Removing Content of Color and Heavy Metals (Pb) in The Waste Liquid Using Batik Industries Membrane Technology NF 270

Kiswanto¹, Nur 'Aini Hamada², Sudarno³, Hartuti Purnaweni⁴

¹ Faculty of Engineering, Universitas Teuku Umar Meulaboh, West Aceh
² Membrane Research Center, Integrated Laboratory, Diponegoro University
^{3,4} Doctoral Study Program of Environmental Science, Diponegoro University Semarang Email: kiswanto@utu.ac.id

Abstract: The development of the batik industry is one of the triggers for economic growth in Indonesia. However, the batik industry wastewater is a problem for the environment. The batik waste produced is cloudy and thick in color. The dye is produced from the remaining dye, the washing process, and the water rinsing. In general, dyes are nonbiodegredable organic compounds that can cause environmental pollution, especially the aquatic environment. The discharge of colored wastewater not only damages the aesthetics of water bodies but also poisons aquatic biota. This research was conducted to analyze the level of rejection of color compounds and Pb metal in the processing of batik production waste using NF270 nanofiltration membranes. This research was conducted at operating pressure (4 bar, 5 bar, and 6 bar), with a concentration of batik waste color before filtration of 743.04 Pt-Co and a Pb concentration of 3.015 Mg / L. The results showed that the rejection value of color concentration and heavy metal Pb after filtration using NF270 membrane with operating pressures (4, 5, 6) bar were (99.59%; 99.84%; 99.87%) and respectively. (100%; 100%; 100%). Based on the quality standards of the Ministry of Environment and Forestry Regulation No.5 of 2004 and Central Java Regional Regulation No.5 of 2012, the color of batik and Pb metal waste water has met the quality standard. Even the processed batik liquid waste has met the quality standards of clean water and drinking water.

Keywords: batik industrial waste, color, lead (Pb), nanofiltration membrane

Introduction

In the production process, the batik industry uses a lot of chemicals and water. This wastewater is alkaline characterized by color and high pH (10-12.5) and has a high salt content (Shu et al., 2005; Aouni et al., 2012). This colored liquid waste causes problems in the aquatic environment if it is immediately disposed of because it contains non-biodegradable organic compounds (Suprihatin, 2012). Disposing of liquid batik waste directly into the environment without any prior treatment can reduce the quality of the environment and damage life in the environment (Purwaningsih, 2008). Therefore, proper liquid batik waste processing needs to be done to obtain the appropriate quality standards before being discharged into the environment (Chakraborty et al., 2005).

The batik industry is one of the producers of liquid waste originating from the coloring process. Apart from the very high dye content, the batik industrial waste also contains synthetic materials which are difficult to decipher. After the coloring process is complete, a cloudy and thick colored liquid waste will be produced; usually, the color of batik wastewater depends on the dye used. Batik liquid waste, which is thick in color, can cause problems for the environment (Lestari, 2017).

The dyes produced from the batik industry are generally non-biodegradable organic compounds that can cause environmental pollution, especially waters. Suppose the waste batik industry can increase COD (Chemical Oxygen Demand) levels. Colors that are widely used in the batik industry are remazol black, red, and golden yellow. In coloring, this compound is only used about 5%, while the remaining 95% will be disposed of as waste. This compound is stable enough so that it is very difficult to degrade in nature and is dangerous for the environment, especially in very large concentrations because it can increase COD (Lestari, 2017). The dyes most widely used in the batik industry include benzonaphthalene derived dyes, azonaphthalene derived dyes, direct (natural) dyes, and reactive dyes (Sumantri et al., 2006). This color density can block the penetration of sunlight so that it inhibits the photosynthesis process in water. As a result, the oxygen needed for aquatic life will decrease (Nasution, 2009).

Color is one of the mandatory physical parameters stipulated by Permenkes RI No.416 / Menkes / PER / IX / 1990. The Kepmenkes RI No. 416 of 1990 states that the maximum color limit for clean water is 50 on the TCU scale. In a color analysis, the instrument used is a spectrophotometer). Apart from dyes, heavy metal ions in other batik wastewater are also quite high (Kiswanto et al., 2019).

