Waste Technology (WasTech)
Journal homepage: http://ejournal.undip.ac.id/index.php/wastech
An International Journal

Treatment of Natural Rubber Wastewater using Photoactive Nanocomposite Membrane PSf/sulfonated ZnO: Performance Evaluation, HAZOP, and Risk Analysis

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Abstract - *The application of nanocomposite membranes for high organic wastewater treatment faces several problems such as impurities and low permeate flux. In this study, sulfonated ZnO nanoparticles were incorporated in the PSf membrane. SEM images reveal that sZnO has good compatibility with PSf polymers and the FTIR spectrum also forms sulfonic acid groups on the composite membrane. The addition of sZnO into PSf increased the PWF value but overloading caused a significant decrease. The surface hydrophilicity of the membrane was also enhanced by the incorporation of sZnO into the PSf membrane. The performance evaluation showed a significant increase in flux from 9.0 to 14.5 L.m^{-2}.h^{-1} and a disappointment rate for ammonium ion (NH_4^+) up to 87%. Increased hydrophilicity was also revealed by decreasing the air contact angle from 79.33° to 55.67°. PVA-coated membranes can increase COD rejection up to ~88%, which is 8 times higher than uncoated composite membranes. The PVA coating also reduced the tendency of organic fouling on the membrane during rubber wastewater filtration by reducing the total fouling resistance from 14.2 x 10^{-11} to 9.91 x 10^{-11} m^{-1}. The HAZOP and risk analysis were also studied in this work regarding on their practical application in industrial scale..*

***Keywords** – Adsorption, Membrane, Natural rubber, Sulfonation, Wastewater, Zinc oxide*
Doi: http://dx.doi.org/10.14710/wastech.10.2.35-49
[How to cite this article: Kusworo, T.D. (2022). Treatment of Natural Rubber Wastewater using Photoactive Nanocomposite Membrane PSf/sulfonated ZnO: Performance Evaluation, HAZOP, and Risk Analysis. Waste Technology, 10(2),35-48 doi: http://dx.doi.org/10.14710/wastech.10.2.35-49]

1. Introduction

The rubber processing industry is an industry that processes latex into semi-finished rubber. The results of rubber processing are sit, crepe, and crumb rubber. The rubber industry in its processing uses chemicals as latex coagulants and water in large quantities to wash the latex tanks and for the milling process. The liquid waste generated from this activity is 400 m^3 per day (Andriani et al., 2019). Rubber factory wastewater contains rubber components (proteins, lipids, carotenoids, and inorganic salts), non-clumping latex, and chemicals added during processing (Nashrullah, 2017).

According to Sarengat and Setyorini (2015), the rubber industry produces liquid waste with concentrations of BOD 94-9433 mg/liter, COD 120-15,069 mg/liter and TSS 30-525 mg/liter. Liquid waste discharged into the environment will pollute the environment because the pollutant content of liquid rubber waste is above the quality standard. Membrane technology has shown potential superiorities including a continuous process, does not require chemical additives, low energy consumption, easy to upgrade, does not require extreme conditions, varied membrane materials and is easily combined with other separation processes (Kusworo et al., 2020). Membrane technology also offers an attractive solution for manufactured water treatment with many advantages such as low maintenance costs, no toxic chemicals, modular installation and operation at room temperature. Membrane-based separation processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis are commonly used to produce water treatment (Kusworo et al., 2020).

In this research, a combination of surface modification of Nano-ZnO and H_2SO_4 will be carried out to close the gap between polymer membranes and inorganic PVA and cross-linking to improve the performance of PSf-Nano ZnO membranes for rubber wastewater treatment. In addition, to increase the performance of the membrane, ultra violet irradiation will be carried out as a pretreatment on the surface of the membrane. With this combination of membrane modifications, it is hoped that it will be able to produce flux, rejection values and a large increase in selectivity in the process of treating rubber waste water into clean water.

