) and removal of disinfectant byproducts such as natural and synthetic organic substances. Material that can be separated NF270 is starch, sugar, pesticides, herbicides, pyrogens, divalent ions, organic, BOD, COD, heavy metals, detergents, and dyes. (Mulder, 2012). This study as a comparison with membrane microfiltration, ultrafiltration, and Reverse Osmosis (RO) membranes.

Microfiltration membrane is a separation of micron or submicron-sized particles to remove particles from water, measuring 0.04 to 100 microns. Microfiltration has limitations for its application in textile wastewater treatment because the process has similarities to conventional filtration processes (Mulder, 2012).

Ultrafiltration membranes are only for separating large and colloidal molecules from liquids (Wenten et al., 2015; Wenten et al., 2010). Ultrafiltration membranes are variants of membrane filtration where the hydrostatic pressure forces the liquid to penetrate the semipermeable membrane. Suspended solids and solvents with high molecular weight are retained, while water and low molecular weight solvents pass through the membrane (Mulder, 1996)

Reverse Osmosis membrane is a raw water filtration system through a TFC (Thin Film Composite) membrane with high pressure, to produce pure water. RO also filters organic and inorganic substances, salts, and ions dissolved in water. This RO system can only work well if the raw water is clear and does not contain much-dissolved solids. It also requires a high press and expensive costs (Wenten, 2015).

Membrane characterization was performed to determine the characteristics of the membrane in the initial conditions. The test begins with a compacting test that is passing Aquadest as bait at certain pressure conditions for 30 minutes. Next, calculate the initial flux value (Jo) by flowing the feed in the form of Aquadest at a variety of operating pressure of 4.5, and 6 kg/cm². Figure 2 shows the Aquadest flux values of three different pressures. The value of distilled water flux measured at operating pressures of 4, 5, and 6 bar for 120 minutes was 42.72 L/m²h; 70.71 L/m²h; and 92.03 L/m²h. The graph shows that operating pressure affected the value of flux. Permeate flux increased with increasing pressure caused by greater force through the membrane so that the permeate flux increased.

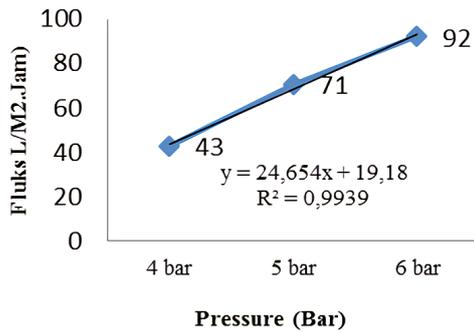


Figure 2. Distilled Water Flux on NF270 Membrane in Different Operating Pressures

The graph in Figure 2 shows that the operating pressure affects the value of the resulting flux. Permeate flux increases with increasing operating pressure caused by a greater thrust through the membrane so that the resulting flux increases.

Effect of Operating Pressure on Membrane Performance

Figure 3 shows the effect of operating pressure on the performance of the 270 nanofiltration membrane from the flux profile for the COD, TSS, TDS, Fe, mixed solution, and coal acid water at 4 bar pressure.

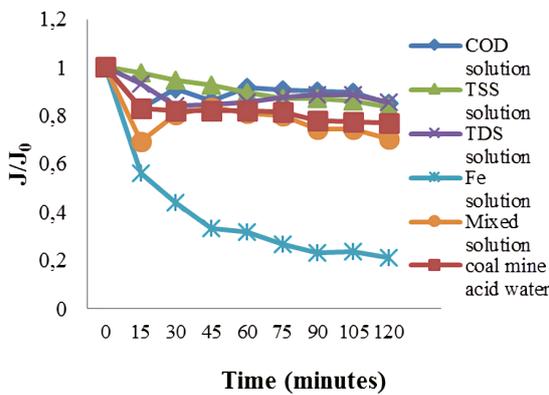


Figure 3. Normalized Flux Profile with NF270 Membrane in 4 Bar

Figure 3 shows the sharpest decrease in flux occurring in Fe solution, followed by the mixed solution, acid mine drainage, COD, TDS, and TSS solution. While figure 4 shows the effect of operating pressure on the performance of the 270 nanofiltration membrane from the flux profile for the COD, TSS, TDS, Fe, mixed solution, and coal mine acid water at 5 bar pressure.

