Laundry Wastewater Treatment Using Membrane Fılter Synthesized from Zeolıte and Chıtosan

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Abstract

The increasing number of laundry industries, has caused the increase of wastewater generation. One method to reduced the pollutant in wastewater was using membrane filtration. Zeolite and chitosan were materials that have been often used as membrane material because it have a good ability in the film-forming, easily processing and availability of abundant. The aim of this research is to analyze the effect of using membranes synthesized from zeolite and chitosan for flux and removing pollutants mainly for the parameter of TSS and surfactant in laundry wastewater. The filtration process used cross-flow method because it required lower operating costs. Variations in this research were the mass composition ratio of zeolite and chitosan 1:1; 2:1 and 1:2 (membrane Z1C1; Z2C1 and Z1C2) with a total mass used of 15 g, and pressure of 2 bar. Where as the concentration of wastewater used in the process was 100% without the addition of distilled water or dilution. The research data showed composition ratio of optimum zeolite and chitosan, the membrane flux and rejection or removal efficienciy. The optimum compotition ratio of zeolite and chitosan was 2:1 (membrane Z2C1). The highest flux in membrane filtration was membrane Z1C1 at 10th minute that was 39,99 L/m^2.jam. Where as the highest TSS and surfactant removal efficiencies at membrane Z2C1 at 20th minute and membrane Z1C2 at 60th minute were 90,71% and 97,04% respectively.

Keywords: laundry wastewater, membrane, zeolite and chitosan

1. INTRODUCTION

The increasing number of population in Surabaya, in both native and immigrant resulted in the increase of laundry business. The increasing number of laundry business is causing more waste produced. This increasing number of laundry industry caused pollution in the water body on the downstream of Surabaya River (Kusumo, 2011). Almost all wastewater from laundry business is disposed through a sewer or septic tank without any advanced processing, which would potentially cause contamination of the groundwater and water bodies in the vicinity. Laundry wastewater contains chemicals originating from detergents with high concentrations, include phosphates, surfactants, ammonia and nitrogen, as well as a high level of dissolved solids (TSS), turbidity, BOD and COD (Ahmad and El-Dessouky, 2008). Thus, the increasing amount of laundry business will lead to an increase of surfactant concentration in the water body if the waste is continuously discharged into water body without any treatment processes.

Meanwhile based on the characteristics test of initial laundry effluent, the obtained TSS value is 560 mg / L and the surfactant concentration is 186,4 mg / L. The level of both parameters either TSS or the surfactant exceeded the applied quality standards in the province of East Java, where the quality standard for TSS is 100 mg/L and surfactant is 10 mg/L (East Java Governor Regulation No. 72 Year 2013).

One method to reduce or lowering the level of contaminants in the wastewater is by using membrane filtration. Membrane filtration is an alternative wastewater treatment technology which has an advantage of its high efficiency for separation. In addition, processing by membrane technology also has advantages for its relatively cheap operating costs, environmentally friendly, and space efficiency (Muliawati, 2012). Some studies have been done to get the right methods of laundry wastewater treatment in order to comply the effluent standards for the laundry business. Nasir, et al (2013) has been conducting a research on laundry wastewater treatment process using ceramic filters made by natural clay and zeolite to lower DS, TSS, pH, COD, BOD, DHL and surfactants.

Membrane is a layer (barrier) or selective barrier, placed between two semipermeable phases which could pass some certain components, and hold the other ones (Mulder, 1996). Membrane material are significantly affecting the separation process. Zeolite and chitosan are materials that can be used as membrane material, because they had good capability in film-forming, processing, and they are also abundant. Chitosan could be obtained from shrimp shells that are abundant in Surabaya.

This study was conducted to analyze the effect of using membranes made from zeolite synthesis and chitosan in pollutants reduction, mainly to the TSS and surfactant parameters in wastewater from laundry business. The use of quality standard for the laundry business in this study is as the effluent control or permeate. The filtration process is using cross-flow stream because it requires lower operating cost. After obtaining the quality of effluent produced, is expected to be the alternative laundry waste treatment so that it can help to overcome the environmental pollution problems.