Lead or Plumbum (Pb) is a metal with black color. Formerly used as a constituent in paints, stamps and is now widely used in gasoline. Organic lead (TEL stands for tetraethyl lead) is deliberately added to gasoline to increase the octane. Pb in poison is systemic. Pb poisoning will cause symptoms: metallic taste in the mouth, black lines on the gums, GI disorders, anorexia, vomiting, clicks, encephalitis, stress drop, irritability, personality changes, paralysis, and blindness. Basophilic stippling of red blood cells is a pathognomonic symptom of Pb poisoning. Other symptoms of poisoning include anemia and albuminuria. Organic Pb tends to cause encephalopathy. In acute poisoning, there will be meninges and general, followed by stupor, coma, and death: high cerebrospinal liquor pressure (CSF), insomnia, and somnolence.

The allowance for dye and Pb is based on a preliminary study of the characteristic test of Batik waste in Pekalongan City which has been carried out that the color and lead parameters exceed the threshold set by the government in the Minister of Environment Regulation No. 5 of 2014, Permenkes 416 of 1990, and Central Java Regional Regulation No. 5/2012. While NF270 was chosen because it has advantages such as low operating costs, low energy requirements, being able to reduce heavy metals, nitrates, sulfates, color, turbidity, and dissolved solids (Bhuyar et al., 2014). 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%. (Kiswanto et al., 2020).

No	Parameters	Unit	Concentration	Quality Standard
1.	pН	-	10,1	6,0-9,0*
2.	Temperature	°C	29,7	38**
4.	Color	Skala Pt-Co (TCU)	743,04	50***
5.	Oil dan Fat	Mg/L	30	$3,0^{*}$
6.	TSS	Mg/L	8420	50^*
8.	COD	Mg/L	12063,33	150^{*}
9.	BOD ₅	Mg/L	3739,53	60^*
10.	Pb	Mg/L	3,015	

Table 1 Characteristics of Batik Wastewater

Source: *) Minister of Environment Regulation No. 05/2014

**) Central Java Provincial Regulation No. 5 of 2012

***) Regulation of the Minister of Health of the Republic of Indonesia No. 416 / IX of 1990

The purpose of this study was to analyze the level of removal of the color parameters and lead oil (Pb) in batik industrial wastewater using NF270 nanofiltration membrane technology. **Table 2**, Characteristics of the NF270 (DOW Filmtec) membrane

Materials	Polyamide Composite
Maximum pressure (bar)	41
Maximum Temperature (C)	45
pH range	2-11
MgSO ₄ rejection (%)	>97% (2000 ppm MgSO ₄ , T = 25°C)

Tool

The tools used include a spectrophotometer (Thermo Scientific with an accuracy of 0.001), ASS Model 210 VGP by Buck Scientific USA at a wavelength of 248 nm, a turbidimeter, a separating funnel, an analytical balance, and a membrane module unit as shown in Figure 1.

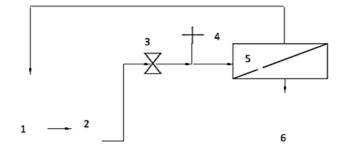


Figure 1. Schematic of the membrane unit with the cross-flow operation.

Information:

- 1. Sample of batik liquid waste in a 300 ml beaker
- 2. Reverse Osmosis Pump with Specifications Nominal Flow Rate: 1.0 PM

Max Pump output: 110 Psi Max Inlet Pressure: 60 Psi Voltage: 24 VDC

- 3. Pressure Regulator
- 4. Pressure Manometer
- 5. The place for the membrane to be tested.
- 6. Permeate (The result of processing with a membrane)

Research Procedure

This research was conducted using commercial NF270 Nanofiltration membranes at 4, 5, and 6 bar pressures. This membrane was obtained from Alfa Laval, Sweden, and printed with a diameter of 4.22 cm and then compaction for 30 minutes to stabilize the pore and membrane structure.