The development of membrane materials has reached the third generation, namely hybrid materials between organic polymers as a continuous phase and inorganic materials as a discrete phase (Mukherjee and De, 2016). Many previous studies have reported the synergistic effect of combining inorganic materials and organic polymers. Some of the improvements obtained include increasing the mechanical properties of the membrane (Wang et al., 2018), reducing the degree of swelling (Tarleton et al., 2006), increasing flux, increasing rejection, and providing anti-fouling properties (Chai et al., 2020) by increasing the surface energy of the membrane (hydrophilicity). Recently, polymer-based membranes have been further developed so that they have certain properties, one of which is a photocatalytic membrane (Du et al., 2020). Photocatalytic membranes are polymer membranes combined with photocatalytic materials so that they have photoactive properties that are effective in degrading organic/foulant content in feed water. So that photocatalytic membranes are currently being developed for the treatment of wastewater with a high organic pollutant content (Lu et al., 2021). In this study, the waste water to be treated is natural rubber industrial waste water which contains a high organic load. Conventional membranes will not be applicable if used to treat the wastewater because fouling will form which will reduce the performance of the membrane. In this study, ZnO nanomaterials will be developed as photoactive materials which will then be embedded in polysulfone polymers (PSf) as basic membrane materials (Ahmad et al., 2015; Kusworo et al., 2020). However, several previous studies reported that at certain concentrations > 1.5 wt-%, ZnO nanomaterials tended to form agglomerates and produce non-selective gaps which caused the separation efficiency to decrease (Kusworo et al., 2019). Therefore, in this study ZnO will be modified using the sulfonate (HSO3-) functionalization method. Sulfonation of ZnO will increase hydrophilicity so that it can provide anti-fouling properties, besides that the presence of sulfonate groups on the surface of ZnO is expected to increase the interaction between nanoparticles and polymer so that non-selective gaps can be removed. Thus, the PSF/sZnO composite membrane becomes more applicable for use in wastewater treatment, especially wastewater from the natural rubber industry.

2. Materials and Methods

2.1 Materials

Materials and chemicals used in this research were real natural rubber wastewater from PTPN VII Bengkulu, PVDF (*polyvinylidene fluoride*) (Sigma-Aldrich Corporation, Germany), *Reduced graphene oxide* (Merck), H_2SO_4 (*Sulfuric Acid*) 95-97% (Merck), $KMnO_4$ *(Potassium Permanganate)* (Merck), Nano partikel ZnO (Shanghai Chemicals Ltd, China), Aquadest (Indrasari Chemicals), PVA (*Polyvinyl Alcohol*) (Merck), and Bentonit (Indrasari Chemicals).

2.2 Synthesis of Sulfonated ZnO

Synthesis of ZnO nanoparticles and sulfonated ZnO (sZnO) using the hydrothermal sol-gel method from the precursor Zinc Nitrate Heptahydrate. The ZnO nanoparticle powders were then sulfonated using concentrated sulfuric acid under thermoflux conditions for 5 hours. The sulfonated ZnO was then washed with distilled water and dried in an oven at 105°C for 24 hours.

2.3 Fabrication of nanocomposite membranes

The production of PSf-sZnO refers to the research by Safarpour et al. (2014). Preparation of the PSf-sZnO nanocomposite begins with making a dope solution consisting of PSf with a concentration of 18%wt and sZnO with variable concentrations (0.5%w/t; 1.0%w/t; and 1.5%w/t) and N-methyl-2-pyrrolidone (NMP) as a solvent. The mixture solution was dispersed using an ultrasonic for 1 hour. Then, the solution was further mixed using a magnetic stirrer at 70°C until a homogeneous solution was formed. Membrane casting refers to research by Kusworo et al. (2018), which is done using the dry-wet phase inversion method with a thickness of 150 μm. The thin layer on the glass plate was irradiated with UV light at room temperature using a UV-lamp for 3 minutes and then put into a coagulation bath filled with water for 1 day at room temperature.

2.4 Membrane performance evaluation

Evaluation of membrane performance was performed for treating natural rubber wastewater obtained from PTPN VII Bengkulu. The filtration process is carried out on a cross-flow system membrane module (Figure 1). The composite membrane was placed in the filter area and then compacted using demineralized water for 30 minutes. Furthermore, wastewater is fed to the membrane at a pressure of 5 bar. Permeate water was collected to measure the volume every 30 minutes. The permeate water was analyzed for its pollutant content to evaluate the membrane separation performance. The permeate flux is calculated using equation (1).

$$J = \frac{V}{A \times t} \qquad (1)$$

Where J is permeate flux ($L.m^{-2}.h^{-1}$), V is permeate volume (L), A is membrane surface area (m^2), and t is filtration time (hours).