2. MATERIALS AND METHODS

2.1. Zeolite Activation

Zeolites that will be used for the membrane forming should be activated. Activation is done chemically by acidification. The goal is to remove inorganic polluter. This acidification will cause the cation exchange with H^+ (Ertan, 2005). The zeolite used in this membrane forming is in the form of powder. Before the chemically activation is done, zeolites are sieved using a sieve (mesh), and taken in a uniform size that is 100 mesh. Afterward, dissolved 250 g zeolite into 350 mL 1 N HCl for 24 hours. Then, after being soaked in HCl, zeolite was rinsed with tap water and distilled until the solution became neutral (pH closer to 7). This washing is done for 6-7 times to make the zeolite neutral. Then zeolites are dried in an oven at 100^o C for 24 hours to remove the liquid on it.

2.2. Solution Preparation and Membrane Molding

The zeolite preparation is begun by weighing the mass of zeolite suitable with the ratio for making membranes that is 7,5 g, 10 g and 5 g. Then put them in a glass beaker and added Iso Propanol Alcohol (IPA) as much as 35 mL and stirred it using a magnetic stirrer for 10 minutes at a speed of 600 rpm to homogenize the solution. The addition of IPA in the membrane forming is to dissolve the zeolite. Next, the zeolite solution was added by a 3,5 ml solution of NH_4Cl. The addition of NH_4Cl solution functioned as a washing solution to remove contaminants that may be present in the zeolite solution, and prevent the growth of microorganisms on the membrane. Afterward, the zeolite solution was stirred again by a magnetic stirrer and settled.

The preparation of chitosan solution started by weighing the chitosan powder in accordance with the mass ratio for the membrane forming, that is 7,5 g, 5 g and 10 g. Then, the chitosan powder was poured in to a beaker glass and added with a 5% solution of acetic acid (CH_3COOH) as much as 100 mL, to dissolve the chitosan. After the acetic acid is added, then it is heated on an electric heater or using a water bath (temperature 95° C) while stirring manually with a stirrer glass for 10-15 minutes until the chitosan is completely dissolved and turned into a homogeneous brownish yellow solution.

In creating membrane, the first step to be done is pouring the zeolite precipitate into chitosan solution, and stirring it manually with a glass stirrer, continued with stirring the solution using a magnetic stirrer with a speed of 600 rpm for 10 minutes to homogenize these two solutions. After being mixed, then heated it on an electric heater. The mixture heating could be done in a saucepan or a larger glass beaker to prevent the solution from being charred or too dry. In addition to the above, heating could also be done in a water bath at a maximum temperature of 95° C. The heating is done for 1 hour while manually stirring the solution by using a glass stirrer.

At the beginning of heating, the mixed solution was added by additive i.e. Poly Vinyl Alcohol (PVA) and Poly Ethylene Glycol (PEG) solution, respectively 30 mL. PVA addition aims to reinforce the membrane or as an adhesive substance (Nisa, 2005). While the PEG addition is functioned as additive which could form more uniform membrane pores. According to Farha and Kusumawati (2012), the addition of a certain amount of PVA could improve the membrane structure itself, increase the strength of membrane and also stabilize the formed membrane, while the use of PEG is for the formation of membrane pores that known as porogen.

After the heating is completed, membrane solution is not given any treatment for a minute in order to make it cooler, and then poured in petri dish with small diameter, 5. Then heat it in oven at a temperature of 100^{o} C for 24 hours to remove or reduce the water content contained in the solution.