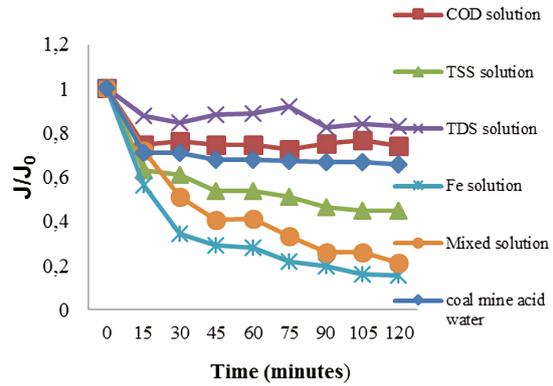


Figure 4. Normalized Flux Profile with NF270 Membrane in 5 Bar

Figure 4 shows the significant decline in flux occurring in Fe, followed by mixed solutions, TSS, acid mine drainage (AMD), COD, and TDS. Figure 5 shows the sharpest decrease in flux occurring in Fe, followed by the mixed solution, TDS, acid mine drainage, TSS, and COD solution.

Figure 5 shows the effect of operating pressure on the performance of the 270 nanofiltration membrane from the flux profile for the COD, TSS, TDS, Fe, mixed solution, and coal mine acid water at 6 bar pressure.

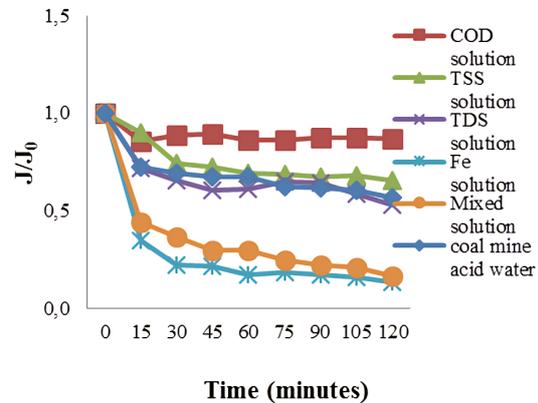


Figure 5. Normalized Flux Profile with NF270 Membrane in 6 Bar

Figure 5 shows the sharpest decrease in flux occurring in Fe, followed by a mixed solution, TDS, mine acid water solution, TSS, and COD.

In TSS, COD, and TDS solutions, there was a sharp decrease in the first 15 minutes, after which there was no noticeable decrease in flux during the filtration process. A significant decrease in the flux of Fe feed solution and synthetic acid mine drainage (AMD) solution occurred in the first 15 minutes to 120 minutes. In comparison, the AMD solution occurs in the first 15 mi-

minutes, after a gradual decline occurs. In general, permeate flux on all graphs had decreased very sharply.

The decrease was due to the fouling and polarization concentration (Almazán et al., 2015) on the membrane surface. Fouling is the deposition of suspended substances or solutes on the surface of the membrane and was irreversible. After that, the flux tended to stabilize as the fouling layer had formed. The other cause of the decline was polarization concentration. According to Almazán et al. (2015), the concentration of polarization occurred due to the accumulation of solutes that are retained on the membrane surface so that it can cause a decrease in flux. The concentration of polarization is reversible.

The separation mechanism that occurs in the nanofiltration membrane is a sieving mechanism and charge exclusion. The sieving mechanism is separation based on pore size and is usually for uncharged solutes. In contrast, charge exclusion is separation based on solute and membrane loads. COD feed solution, which uses humic acid as a material for making synthetic mine acid water, the separation mechanism occurred by the sieving mechanism. As for the TDS, TSS, and Fe feed solutions, the separation occurred by charge exclusion.

The separation that occurred in humic acid was because humic acid was neutral so that the membrane charge and the pH of the solution did not affect the separation process, the particle size larger than the pore size of the membrane retained on the membrane surface while the smaller particles passed as permeate. According to Hilal (2015), ion separation in nanofiltration membranes occurs due to electrostatic interactions between ions and the membrane surface. This separation process occurred in the TDS, TSS, and Fe feed solutions. In TDS and TSS, the separation process was influenced by the pH value of the feed solution, which was 6. At a pH of 6, the NF270 membrane was negatively charged because it was above its isoelectric point between pH 3 and 4 (Tu, 2013; and Hilal, 2015). Because kaolin, Cl⁻ charge, and the NF270 membrane are negative, there was resistance between the two charges called electrostatic repulsion, which caused the particle could not pass through the membrane as permeate.