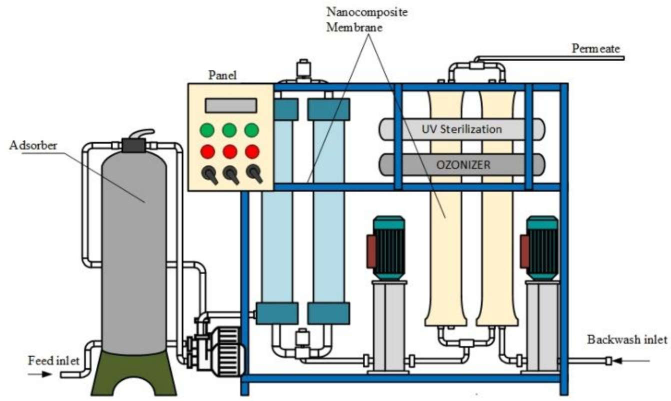


Figure 1. Membrane filtration system for natural rubber wastewater treatment

Rejection (R) is defined as a measure of the ability of a membrane to retain or pass certain components (Murni and Sudarmi, 2010). In this study, rejection was based on the ability to retain total dissolved solids (TDS) and Chemical Oxygen Demand (COD) in liquid rubber waste. Noble and Stern (2006) in Kurniawan and Mariadi (2016) state that the rejection coefficient is the fraction of solute concentration that does not penetrate the membrane and is expressed in equation (2):

$$R = \left(1 - \frac{C_P}{C_f}\right) \times 100\% \qquad (2)$$

Where R is pollutant rejection (%), CP and Cf are concentrations of solutes (contaminants) in the permeate and feed.

2.5 Nanocomposite membrane characterization

Fourier transform infrared (FTIR) characterization is used to determine changes in organic functional groups in the membrane. In this study, the FTIR test aims to determine the effect of the modifications that have been made on the PSf/sZnO nanocomposite membrane. Scanning electron microscope (SEM) characterization was used to observe the morphology of PSf/sZnO membranes. The hydrophilicity of the membrane was analyzed by measuring the water contact angle. Porosity and estimated pore size of the membrane are calculated using the following equations (3) and (4).

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times \rho_w} \qquad (3)$$

$$r = \sqrt{\frac{8\eta\delta Q \times (2.9 - 1.75\varepsilon)}{\varepsilon \times A \times \Delta P}} \qquad (4)$$

Where, ω_1 is the weight of the membrane in a wet state (grams), ω_2 is the weight of the membrane in a dry state (grams), A is the area of the membrane (m^2), δ is the thickness of the membrane (m) and ρ_w is the density of water (0.998 gram/cm^3) (Hartini et al. al., 2018). η is the viscosity of water at room temperature (8.9 x 10-4 Pa.s), Q is the permeate flow rate ($m^3.s^{-1}$), and ΔP indicates pressure (Pa) (Ndlwana et al ., 2020).

2.6 Photocatalytic activity tes and fouling evaluation

The photocatalytic activity test of the PSf/sZnO composite membrane will be carried out based on a procedure that refers to research conducted by Kusworo et al. (2020), namely by evaluating the rate of organic degradation which can be demonstrated by a decrease in the COD value in rubber liquid waste. The series of equipment for the photocatalytic activity test is presented in Figure 2.

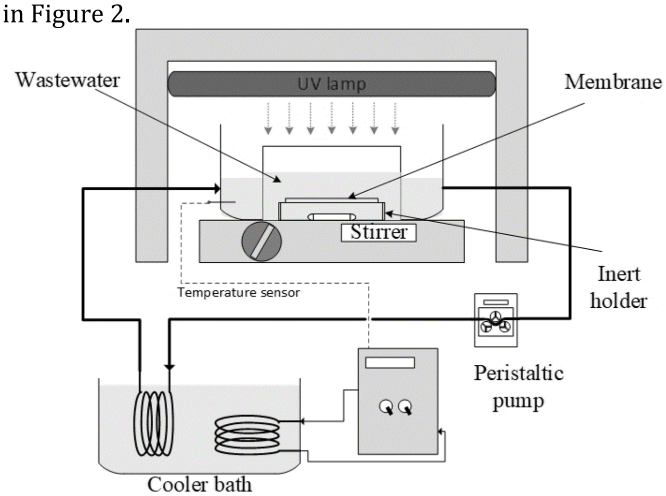


Figure 2. Equipment set for photocatalytic activity test

The fouling phenomena of the membrane during wastewater filtration was evaluated using fouling resistance measurement. The fouling resistance was evaluated according to Darcy theory of fluid flow in mesoporous material. A series model of fouling resistance formula is presented in Eq. (5) – (7).

$$R_m = \frac{\Delta P}{\mu \times J_0} \qquad (5)$$

$$R_a = \frac{\Delta P}{\mu \times J_a} - R_m \qquad (6)$$

$$R_c = \frac{\Delta P}{\mu \times J_f} - R_m - R_a \qquad (7)$$

In this study, the fouling mechanism is evaluated based on three major fouling mechanism theory such as complete blocking model, cake filtration, and combined mechanistic model as presented in Eq. (8) – (9). The values of root mean square errors and determination coefficient (R^2) were used to compare the accuracy of proposed models with experimental data set.