2.3. Membrane Reactor Application

The steps in membrane reactor application is as follows (Sari and Damayanti, 2015) :

a. Membrane result of zeolite synthesis and the membrane are molded in ± 5 cm diameter by using a dish.
b. Membranes that had formed were tested on crossflow reactor.
c. The membrane is placed in the hole where the permeate discharges. The laying of membrane must be ensured to cover the hole tightly to prevent leakage. The membrane reactor laying is done with an array of rubber-gauze coarse-fine gauze-membrane-fine-mesh gauze rough-cover.
d. The liquid waste in a storage tank (feed) with capacity of 10 L which will be pumped by a booster pump to the membrane reactor. To made the membrane pores work effectively, distilled water is flowed to the membrane for ± 1 hour. Then the waste water flowed into the reactor at a pressure of 2 bar (Gustian, 2006).
e. In the initial running, the valve and by pass are opened and closed gradually to increase or reduce the pressure up to 2 bar. After reaching a pressure of 2 bar, the permeate is accommodated in a tube or tub for TSS and level of surfactant analysis next. The water coming out of the by-pass will be accommodated in a tank as retentate or concentrate. The membrane test is done 60 minutes (1 hour) with each variant and the permeate is taken every 10 minutes.
f. The resulting permeate volume is measured, and calculate membrane flux.
g. The resulting permeate is analyzed for TSS and surfactant parameters, and then calculate TSS removal efficiency.

2.4. Permeate Analysis

The analyzed pollutant parameters were TSS and surfactant parameters. TSS analysis is done by using gravimetric analysis method in reference to the SNI 06-6989.3-2004. For the analysis of surfactants or detergents using MBAS method (APHA, 2005).

2.5. Membrane Morphology Analysis

Analysis of membrane morphology is using a Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX). SEM analysis is conducted to determine the membrane pores while EDX is determining the composition of elements contained in the membrane. SEM analysis is performed before and after the membrane used for laundry wastewater filtration process. Membranes used for the SEM-EDX analysis is the membrane that produces the highest flux value.

The first step that had to be done in SEM EDX analysis is to dry the sample, the membrane must in dry condition. Then the membrane is immersed in nitrogen liquid for a few seconds until the shape is hardened (Muliawati, 2012). Then the pieces of membrane which will be used is cut by tweezers and covered with pure gold (coating). Pure gold serves as a conductor. The next step is to take a picture of membrane surface with a certain magnification. Magnification used in this study is 1000 times magnification.

3. RESULTS AND DISCUSSIONS

3.1. Effects of Membrane Filtration on Permeate Flux

Diametre of the membrane which is contacted with the foul water when operating membrane reactor is 2,9 cm, so the area (A) that used for the flux value calculation is 0,00066 m^2. The membrane is operated for 60 minutes or an hour with permeate sample taken at 10 minutes interval, so the time value (t) used for the calculation is 0,167 hour. The permeate volume (V) which obtained from the operation is measured in mL unit, then in the volume value converted to Liter unit. In conclusion, the flux value will use L/m^2.hour unit as measurement.

Table 1. Membrane flux value

Time (minute)	**Z1C1**		**Z2C1**		**Z1C2**	
	Volume (mL)	Flux (L/m^2.h)	Volume (mL)	Flux (L/m^2.h)	Volume (mL)	Flux (L/m^2.h)
10	4,4	39,99	4,2	38,17	3,3	29,99
20	3,2	29,08	2,9	26,36	2,2	19,99
30	2,3	20,90	2,2	19,99	1,8	16,36
40	1,1	10,00	1,9	17,27	1,5	13,63
50	0,9	8,18	1,6	14,54	1,5	13,63
60	0,6	5,45	1,3	11,81	1,2	10,91

From the value shown in Table 1 it can be concluded that the membrane flux value which obtained from the operation are mostly categorized in the ultrafiltation membrane type, in which the value are around 10 – 50 L/m^2.hour (Mulder, 1996). The membrane tends to produces smaller value of permeate volume and flux value as the operation time goes on. From the obtained result, the highest value of permeate volume and flux value is obtained using Z2C1 membrane. The average volume and rejection value produced by Z2C1 membrane are 2,35 mL and 21,36 L/m^2.hour.

Based on Ciabatti *et al.*, (2009), and Sari and Damayanti (2014) the flux value tend to decrease as the time goes on. This phenomon is caused by the occurence of fouling at the membrane which triggered by adsorbtion of pollutant into the membrane, accumulating the particles and making a layer on the surface and pores inside the membrane which will causing the decrease of membrane's flux (Nasir, *et al.*, 2013).