Prefiltration using filter paper is carried out before the waste enters the membrane unit. This aims to reduce the number of suspended solids, which can increase the occurrence of membrane blockage. The research was carried out by cross-flow filtration and carried out for 3 hours with a permeate taking time every 15 minutes to measure the permeability with the formula :

$$J = \frac{V}{A x t}$$

Where V is the permeate volume (liters), A is the membrane surface area (m^2) , time (hours). Furthermore, the color rejection and Timabl (Pb) of the resulting permeate are also calculated with the formula:

$$R = 1 - \frac{C_p}{C_f} \times 100\%$$

Where Cp is the solute concentration in the permeate, and Cf is the solute concentration in the feed.

Method of Analysis

Analysis of the color of the batik liquid waste feed and permeate used a spectrophotometer while heavy metal analysis (Pb) used AAS Model 210 VGP by Buck Scientific USA at a wavelength of 248 nm.

Results and Discussion Flux Test

Feed The feed flux profile in the form of batik waste liquid waste in Pekalongan City when it passes through the NF270 membrane is presented in Figure 2.

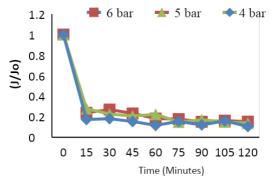


Figure 2. Flux profile (J / Jo) on filtration using NF270 membrane

Figure 2 above shows that the addition of pressure has an effect on decreasing flux. The higher the pressure, the faster the flux decreases over time. In the picture above, the highest decrease in flux is at a pressure of 6 bar, 5 bar, and 4 bar. The higher the pressure, allowing the feed to pass through the membrane quickly and the more fouling accumulated on the membrane surface and membrane structure, causing pore-clogging faster than at low pressure (Zhou, 2010).

The sieving mechanism occurs during the processing of batik liquid waste using the NF 270 membrane unit, causing the feed to separate based on size according to the pore size of the membrane used. The length of time of operation also affects the amount of flux produced. The longer the time, the smaller the flux produced. According to Mulder (1996), this is caused by fouling, which includes concentrations of polarization, adsorption, the formation of gel layers, and clogging of pores.

Membrane Rejection

Membrane performance is also determined by the ability to rejection of several parameters, namely Color and Metal Pb.

Color

The batik liquid waste feed has a color parameter value of 743.04 Pt-Co (TCU). Pretreatment or prefiltration is necessary if the turbidity value of the feed is above 10 Pt-Co and is done to reduce the concentration of dissolved solids before entering the membrane unit (Joseph and Roger in AWWA Manual, 2005). The value of the feed color and permeate parameters after being treated with a membrane unit is presented in Table 3.

Table 3. The value of batik waste color rejection with a concentration of 743.04 (Pt-Co)								
		4 Bar	5 Bar	6 Bar				
	Initial Concentration	743,04	743,04,08	743,04				
	Final Concentration	3,04	1,15	0,90				
	Rejection Rate	99,59%	99,84%	99,87%				

Based on the results of the study, the 270 Nanofiltration membrane was able to produce permeate/products with low color values. Nanofiltration membranes have better rejection rates for color separation than microfiltration membranes. The reduction in rejection rate for 4 bar pressure is 99.59%, 5 bar is 99.84%, and for 6 bar, it is 99.87%. This is in accordance with research (Kiswanto et al., 2019) that the higher the operating pressure, the greater the rejection. In dye removal, the higher the pressure used, the decrease in relative flux decreased (Figure 4.). It can be explained that the dye has a strong interaction (ionic and H-bonding) with the membrane surface, especially in nitrogenous fibers such as polyamide. With the high operating pressure, the dye is pushed or deposited on the membrane surface. This statement was conveyed by Akbari (2002). As a result, dye deposits on the membrane surface reduce the relative flux (Schafer 2004; Manttari et al., 2004; Fersi et al., 2009; Susanto, 2011).