According to Tu (2013), the process of salt separation in membranes occurred because the membrane was charged rejected co-ions (ions which had the same charge as the membrane surface). As for the need for electron neutrality in the solution, counter-ions (ions whose charge differed from the membrane surface), which is Na⁺,

was also rejected by the membrane so that salt retention happened.

The mechanism of Fe separation in NF270 also occurred due to electrostatic interactions between ions and the membrane surface. According to Tu (2013), when the membrane was contacted with FeCl₃, the membrane surface charge density became positive. It could be influenced by the pH of the solution, which was three at the isoelectric point value of the NF270 membrane, which made it possible to make a positively charged, negative, or neutral membrane. In this case, in addition to electrostatic interactions, separation based on pore size also played a role in the separation of Fe. According to Hilal (2015) that the separation of salt by NF270 membrane is more complicated and can occur in combination based on molecular size and the effect of Donnan Exclusion (electrostatic interaction) and high salt rejection (NaCl) with increasing flux (Bargeman et al., 2014).

Rate of Rejection of Single, Mixed, and AMD Solutions

Tables 3, 4, and 5 show the different rates of rejection for each parameter in a single feed, mixed, and acid mine drainage (AMD). The rate of rejection generated on the COD parameter at all operating pressures reached 56.4 - 93.1%. It is not much different from the previous results of research done by Christy et al. (2015) because the COD removal reached 85-98%. Besides, according to Kiswanto et al. (2019) and Amalia et al. (2016), the nanofiltration membrane was able to set aside glucose $90 \pm 2.4\%$.

The rejection rate for the TDS parameter was following Hilal's research (2015) in the range of 40.2 - 83.1% depending on the concentration of the feed, pressure, pH, and temperature. The chloride ion rejection rate increased with increasing operating pressure due to the rate of water transfer across the membrane, which was faster than the rate of chloride ion transfer. The rejection rate produced was higher, along with the tremendous pressure used. It is consistent with the study of Bargeman et al. (2014), which stated that the level of salt rejection (NaCl) would increase with increasing flux. The NF270 nanofiltration membrane was capable of removing TSS and Fe with a 100% rejection rate at all operating pressures used. Following the results of Futry's research (2015), the rejection rate of NF270 to Fe reached 100%.

Permeate quality presented in Tables 4 and 5 are then compared with the Minister of Health Regulation no. 492 of 2010 concerning Drinking Water Quality Requirements. All the parameters

tested at three operating pressures, both single and mixed feeds, the permeate quality produced met the quality standards for COD, TSS, and Fe parameters. Whereas the TDS parameter only met quality standards at 6 bar pressure. Overall, these results indicate that the performance of the NF270 nanofiltration membrane in reducing the concentration of COD, TSS, TDS, and Fe pollutants had been excellent at the pressure of 6 bar.

The 6 bar pressure was then used to compare the flux phenomenon that occurred, and the rejection rate generated in the feed solution of coal mine acid water.

In table 3 shows the different rejection rates for each parameter in a single feed solution. The level of rejection produced on the feed parameters COD, TSS, TDS, and Fe are at operating pressures of 4, 5, and 6 bar.

Table 3. The Concentration of Feed and Permeate of Single Solution at Different Pressure

Parameter	Initial Value (ppm)	Single Feed					
		4 bar		5 bar		6 bar	
		ppm	%R	ppm	%R	ppm	%R
COD	99,3	43,3	56,4	31,4	68,4	15	84,9
TSS	522	112	78,5	68	86,9	40	92,3
TDS	200	114	43	109	45,5	82	59
Fe	7,6	2,57	66,2	1,51	80,13	0,72	90,5

In table 3, the difference in the rejection rate for each parameter in a single feed resulted in the COD, TSS, TDS, and Fe parameters at all operating pressures respectively reaching (56.4-84.9%); (78.5-92,3%); (43-59%); and (66.2-90.5%).

Table 4 shows the different rejection rates for each parameter in a single feed solution. The level of rejection produced on the feed parameters COD, TSS, TDS, and ion Fe is at operating pressures of 4, 5, and 6 bar.