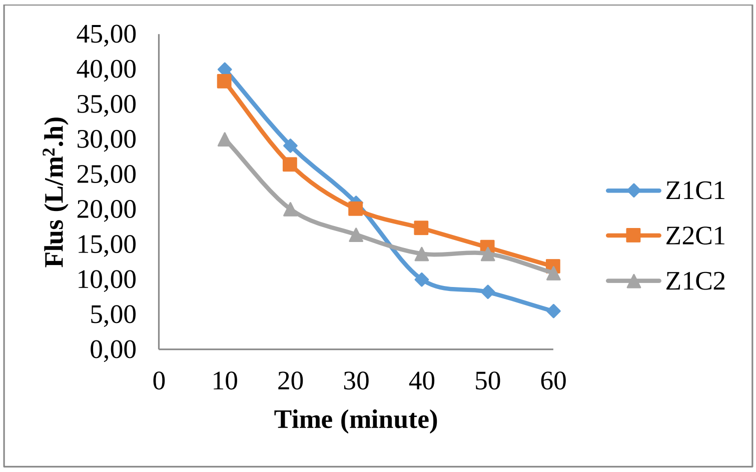

Figure 1. Membrane flux value

3.2. Effects of Membrane Filtration on TSS Rejection

Determining TSS value is useful for measuring the level of foul water pollution and determining the efficiency of water processor unit. Too much TSS can hindering sun light to pass through the water layer, interfering with the photosynthesis process, urging the necessities to determine the TSS limit value for processing foul water before dispatched to the water body (Rahmawati and Azizah, 2005). The measurement of the TSS level is conducted with the use of gravimetric method (APHA, 2005). The initial TSS concentration value of laundry foul water before filtrated is 560 mg/L.

Table 2. Permeate concentration and TSS rejection

Time (minute)	Z1C1		Z2C1		Z1C2	
	Concentration (mg/L)	Rejection (%)	Concentration (mg/L)	Rejection (%)	Concentration (mg/L)	Rejection (%)
10	120,0	78,57	72,0	87,14	140,0	75,00
20	128,0	77,14	52,0	90,71	124,0	77,86
30	144,0	74,29	156,0	72,14	164,0	70,71
40	80,0	85,71	140,0	75,00	148,0	73,57
50	92,0	83,57	128,0	77,14	108,0	80,71
60	76,0	86,43	140,0	75,00	100,0	82,14

Based on Table 2, the highest value of TSS rejection value obtained from the variant composition ratio of zeolith and kitosan 2:1 (Z2C1) at the 20th minute with 90,71%. While the lowest value of TSS rejection value obtained from the variant composition ratio of zeolith and kitosan 1:2 (Z1C2) at the 30th minute with 70,71%.

The TSS rejection value tends to rise as the operation time goes on. This phenomon is caused by the occurence of fouling at the membrane which made the selectifity capability risened because of the diminution of the membrane pores, the longer time the operation takes the more pollutant takes place and trapped inside the membrane's pore causing the pore to keep diminuting, making the pollutant harder to pass through the membrane pores (Wahyuni and Damayanti, 2015).