Metal Pb

The value of heavy metal Pb in batik liquid waste feed is 3.015 mg / 1. Prefiltration using filter paper has not been able to reduce the Pb metal content in the feed. And it still exceeds the quality standard, so that processing needs to be done using a membrane unit. Table 4. Shows the Pb rejection for the NF270 membrane at an operating pressure of 4, 5, 6 bars.

	4 Bar	5 Bar	6 Bar	
Initial Concentration	3,015	3,015	3,015	
Final Concentration	0	0	0	
Rejection Rate	100%	100%	100%	

Table 4: Initial concentration of Pb rejection value 3.015 mg / 1 Pressure (4, 5, and 6 bar).

The removal of Pb in the Nanofiltration membrane 270 also occurs due to electrostatic interactions between ions and the membrane surface. According to Tu (2013), when the membrane is brought into contact with metal ions, the surface charge density of the membrane becomes positive. Nanofiltration membrane that allows making the membrane positively, negatively or neutral charged. Separation based on pore size also plays a role in Pb separation. The nanofiltration membrane process can remove suspended solids, natural organic matter, bacteria, viruses, salts, and divalent ions present in water. Nanofiltration operates at a lower pressure than reverse osmosis, between 50-150 psi (Seungkwa, 1997).

From the research results shown in table 4. It can be seen that the pore size expressed in molecular weight cutoff (MWCO) affects the removal of Pb metal parameters. NF270 membrane has a good rejection rate in removing heavy metals in wastewater. According to research conducted by (Boussu 2007) that the smaller the pore size, the rejection rate of PB

metal parameters will increase. Because this is because the NF270 membrane is the best membrane for removing heavy metals and divalent compounds.

Another factor that affects the rate of rejection of Pb metal parameters is pressure. An increase in the rejection rate on the NF 270 membrane at a pressure of 6 bar resulted in the faster formation of fouling on the surface and membrane structure so as to reduce the pore size of the membrane and increase the ability of the membrane to re-probe Pb parameters.

The rejection that decreases with the addition of pressure can be due to the increase in pressure, the process of shrinking the pore surface of the membrane is inhibited, thereby reducing the performance of the membrane in the sifting process (Syarfi, 2007).

Conclusion

NF270 membrane is proven to be able to remove dyes and Pb metal in batik industrial wastewater. At different operating pressures (4.5 and 6 bar), the resulting rejection value was 99.59%; 99.84%; 99.87% for color, while the Pb metal rejection value was 100% for all operating pressures. The highest rejection value is at an operating pressure of 6 bar so that a pressure of 6 bar is proven to be effective in removing color from batik waste. The higher the operating pressure, the higher the reaction value.

Acknowledgments

The author would like to thank the Mer-C laboratory staff who have helped provide laboratory materials and equipment in this research.

References

- Akbari, A., Remy, J. C., & Aptel, P. 2002. Treatment of textile dye effluent using a polyamidebased nanofiltration membrane. Journal of Chemical Engineering and Processing: Process Intensification, 41(7),601-609.
- Aouni A., Farsi C., Cuartas-Uribe B., Bes-Pia A., Alcaina-Miranda M.I., Dhahbi M. 2012. Reactive dyes rejection and textile effluent treatment study using ultrafiltration and nanofiltration processes. Journal of Desalination 297, 87-96.
- Bayar, K. D., Loharkar, K. A., & Solanki, R. Design & Fabrication of Nanofiltration Unit: A Review. 2014. International Journal of Innovations in Engineering and Technology Vol. 4, ISSBN: 2319-1058.
- Boussu, K. Applicability of Nanofiltration in the Carwash Industry. Separation and Purification Technology 54 (2007) 139-146
- Chakraborty, S., De. S., Basu, J.K., DasGupta, S. 2005. Treatment of A Textile Effluent: Application of A Combination Method Involving Adsorption and Nanofiltration. Journal of Desalination 174, 73-85.
- Farsi, C., Lassaad Gaara, Mahmoud Dhahbi. 2009. Flux Decline Study for Textile Wastewater Treatment by Membrane Processes. Journal of Desalination 244 (2009) 321–332.
- G.Jacangelo, Joseph., K.Noack Roger. System Concepts. AWWA Manual Chapter 4 (2005) Page: 166.
- Kiswanto, Laila Nur Rahayu, Wintah. 2019. Pengolahan Limbah Cair Batik Menggunakan Teknologi Membran Nanofiltrasi Di Kota Pekalongan. Jurnal Litbang Kota Pekalongan Vol. 17 Tahun 2019
- Kiswanto, Susanto. H, Sudarno, 2020. Treatment Of Coal Mine Acid Water Using Nf270 Membrane As Environmentally Friendly Technology , 9(3), Pp.439–450