Table 4. The Concentration of Feed and Permeate of Mixed Solution at Different Pressure

Parameter	Initial Value (ppm)	Mixed Feed					
		4 bar		5 bar		6 bar	
		ppm	%R	ppm	%R	ppm	%R
COD	103	14,31	86	23,06	78	12,1	88
TSS	522	0	100	0	100	0	100
TDS	206,9	123,02	41	111,03	46	83,7	60
Fe	8	0	100	0	100	0	100

In table 4, the different rejection rates for each parameter in the mixed solution feed were generated on the COD, TSS, TDS, and Fe parameters at all operating pressures respectively (78-88%); (100%); (41- 60%); and (100%). NF270 membrane is capable of removing the permeate feed parameters TSS and Fe for pressures of 4, 5,

and 6 bars reaching 100%. It means that the concentration of TSS and Fe results from filtration with an NF270 value of 0.

Table 5 shows the different levels of rejection for each parameter in the acid mine drainage (AMD). The level of rejection generated on the COD, TSS, TDS, and Fe parameters at all operating pressures

Table 5. The Concentration of Feed and Permeate of AMD Solution at Different Pressure

Parameter	Initial Value (ppm)	AMD Solution					
		4 bar		5 bar		6 bar	
		ppm	%R	ppm	%R	ppm	%R
COD	103	30,4	70,5	13,1	87,3	7,1	93,1
TSS	522	0,4	99,9	0	100	0	100
TDS	207	92	55,5	90	56,5	63,5	69,3
Fe	8	0,1	99,3	0	99,6	0	100

In table 5, the different rejection rates for each parameter in the acid mine feed water are generated in the COD, TSS, TDS, and Fe parameters at all operating pressures reaching respectively (70.5-93.1%);(99.9-100%);(55.5-69.3%);(99.3-100%). NF270 membrane is capable of removing the permeate feed parameters TSS and Fe for pressures of 5 and 6 bars reaching 100%. It means that the concentration of TSS and Fe results from filtration with an NF270 value of 0. The

NF270 nanofiltration membrane is capable of removing TSS and Fe with rejection rates 100% at all operating pressures used (Christy et al., 2015; Amalia et al., 2016; Yildirim et al., 2019)

Coal Mine Acid Water Treatment at Optimum Pressure of 6 Bar

Figure 6 shows the gradual decrease in flux until 120 minutes due to the initial deposition/adsorption of foulant on the membrane surface.

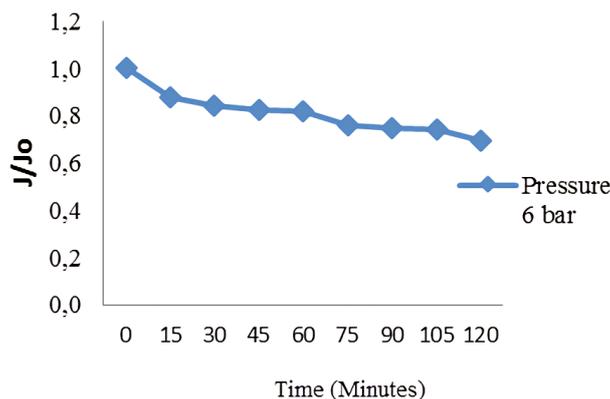


Figure 6. Normalized Flux Profile of NF270 Membrane in PTBA's Coal Mine Acid Water Feed

In another study, Simon et al. (2013) reported that membrane fouling occurred due to the deposition of organic and inorganic compounds and/or the formation of layers on the membrane surface, thereby reducing membrane permeability over time.

The decrease in flux that occurred was different from that which occurred in single or mixed feeds. The impurity could cause this in acid mine water, which was more varied than other parameters besides the parameters so that fouling occurred faster. Also, it was due to the difference in concentration between synthetic feed and the

mine acid water feed from PTBA. More solutes adsorbed on the membrane surface could cause a decrease in flux and affected the rejection rate. The rate of rejection produced from the PTBA's mine acid water sample was not much different from the synthetic mine acid water sample.

The level of rejection produced from samples of original coal mine acid water is not much different from samples of synthetic coal mine acid water. Table 6 shows the difference in the level of rejection of original coal mine acid water with synthetic mine acid water.