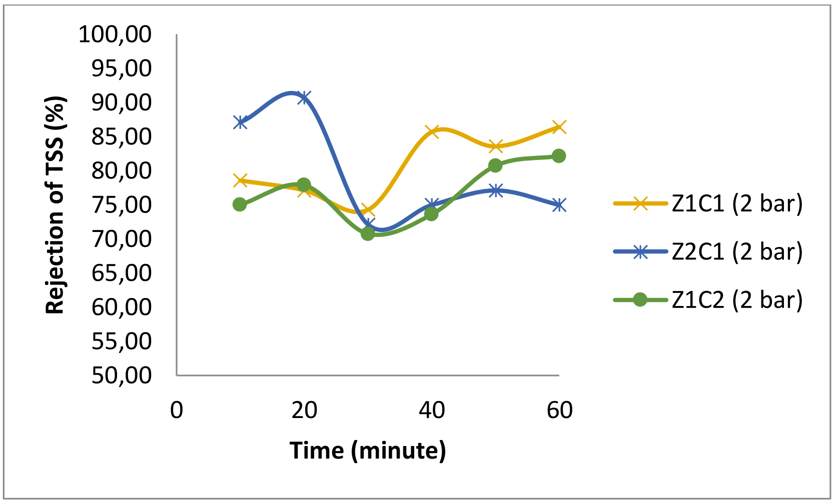

Figure 2. TSS rejection of membrane

3.3. Effects of Membrane Filtration on Surfactant Rejection

Surfactant analysis is performed using MBAs (Methylen Blue Active Surfactant) by adding methylene blue substance that binds to surfactant and analyzed by UV-Vis spectrophotometer (APHA, 2005). The legible concentration is the level of anionic surfactant in the waste sample that binds to the methylene blue. The surfactant concentration of the analysis before the wastewater treatment using membrane filtration is 186,4 mg/L.

Table 3. Permeate concentration and surfactant rejection

Time (minute)	**Z1C1**		**Z2C1**		**Z1C2**	
	Concentration (mg/L)	Rejection (%)	Concentration (mg/L)	Rejection (%)	Concentration (mg/L)	Rejection (%)
10	31,9	82,87	18,7	89,95	29,3	84,26
20	27,5	85,27	14,7	92,10	16,1	91,35
30	24,2	87,04	14,2	92,36	15,4	91,73
40	23,2	87,55	9,5	94,89	14,0	92,48
50	21,8	88,31	9,1	95,14	11,9	93,62
60	18,7	89,95	5,5	97,04	9,3	95,01

Based on Table 3, it is known that the highest surfactant rejection value was obtained on the 2:1 variant composition ratio of zeolite and chitosan (Z2C1) in the 60th minute with an amount of 97,04%. While the lowest possible surfactant rejection value obtained on the 1:1 variant ratio composition of zeolite and chitosan (Z1C1) in the 10th minute with an amount of 82,87%.

Surfactant rejection is increased due to the increasing of operating time. But there is a difference in the increasing rejection of each variant. When the surface of membrane has been contaminated, the membrane pore is getting narrower and in longer time it will form a cake, when it was formed, then the solute will also restrained which caused the rising of rejection coefficient (Espendiller *et al*., 2010).

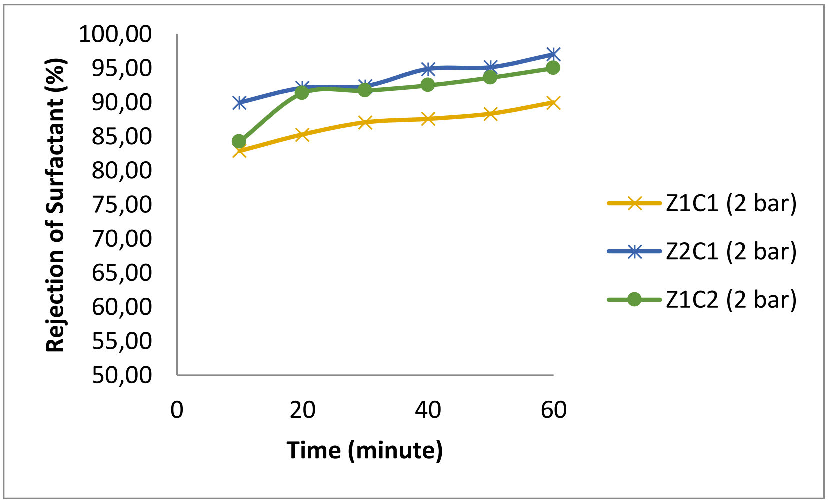

Figure 3. Surfactant rejection

3.4. Membrane Morphology Analysis

Analysis of membrane morphology is using a Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX). SEM analysis was conducted to determine the membrane pores, while for EDX is to determine the composition of elements contained in the membrane. SEM analysis was performed before and after the membrane is used for laundry wastewater filtration process. Membranes used for SEM-EDX analysis is the membrane that produces the highest flux value that is Z2C1 membrane which produces total flux in the amount of 128,15 L/m^2.hour.