- Lestari, N.D. dan Tuhu, A. 2017. Penurunan TSS Dan Warna Limbah Industri Batik Secara Elektro Koagulasi. Jurnal Ilmiah Teknik Lingkungan, 6 (1): 37-38.
- Mantri, M., Pekuri, T., Nystrom, M., 2004. NF270, A New Membrane is having Promising Characteristics and being Suitable for Treatment of Dilute Effluents from The Paper Industry. Journal of Membrane Science 242, 107-116.
- Mulder, M. Basic Principle of Membrane Technology. Dordrecht: Kluwer Academic Publishers. 1996.
- Nasution, 2009, Metode research, Bumi aksara, Jakarta
- Peraturan Daerah Provinsi Jawa Tengah Nomor 5 Tahun 2012. Baku Mutu Air Limbah. Peraturan Menteri Kesehatan Nomor: 416/MEN.KES/PER/IX/1990. Syarat-syarat dan Pengawasan Kualitas Air.
- Peraturan Menteri Lingkungan Republik Indonesia Hidup No 5 Tahun 2014. Baku Mutu Air Limbah.
- Purwaningsih, I. 2008. Pengolahan Limbah Cair Industri Batik CV. Batik Indah Rorojonggrang Yogyakarta dengan Metode Elektrokoagulasi Ditinjau dari Parameter COD dan Warna. Tugas Akhir pada Jurusan Tenik Lingkungan UII.
- Schafer, A.I., Andritsos, N., Karabellas, A.J., Hoek, E.M.V., Schneider, R., and Nystrom, M. 2004. Fouling in Nanofiltration in Nanofiltration–Principles and Applications, Chapter 20: 169-239.
- Seungkwan Hong, Menachem Elimelech, Chemical and Physical Aspect of natural organic matter (NOM) fouling of nanofiltration membrane. Journal of membrane science 132 (1997) 159-181.
- Shu, L., Waite, T. D., Bliss, P. J., Fane, A., Jegatheesan, V. 2005. Nanofiltration for The Possible Reuse of Water and Recovery of Sodium Chloride Salt from Textile Effluent. Journal of Desalination 172, 235-243.
- Sumantri, I., Sumarno, A., Nugroho., Istad.i, dan Buchori, L. 2006.Pengolahan Limbah Cair Industri Kecil Batik dengan Bak Anaerobik Bersekat (Anaerobic Baffled Reaktor). Undip Semarang.
- Suprihatin, H. 2012. Kandungan Organik Limbah Cair Idustri Batik Jetis Sidoarjo dan Alternatif Pengolahannya. Riau: PPLH Universitas Riau.
- Susanto, Heru. Teknologi Membran. Semarang: UPT UNDIP Press. 2011
- Syarfi, Syamsu Herman. Rejeksi Zat Organik Air Gambut Dengan Membran Ultrafiltrasi. Tugas Akhir Teknik Kimia Universitas Riau: Pekanbaru. Sains dan Teknologi 6 (2007) 1-4.
- Tu, N.P. 2013. Role of Charge Effect During Membrane Filtration. Disertasi. Universiteit Gent.Belgia.
- Zhou, Nina. Parametric Study Of Ultrafiltration Membrane System and Development of Fouling Control Mechanism. Thesis Master of Science in Engineering. Purdue University. Hammond, Indiana. (2010) Page:21