Complete blocking model:

$$J = J_0 \frac{1}{\sqrt{\left(1 + 2K_{cf} J_0^{\,2} t\right)}} \qquad (8)$$

Cake filtration model:

$$J = J_0 \exp^{(-K_{cb} t)} \qquad (9)$$

Combination of mechanistic model:

$$J = J_0 \exp\left(\frac{-K_{cb}}{K_{cf} J_0^{\,2}} \left(\sqrt{\left(1 + 2K_{cf} J_0^{\,2} t\right)} - 1 \right) \right) \quad (10)$$

3. Results and Discussion

3.1 Morphological properties and FTIR analysis

SEM images of the surface and cross-sectional morphology of the PSf/sZnO composite membrane are shown in Figure 3. The surface morphology of the flat membrane no cavities were observed at this magnification and there were many white nodules which might be associated as sZnO embedded. The difference in the gap between the sZnO nanoparticles and the PSf polymer was not observed, this indicates that the sulfonated ZnO nanoparticles have good compatibility with PSf through sulfonate-sulfone interactions. SEM cross-sectional images as presented in Figure 3(b) show an asymmetrical structure consisting of a dense upper layer, a porous finger-like layer, and a lower layer. The top dense layer plays an important role in the selectivity behavior of the membrane while the finger-like porous layer contributes in water permeation and structural stability of the membrane during the filtration process.

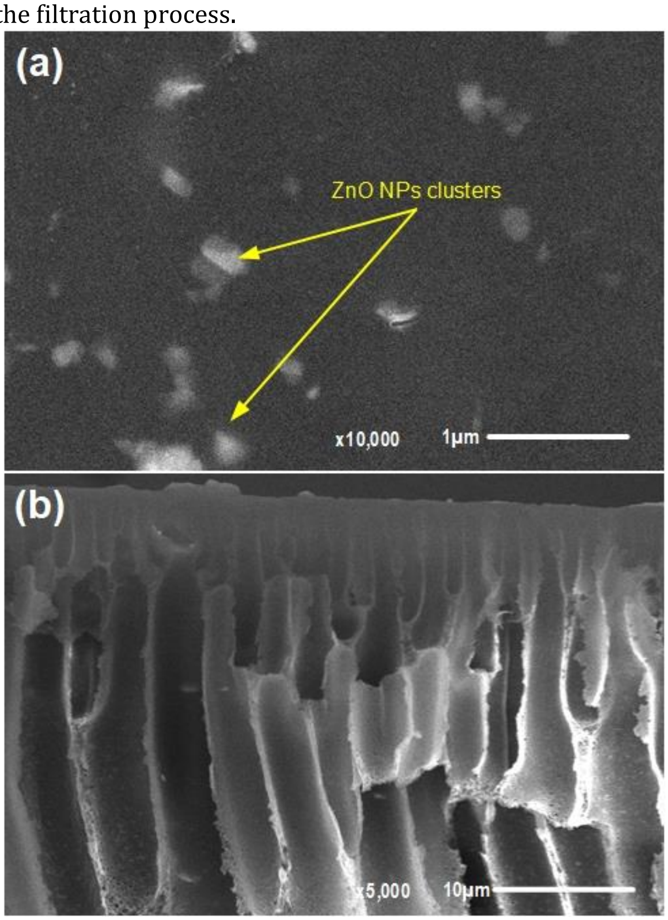


Figure 3. SEM images of PSf/sZnO nanocomposite membrane (a) surface at x10,000 magnification (b) cross-section at x5,000 magnification

Investigation of the chemical structure of fabricated membranes is very important to evaluate the success of modification procedures. The FTIR spectra of the pure PSf and sZnO-PSf composite membranes are presented in Figure 4. The FTIR spectra of the pure PSf and sZnO-PSf membranes are similar. There is an absorption consistency at 1300–1350 cm^{-1} which can be attributed to the sulfone groups (S=O) of polysulfone and a strong peak at 1248 cm^{-1} belonging to vinyl ether (-O-) with aromatic derivatives from the PSF backbone. The FTIR spectrum of sZnO-PSf shows an additional weak peak at 1367 cm^{-1} which is associated with a sulfonate group (-SO_3-H) as an effect of the sulfonation process. FTIR analysis revealed that the sulfonation process of ZnO nanoparticles was successfully carried out.