Table 6. Rejection Rates of Synthetic Coal Mine Acid Water and PTBA's Coal Mine Acid Water

Parameter	Initial Value (ppm)	Synthetic Coal Mine Acid		PTBA's Coal Mine Acid	
		ppm	%R	ppm	%R
COD	103	12,1	88	7,1	93,1
TSS	522	0	100	0	100
TDS	207	83,7	60	63,5	69,3
Fe	8	0	100	0	100

For the COD parameter, the rejection rate of the PTBA's mine acid water feed was higher than the synthetic feed, which was 93% and 88%. Whereas the TDS parameter, the rejection rate of synthetic mine acid water feed was not much

different from the original mine acid water sample, which was 60% and 69%. As for the TSS and Fe parameters in PTBA's and synthetic mine acid water, they reached a rejection of 100%. The high level of Fe rejection could occur because in

the PTBA's mine acid water contained Fe (II), which can be oxidized due to aeration (Zamani et al., 2015). As for the TSS and Fe parameters on NF270, the rejection rates both reached 100% as well. Differences in the rejection rate that occurred in all parameters could occur due to the influence of pH and concentration.

Characteristics of Fouling on a Membrane Surface with SEM

Figure 7 shows the presence of fouling on the membrane surface of synthetic mine acid water solution and PTBA's mine acid water. The fouling occurred during the process was due to gel/cake layer formation. This gel/cake layer was formed from humic acid. The formation of this layer also resulted in an increased sieving mechanism shown in Figure 8 because there were particles attached to the gel layer. The presence of salt and kaolin in the feed also affected the pro-

cess of fouling. The presence of NaCl and FeCl₃ could lead the formation of an Electrical Double Layer (EDL) on the surface of kaolin, which could reduce the kaolin load so that the stability of colloids was disrupted to form aggregates between kaolin particles. The addition of cations can reduce the nature of the charge and can change the nature of particle electricity and particle size, which is related to the tensile strength between particles and the membrane surface, which causes fouling (Chang et al., 2016; Motsa et al., 2014).

When this ion exchange occurred, the EDL thickness increased as it increased. At the same time, the kaolin potential zeta due to divalent cations (in this case, Fe³⁺) was smaller than monovalent cations. The higher the ion concentration or, the more valence of the ion, the EDL went thinner and caused the lower zeta potential.

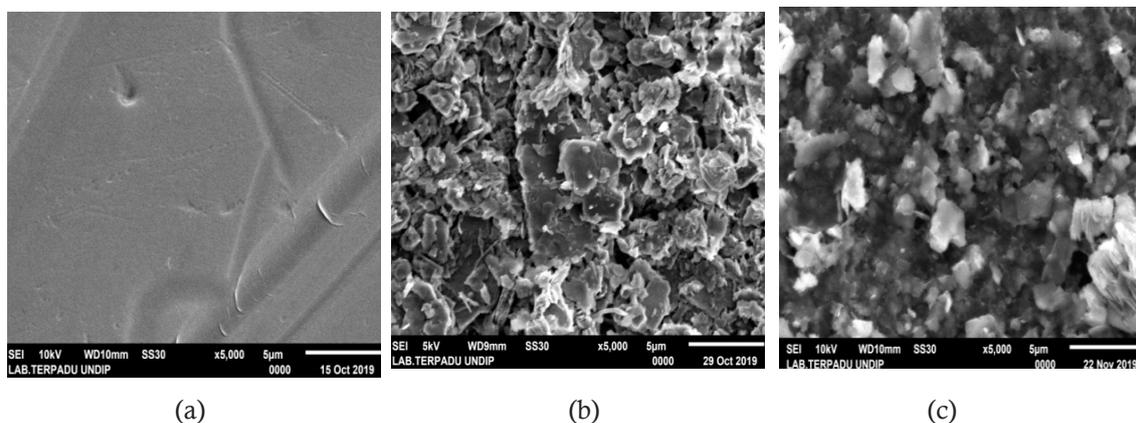


Figure 7. Results of SEM Analysis at 5000x. (a) Fresh Membrane, (b) Membrane for Synthetic Acid Mine Water, (c) Membrane for PTBA's Acid Mine Water

The presence of a reaction between colloids and cations affected fouling and rejection rates. The more cations adsorbed on kaolin, the

higher the salt rejection rate was. Figure 8 shows that fouling mechanisms for synthetic acid mine water feed are as follows:

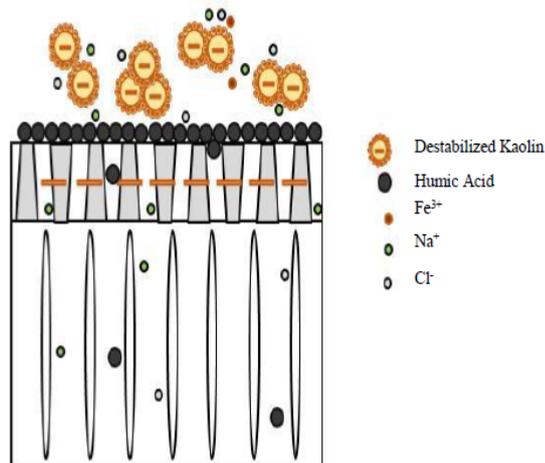


Figure 8. Fouling Mechanism in Synthetic Coal Mine Acid Water

The phenomenon of fouling in synthetic mine acid water was slightly different from what occurred in PTBA's mine acidic water. In Fig. 8c, it can be seen that fouling formed in the PTBA's coal mine acid water was cake/gel formation whose structure was more incompressible than synthetic mine acid water. It happened because many organic and inorganic compounds affected the formation of the gel layer. Fouling in PTBA's mine acid water occurred from organic and inorganic compounds. The existence of these compounds made it possible to interact with each other so that it caused a layer of fouling and ultimately affected the flux and rejection rate.

As stated by Hao et al. (2011), the deposition of more massive particles on the membrane surface can cause gel formation by the addition of Fe^{2+} metal ions. Various things could cause the formation of this gel layer. One of them is because there were still suspended solids that had not been removed from the NF270 membrane. Besides, other organic and inorganic compounds also played an essential role in the formation of fouling because it allowed interaction between existing components. Possible interactions were organic compounds with colloids, organic compounds with metals, and metals with colloids. According to Shon et al. (2013), fouling on NF270 membranes could be caused by precipitation of inorganic compounds, colloidal fouling, adsorption of organic compounds, and/or biofouling.

In contrast to synthetic mine acid water, which only used glucose, which is neutral in charge, in the original leachate, there were more types of organic compounds whose payload varied. Moreover, organic fouling was a decrease in irreversible flux due to the adsorption or deposition of colloidal or dissolved organic compounds. Organic compounds might be adsorbed or deposited on the membrane surface or in colloids.

Natural colloidal compounds in the environment are usually negatively charged due to the adsorption layer of NOM (Natural Organic Matter), which affects the stability of colloids. One example of NOM in water or wastewater is humic acid (humic acid), which can cause fouling due to adsorbed or accumulated on the surface (pore blocking). The existence of cations can influence the phenomenon of fouling because the presence of electrolytes can reduce the repulsion of a charge (Chang et al., 2016; Hao et al., 2011; Motsa et al., 2014).

Besides, cations could act as a bridge between charged foulants and membranes. The stronger the adsorption of compounds on the membrane, the sharper the decrease in flux.

CONCLUSION

From the results, it can be concluded that higher operating pressure results in greater flux values and affects the rejection rate. The optimal operating pressure used is 6 bar.

The flux that occurs in the solution of acid mine feed water decreases significantly in the first 15 minutes and is stable after that. This sharp decrease occurs rapidly so that fouling occurs as indicated by the results of membrane characterization with SEM. The level of rejection that results in acid mine drainage does not show a massive difference.

NF 270 membrane was able to remove COD, TSS, TDS, and Fe respectively by 56.4-93.1%, 78.5-100%, 43-69.3%, 67-100%. All levels of rejection result in permeate quality that meets the standards of the Indonesian Ministry of Health Regulation. (2010). Minister of Health Regulation Number 492 / MENKES / PER / IV / 2010 of 2010 concerning Requirements for Drinking Water Quality. Ministry of Health. Jakarta. Thus, NF270 membrane technology can be used to process coal mine acid water into environmentally friendly drinking water.