The first step done for SEM EDX analysis is drying the sample, so the membrane must be dry. Afterwards, the membrane is immersed in nitrogen liquid for a few seconds until it is hardened (Muliawati, 2012). Then the pieces of to-be-used membrane is cut with tweezers and covered with pure gold (coating). Pure gold is functioned as a conductor. The next step is to take a picture of the surface of membrane with a certain magnification. The magnification used in this study is 1000 times magnification.

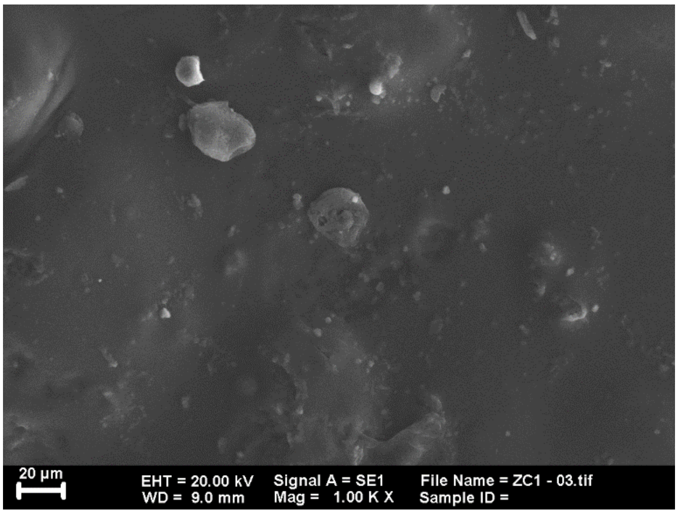

Figure 4. SEM analysis of membrane before operation

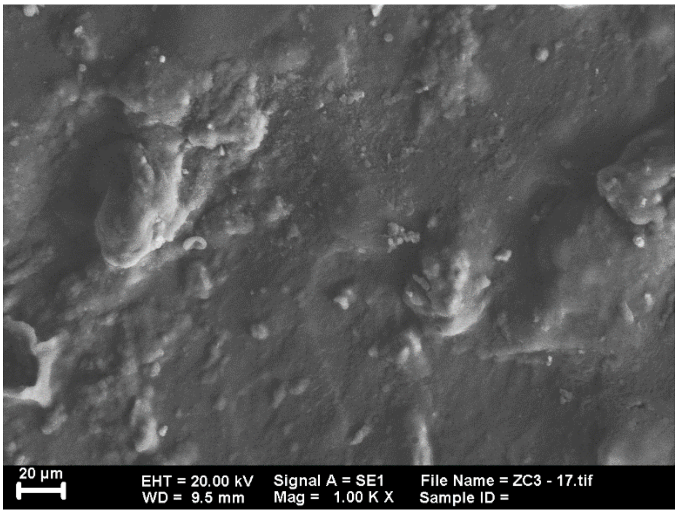

Figure 5. SEM analysis of membrane after operation

Based on Sari and Damayanti (2014) research, the membrane looks increasingly congested due to the fouling. Fouling causes blockage on the pores of membrane due to a material buildup on the surface of membrane. Membrane fouling occurs not only at the top surface or outer layer of membrane which made up a cake but it is also possible to be happened in the membrane lining. Pollutants entering into the inner layer occurs due to the pressure exerted during the membrane operation. The pressure will push the deposition of particles on the surface of membrane.

4. CONCLUSION

From this research, we can take some conclusions, as follows:

1. The best membrane is membrane with 2: 1 zeolite and chitosan ratio (Z2C1) because it produces permeate volume and total flux as much as 14.1 mL and 128.15 L/m^2.hour.
2. The best flux value is 39,99 L / m2.hour obtained from the variant of membrane with 1:1 zeolite and chitosan ratio (Z1C1) in the 10th minute.
3. The best TSS rejection coefficient with a percentage of 90,71% found on the membrane with 2:1 zeolite and chitosan ratio (Z2C1) in the 20th minute. While the best surfactant rejection coefficient with a value of 97,04% found in the membrane with 1:2 zeolite and chitosan ratio (Z1C2) in the 60th minute.