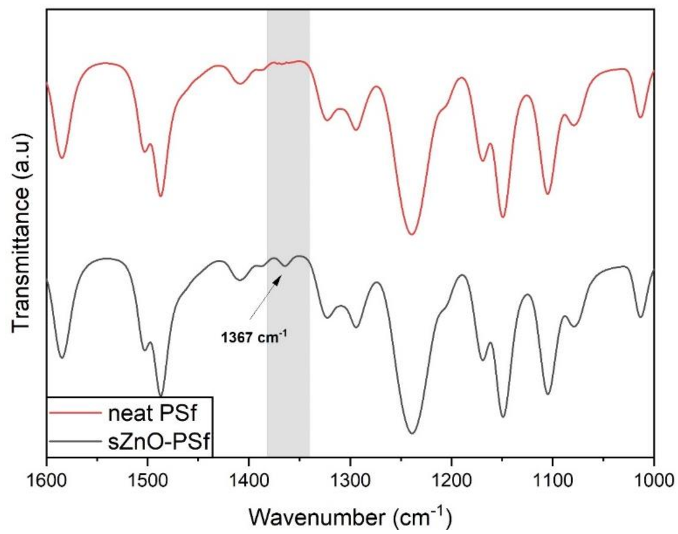


Figure 4. FTIR spectra of pure PSf and nanocomposite PSf/sZnO

3.2 Pure water flux and membrane hydrophilicity

Table 1 shows the PWF profile of the sZnO-PSf composite membrane. The PWF value increased with increasing sZnO concentration in the polymer matrix. The increase in PWF might be attributed to the introduction of water-attracting fillers into the PSf polymer that increases its affinity for water molecules. In addition, the presence of sZnO nanoparticles in the polymer forms unclogged channels that allow water molecules to pass through the membrane barrier. According to previous studies, the addition of ZnO nanoparticles to polymer membranes increases the porosity of the resulting membrane thereby increasing water permeation (Wenten et al., 2020). However, concentration overloading can cause the opposite effect whereby the nanoparticles form agglomerates which increase the membrane resistance which leads to a decrease in PWF. The water contact angle profile of the membrane as presented in Table 1 confirms the increased surface hydrophilicity of the membrane. The pure PSf membrane contact angle value was 79.33° indicating that PSf is naturally slightly hydrophobic. The contact angle decreased significantly to 72.83° with the addition of 0.5

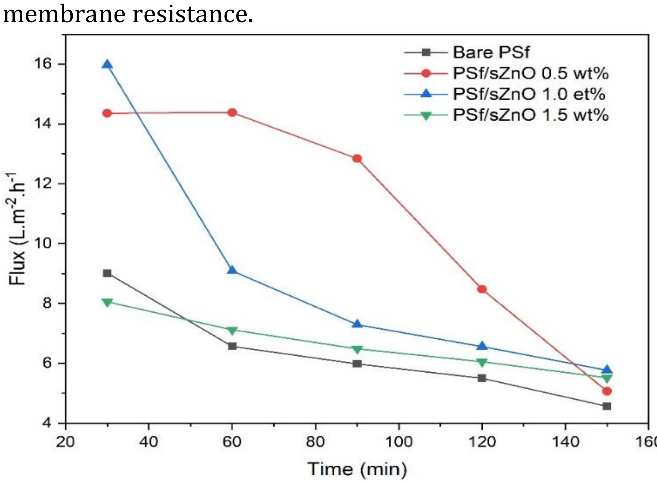
wt% sZnO and continued to decrease to 56.33° after the addition of 1.5 wt% sZnO. The ZnO nanoparticles themselves are naturally hydrophilic with an oxygen molecule attached acting as a water-attracting site. The addition of sulfonate groups on the ZnO surface increases the water-attracting sites. According to these results, the incorporation of sZnO has shown an important role in increasing the hydrophilicity and wettability of the composite membrane.