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REFERENCES

- Afrianty, C., Gustin, L., & Dewi, T. K. (2012). Pengolahan Limbah Air Asam Tambang Menggunakan Teknologi Membran Keramik. *Jurnal Teknik Kimia*, 18(3).
- Almazán, J. E., Romero-Dondiz, E. M., Rajal, V. B., & Castro-Vidaurre, E. F. (2015). Nano-filtration of glucose: Analysis of parameters and membrane characterization. *Chemical engineering research and design*, 94, 485-493.
- Amalia, D. A., Susanto, H., & Istirokhatun, T. (2016). *Pengolahan Limbah Lindi Menggunakan Membran Nanofiltrasi Nf99* (Doctoral dissertation, Diponegoro University).
- Al-Zoubi, H., Rieger, A., Steinberger, P., Pelz, W., Haseneder, R., & Härtel, G. (2010). Optimization study for treatment of acid mine drainage using membrane technology. *Separation Science and Technology*, 45(14), 2004-2016.
- Ashari, A., Budianta, D., & Setiabudidaya, D. (2015). Efektivitas elektroda pada proses elektrokoagulasi untuk pengolahan air asam tambang. *Jurnal Penelitian Sains*, 17(2).

- Bargeman, G., Westerink, J. B., Miguez, O. G., & Wessling, M. (2014). The effect of NaCl and glucose concentration on retentions for nanofiltration membranes processing concentrated solutions. *Separation and purification technology*, 134, 46-57.
- Chang, H., Liang, H., Qu, F., Shao, S., Yu, H., Liu, B., ... & Li, G. (2016). Role of backwash water composition in alleviating ultrafiltration membrane fouling by sodium alginate and the effectiveness of salt backwashing. *Journal of Membrane Science*, 499, 429-441.
- Christy, F. T., Susanto, H., & Sudarno, S. (2015). *Pengolahan Limbah Lindi Menggunakan Membran Nanofiltrasi Nf270* (Doctoral dissertation, Diponegoro University).
- Dalwani, M. (2011). Thin film composite nanofiltration membranes for extreme conditions. *Gilden Print Drukkerij, Enschede, The Netherland*.
- Dandautiya, R. (2012). Comparative study of existing leachate treatment methods. In *International Conference on Recent Trends in Engineering and Technology (ICRTET)* (pp. 192-202).
- Dewi, S. S. (2015). Nanofiltrasi sebagai "Best Available Technology" untuk Pengolahan Air.
- Fane, A. T., Wang, R., & Jia, Y. (2011). Membrane technology: past, present and future. In *Membrane and Desalination Technologies* (pp. 1-45). Humana Press, Totowa, NJ.
- Galanakis, C. M., Fountoulis, G., & Gekas, V. (2012). Nano-filtration of brackish groundwater by using a polypiperazine membrane. *Desalination*, 286, 277-284.
- Gautama, R. S. (2014). Pembentukan, pengendalian dan pengelolaan air asam tambang. *Bandung: Institut Teknologi Bandung*.
- Gomes, S., Cavaco, S. A., Quina, M. J., & Gando-Ferreira, L. M. (2010). Nanofiltration process for separating Cr (III) from acid solutions: experimental and modelling analysis. *Desalination*, 254(1-3), 80-89.
- Hao, Y., Moriya, A., Maruyama, T., Ohmukai, Y., & Matsuyama, H. (2011). Effect of metal ions on humic acid fouling of hollow fiber ultrafiltration membrane. *Journal of membrane science*, 376(1-2), 247-253.
- Hilal, N., Kochkodan, V., Al Abdulgader, H., & Johnson, D. (2015). A combined ion exchange-nanofiltration process for water desalination: II. Membrane selection. *Desalination*, 363, 51-57.
- Hidalgo, A. M., León, G., Gómez, M., Murcia, M. D., Gómez, E., & Gómez, J. L. (2013). Application of the Spiegler-Kedem-Kachalsky model to the removal of 4-chlorophenol by different nanofiltration membranes. *Desalination*, 315, 70-75.
- Ji, Y., Qian, W., Yu, Y., An, Q., Liu, L., Zhou, Y., & Gao, C. (2017). Recent developments in nanofiltration membranes based on nanomaterials. *Chinese Journal of Chemical Engineering*, 25(11), 1639-1652.
- Kedang, Y. I. (2019). Membran Nanofiltrasi untuk Aplikasi Pemisah Zat. *Jurnal Saintek Lahan Kerinci*, 2(1), 27-29.
- Kiswanto, K., Rahayu, L. N., & Wintah, W. (2019). Pengolahan Limbah Cair Batik Menggunakan Teknologi Membran Nanofiltrasi Di Kota Pekalongan. *Jurnal Litbang Kota Pekalongan*, 17.
- Kootenaeci, F. G., & Rad, H. A. (2013). Treatment of hospital wastewater by novel nanofiltration membrane bioreactor (NF-MBR). *Iranica Journal of Energy and Environment, Special Issue on Nanotechnology*, 4(1), 60-67.
- Madsen, H. T., & Søgaard, E. G. (2014). Applicability and modelling of nanofiltration and reverse osmosis for remediation of groundwater polluted with pesticides and pesticide transformation products. *Separation and Purification Technology*, 125, 111-119.
- Motsa, M. M., Mamba, B. B., D'Haese, A., Hoek, E. M., & Verliefde, A. R. (2014). Organic fouling in forward osmosis membranes: The role of feed solution chemistry and membrane structural properties. *Journal of Membrane Science*, 460, 99-109.
- Mulder, M. (1996). Preparation of synthetic membranes. In *Basic principles of membrane technology* (pp. 71-156). Springer, Dordrecht.
- Mulder, M. (2012). *Basic principles of membrane technology*. Springer Science & Business Media.
- Nasir, S., Purba, M., & Sihombing, O. (2014). Pengolahan air asam tambang dengan menggunakan membran keramik berbahan tanah liat, tepung jagung dan serbuk besi. *Jurnal Teknik Kimia*, 20(3).
- Oreamuno, F. A. P. (2011). *Microscopic characterization of the nanostructure of polyamide thin films in reverse osmosis and nanofiltration membranes* (Doctoral dissertation, Stanford University).
- Peters, T. (2010). Membrane technology for water treatment. *Chemical engineering & technology*, 33(8), 1233-1240.
- Said, N. I. (2014). Teknologi Pengolahan Air Asam Tambang Batubara "Alternatif Pemilihan Teknologi". *Jurnal Air Indonesia*, 7(2).
- Salehi, F. (2014). Current and future applications for nanofiltration technology in the food processing. *Food and Bioproducts Processing*, 92(2), 161-177.
- Shon, H. K., Phuntsho, S., Chaudhary, D. S., Vigneswaran, S., & Cho, J. (2013). Nano-filtration for water and wastewater treatment-a mini review. *Drinking Water Engineering and Science*.
- Simon, A., Price, W. E., & Nghiem, L. D. (2013). Changes in surface properties and separation efficiency of a nanofiltration membrane after repeated fouling and chemical cleaning cycles. *Separation and Purification Technology*, 113, 42-50.
- Susanto, H. (2011). *Teknologi Membran*. Semarang: Badan Penerbit Universitas Diponegoro.
- Susanto, H. (2018). Characterization Of Coal Acid Water In Void Pools Of Coal Mining In South