REFERENCES

[1] Ahmad, J., and El-Dessouky, H. Design of a Modified Low Cost Treatment System for The Recycling and Reuse of Laundry Waste Water. Resources, Conservation and Recycling 2008: 52, 973–978.

[2] APHA, AWWA and WPFC. Standard Methods For Examination Of Water And Wastewater**,** 21st.Ed. Washington, DC: 2005.

[3] Ciabatti, I., F. Cesaro, L. Faralli, E. Fatarella and F. Tognotti. Demonstration of a Treatment System for Purification and Reuse of Laundry Wastewater. Jur. of Desalination 2009: 204, 78-86.

[4] Ertan, A. and Ozkan. CO_2 and N_2 Adsorption on The Acid (HCl, HNO_3, H_2SO_4 and H_3PO_4) Trated Zeolites". Adsorption 2005 : Vol. 11, 151-156.

[5] Espendiller, C., Nghiem, L.D., and Coleman, P.J. Mechanisms Underlying The Effects Of Membrane Fouling On The Nanofiltration Of Trace Organic Contaminants. Desalination 2010: 250, 682-687.

[6] Gustian, I. Karakterisasi Kinerja dari Beberapa Membran Datar. Jurnal Gradien, Vol. 2 No. 2 Juli 2006: 187-191.

[7] Kusumo, A. H. Penurunan Konsentrasi Kekeruhan dalam Limbah Cair Laundry dengan Adsorpsi Menggunakan Arang Batok Kelapa (Coconut Shells) Komersil. Teknik Lingkungan ITS, Surabaya: 2011.

[8] Mulder, M. Basic and Principles of Membrane Technology. Kluwer, London: 1996.

[9] Muliawati, E. C. Pembuatan dan Karakterisasi Membran Nanofiltrasi untuk Pengolahan Air. Magister Teknik Kimia UNDIP, Semarang: 2012.

[10] Nasir, S., Teguh, B.S.A, and Silviaty, I. Aplikasi Filter Keramik Berbasis Tanah Liat Alam dan Zeolit Pada Pengolahan Air Limbah Hasil Proses Laundry. Jurnal Bumi Lestari, Volume 13 No. 1, Februari 2013: 45-51.

[11] Nisa, K. Karakteristik Fluks Membran Kitosan Termodifikasi Poli (Vinil Alkohol) dengan Variasi Poli (Etilena Glikol) sebagai Porogen. Kimia IPB, Bogor: 2005.

[12] Peraturan Gubernur Jawa Timur. 2013. *Baku Mutu Air Limbah bagi Industri dan/atau Kegiatan Usaha Lainnya.* No. 72 tahun 2013. Surabaya.

[13] Rahmawati, A.A. and R. Azizah. Perbedaan Kadar BOD, COD, TSS, dan MPN Coliform Pada Air Limbah, Sebelum dan Sesudah Pengolahan di RSUD Nganjuk. Jurnal Kesehatan Lingkungan, 2005: 2(1), 97-110.

[14] Sari, T.K and Damayanti, A. Pengolahan Limbah Laundry Menggunakan Membran Nanofiltrasi Zeolit Aliran Cross Flow untuk Filtrasi Kekeruhan dan Fosfat. Skripsi. Jurusan Teknik Lingkungan, Institut Teknologi Sepuluh Nopember, Surabaya: 2014.

[15] Sari, T.K and Damayanti, A. Filtrasi Limbah Cair Kelapa Sawit dengan Membran Zeolit-Silika untuk Menurunkan BOD, COD dan TSS. Tesis. Jurusan Teknik Lingkungan, Institut Teknologi Sepuluh Nopember, Surabaya: 2015.

[16] Wahyuni, S., and Damayanti A. Studi Pembuatan dan Penggunaan Membran Chitosan sebagai Membran Ultrafiltrasi dalam Pengolahan Limbah POME (Palm Oil Mill Effluent). Tesis. Jurusan Teknik Lingkungan, Institut Teknologi Sepuluh Nopember, Surabaya: 2015.