Table 1. Water contact angle value and pure water flux

No.	Membrane	Water contact angle	Pure water flux
1	Neat PSf	79.33 ± 2.15	37.12 ± 3.47
2	PSf/sZnO 0.5 wt%	72.83 ± 1.54	55.21 ± 4.21
3	PSf/sZnO 1.0 wt%	69.81 ± 1.98	63.74 ± 3.86
4	PSf/sZnO 1.5 wt%	56.33 ± 2.31	35.48 ± 2.69

3.3 Membrane performance evaluation

Evaluation of membrane performance was carried out by measuring permeate flux and pollutant rejection in natural rubber wastewater treatment. Figure 6 presents the permeate flux profiles for pure PSf membranes and sZnO-PSf composite membranes with various loading concentrations of sZnO. Overall, the profile shows a significant decrease in flux at initial filtration caused by membrane compaction. The addition of 0.5 wt% sZnO significantly increased the initial flux from 9.0 to 14.5 $L.m^{-2}.h^{-1}$. This increase in flux could be due to the formation of a hydration layer on the surface of the membrane as an effect of water-attracting sites embedded in the PSf membrane. The 0.5 wt% sZnO-PSf membrane flux slightly decreased during initial filtration, possibly due to the contribution of sZnO nanoparticles absorbing the trans-membrane pressure energy load and maintaining the membrane structure from compaction (Dipheko et al., 2017). Further loading sZnO at 1.5 wt%, the permeate flux decreased even lower than that of pure PSf membranes at 8.24 $L.m^{-2}h^{-1}$. This phenomenon can be caused by the formation of nanoparticle agglomeration which increases the intrinsic membrane resistance.



Gambar 6. Flux profile of prepared membranes in natural rubber wastewater filtration process

Table 2 shows the rejection of pollutants represented by the rejection of TDS, COD, and NH3. The rejection efficiency for all parameters increased with increasing sZnO loading concentration. A significant increase was shown by the rejection of NH_3 wherein the rejection rate was increased from 10.94% to 88.41% with 1.5 wt% loading concentration of sZnO. This can occur due to the presence of a sulfonic acid group (-SO3-H) which gives a positive electrostatic charge from Bronsted Acid, while NH3 dissolves in water in the form of NH4+ ions which also contain Bronsted Acid (Kusworo et al., 2021). NH4+ ions are rejected via the Donnan exclusion mechanism as a result of the same electrostatic charge (Tran et al., 2019). Based on this study, sZnO-embedded PSf membranes are selective for positively electrostatically charged ions or particles.

Table 2. Pollutants rejection efficiencies of fabricated membranes

No	Membrane	Rejection (%)		
		TDS	COD	NH_3
1	Bare PSf	6.54	5.22	10.94
2	PSf/sZnO 0.5 wt%	6.88	5.59	24.78
3	PSf/sZnO 1.0 wt%	9.22	12.39	74.85
4	PSf/sZnO 1.5 wt%	17.16	22.31	88.41

3.4 Membrane fouling evaluation

Natural rubber wastewater contains fatty acids, peptides, lipids, ammonia and other organic contaminants which can cause membrane fouling. A rapid decrease in permeate flux was observed during the screening of rubber wastewater in cross-flow mode. The fouling deposition behavior on the membrane was evaluated by measuring the resistance using Darcy's theory of fluid permeation through porous media. Intrinsic membrane resistance (R_m), resistance of adsorbed foulant (R_a), cake foulant resistance (R_c) and total resistance (R_T) are presented in Table 3. The nanocomposite membrane R_m is lower than that of pure PSf membranes. The possible answer to this phenomenon is the presence of sZnO NPs in the doping solution which causes a more porous structure due to the rapid de-mixing process during phase inversion. In addition, the sulfonate groups on ZnO provide hydrophilic properties on the membrane surface. This is also consistent with previous studies where hydrophilic surfaces have a lower tendency for organic fouling (Bidsorkhi et al., 2016; Kusworo et al., 2021).

Tabel 1. Fouling resistance of bare membrane and nanocomposites

Membrane	**R_m x 10^{11} (m^{-1})**	**R_a x 10^{11} (m^{-1})**	**R_c x 10^{11} (m^{-1})**	**R_T x 10^{11} (m^{-1})**
Neat PSf	7.41	4.77	2.02	14.20
PSf/sZnO	5.95	1.44	3.13	10.52

3.4 HAZOP and risk analysis

In addition to considering the variable aspects of operating conditions, to control the performance of membrane separation in addition to a complete analysis, the safety conditions of the membrane unit must be considered. Security (safety) is an important factor that must be considered when it has to do with the use of machinery, equipment and chemicals. It is vital to identify all potential hazards to prevent accidents and to protect workers. Exposure to extremely high pressures and temperatures should always be a top priority when dealing with industrial processes. There should always be safety protocols in place in the event of an accident, such as an explosion. First and foremost, high temperatures pose a hazard to equipment and workers. Construction materials are a serious consideration in everything from piping to reactors and heaters. The HAZOP technique has generally been widely applied in the design of industrial processes including membrane processes. HAZOP analysis is a technique widely used in chemical process design based on its potential to detect critical points in the production cycle: hazards to operator and environmental health and safety, plant or equipment damage under severe working conditions and loss of productivity for unforeseen circumstances. factory closure. A schematic representation of the main actions required in the development of this approach is summarized in an algorithm for implementing HAZOP in a process system presented in Figure 7.