- Kalimantan. In *E3S Web of Conferences* (Vol. 73, p. 05030). EDP Sciences.
- Sun, H., Peng, Y., & Shi, X. (2015). Advanced treatment of landfill leachate using anaerobic-aerobic process: Organic removal by simultaneous denitrification and methanogenesis and nitrogen removal via nitrite. *Bioresource technology*, 177, 337-345.
- Teixeira, M. R., Rosa, S. M., & Sousa, V. (2011). Natural organic matter and disinfection byproducts formation potential in water treatment. *Water resources management*, 25(12), 3005-3015.
- Tu, N. P. (2013). Role of charge effects during membrane filtration. *Ghent. Universiteit Gent*.
- Wenten, I. G., Khoiruddin, K., Aryanti, P. T. P., & Hakim, A. N. (2010). Pengantar Teknologi Membran. *Teknik Kimia Institut Teknologi Bandung*.
- Wenten, I. G. (2015). Teknologi Membran: Prospek dan Tantangannya. *Teknik Kimia Institut Teknologi Bandung*.
- Yildirim, Y., Topaloğlu, A. K., Ince, M., & Kajama, M. N. (2019). The use of NF and RO membrane system for reclamation and recycling of wastewaters generated from a hard coal mining. *Nigerian Journal of Technology*, 38(4), 1048-1055.
- Zaman, B. (2013). Efisiensi Pengolahan Amonium Berkonsentrasi Tinggi Dalam Lindi Pada Sistem Evapotranspirasi-Anaerobik Secara Kontinyu.
- Zamani, M. F., Istirokhatun, T., & Susanto, H. (2015). *Pengolahan Leachate Tempat Pembuangan Akhir Sampah Menggunakan Kombinasi Teknologi Membran Mikrofiltrasi Dan Nanofiltrasi* (Doctoral dissertation, Diponegoro University).