The membrane filtration system will be used to treat wastewater with high feed characteristics of organic matter and is acidic. Therefore, the equipment must have a construction material that is corrosion resistant and of sufficient thickness. The biggest hazard of this equipment is leakage, which can damage the process equipment. The pump can overheat and can cause severe burns if used for a long time and not properly maintained. In the event of overheating, the pump should be temporarily shut down and allowed to cool back to proper operating temperature.

The results of the HAZOP study are presented in Table 4. Flow variations are caused directly by mechanical and electrical failures of valves, pipelines and control instrumentation and indirectly affect membrane damage due to uncontrolled pressure changes or inefficient filtration systems. Changes in pressure with respect to the set point value are exclusively associated with inappropriate pollutant loads in the feed water as a result of blockages in the filter media and membranes. The sudden uncontrollable pressure deviation can cause serious problems to the membrane material and environmental safety.

Relief valves, control and alarm instrumentation with systematic inspection and maintenance protocols can reduce risks significantly for humans (operators) and the environment especially when hazardous materials are involved in the reaction process. The membrane unit for its simplicity requires only a few additional units and related instrumentation which adds little to the complexity of the whole system. So that the analysis of operational process problems allows for the investigation of problems that occur more frequently individually during operations. The absence of additives in the separation process can reduce the risk of explosion through the intrinsic control of operating temperature and pressure. Furthermore, controlled administration of the reagents avoids the contamination limits of a particular mixture.

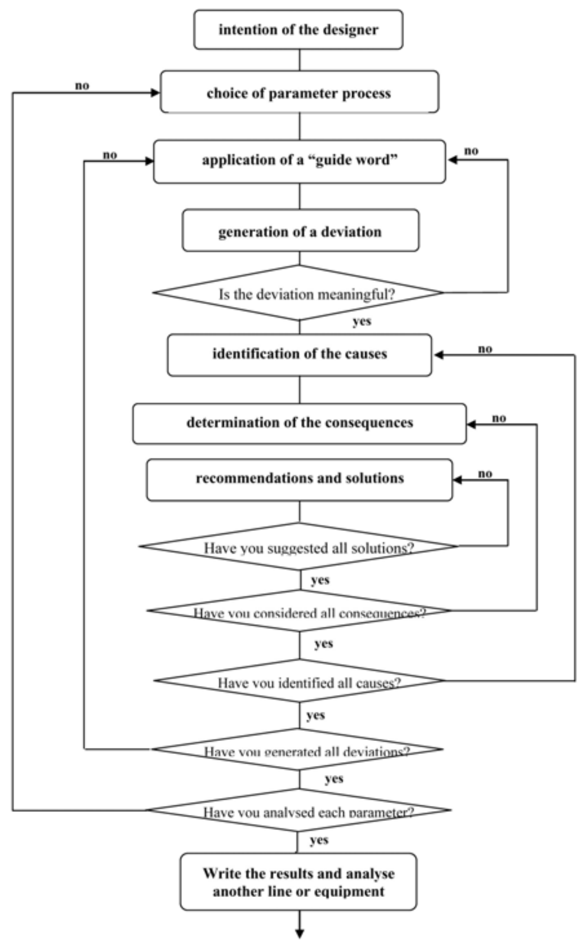


Figure 7. HAZOP evaluation algorithm in every process stage

Table 4. HAZOP identification of membrane filtration process

Equipment Part		Multimedia pre-filter, cartridge microfilter				Activity:	Filtering large size contaminants such as TSS
Operating Condition Data		Pressure (atm-g)	Temp. (°C)	Flow (gal/day)	Vaccum	Material:	Natural Rubber Wastewater
		0.1 – 0.5	ambient	10.000	-	Source:	Feed tank of wastewater

Parameter	Keyword	Possibility Cause	Consequences	Safety guards	Action
General	General	• Feed contains large size contaminants • pH of wastewater potentially damage equipment • Corrosion	• Filter blocking • Thinning of column FRP material • Damage equipment from metal	• Intensive backwash • Extreme pH durable material • Using stainless steel	Strainer installation to prevent blocking
Flow	High	• The by-pass valve of the feed pump is closed	• The screening process is not effective because of the short residence time	• Adjust the by-pass valve to get the appropriate flow	There is no specific action
	Low	• The by-pass valve of the feed pump is fully open • The level of feed water in the tank is reduced	• Pump cavitation	• Adjust the by-pass valve to get the appropriate flow • Make sure the water level is sufficient	Inspect the pump for cavitation damage
	No Flow	• Empty feed tank • Terjad total blocking in the pre-filter column • The booster pump is not working	• target management capacity not achieved • Potential increase in pressure in the pipeline • possibility of damaging equipment, possibly causing operator accidents	• • periodic backwashing process • • control panel inspection, and electricity	Check the pump if it doesn't work
	Back flow	• Pump is not working	• Vacuum in pipeline system	• Installation of a back stop system in the event of a feed failure	There is no significant action
Tekanan	High	• There is a blockage in the pre-filter column • By-pass valve does not open	• Potential for device leaks and damage to pressure gauges	• Perform regular backwashing • Setting by-pass valves	There is no significant action
	Low	• Pump motor trouble	• Water pressure is unable to overcome the resistance of the filter media	• Check pump condition	Use back-up pump

Equipment Part	Multimedia pre-filter, cartridge microfilter				Activity:	Filtering large size contaminants such as TSS
Operating Condition Data	Pressure (atm-g)	Temp. (°C)	Flow (gal/day)	Vaccum	Material:	Natural Rubber Wastewater
	0.1 – 0.5	ambient	10.000	-	Source:	Feed tank of wastewater

Parameter	**Keyword**	**Possibility Cause**	**Consequences**	**Safety guards**	**Action**
General	General	• Ozone oxidation reaction with phosphate compounds that form colloids • Oxidation of reactor materials with ozone	• Causing a deadlock on a stream • Pollutant oxidation efficiency is reduced • Damage to reactor materials	• Perform regular desludging of sludge • Injecting a pH adjuster to oxidize phosphates • Inert reactor material	It is necessary to determine the schedule for desludging sludge in the ozonation reactor
Flow	High	• Valve by-pass is closed	• • The residence time of the material in the reactor is short so that the oxidation is not optimal	Adjust the by-pass valve to get the appropriate flow	There is no specific action
	Low	• A problem has occurred with the pump • Valve-by-pass open too large	• The operating capacity target was not achieved • A lot of O3 gas is wasted, thus endangering the operator	• Adjust the by-pass valve to get the appropriate flow • Perform periodic pump checks	There is no specific action
	No Flow	• Empty feed tank • There is a complete blockage • Valve control does not work • Pump is not working	• target processing capacity not achieved • The pressure in the pre-filter column is too high • the possibility of damaging the equipment, possibility cause an operator accident	• ensure the tank is filled with bait to a sufficient height • perform CIP cleaning (cleaning in process) • check control valve and pump	Perform periodic and regular CIP cleaning and backwashing
	Impurities	• soil, sand and colloids	• Sludge accumulation occurs in the reactor	• carry out regular desludging	There is no specific action

Equipment Part	Multimedia pre-filter, cartridge microfilter				Activity:	Filtering large size contaminants such as TSS
Operating Condition Data	Pressure (atm-g)	Temp. (°C)	Flow (gal/day)	Vaccum	Material:	Natural Rubber Wastewater
	0.1 – 0.5	ambient	10.000	-	Source:	Feed tank of wastewater

Parameter	**Keyword**	**Possibility Cause**	**Consequences**	**Safety guards**	**Action**
General	General	• The feed stream still contains large amounts of impurities. • Cleaning liquid that has the potential to damage the membrane material • Corrosion	• The membrane is stuck • Damage to the membrane material which reduces separation efficiency • Damage to the membrane housing	• Perform CIP cleaning procedures • Perform periodic backwash • Using housing with anti-corrosion/inert material	There is no specific action
Flow	High	• By-pass valve does not open • Totally open retentate valve	• Increased system pressure • Potentially damaging to membrane materials	Adjust the by-pass valve	There is no specific action
	Low	• The by-pass valve is too large open • Faulty pump	• The operating capacity target was not achieved • Transmembrane pressure is not reached	• Adjust valve-by-pass • Checking the condition of the pump	Immediately perform pump maintenance if a problem is found
	No flow	• The pump is not working • Closed retentate valve • Total blockage occurs	• The pump is not working • Closed retentate valve • Total blockage occurs	• Make sure the pump is working. • Pressing emergency stop if there is no flow	Do maintenance thoroughly
	Back flow	• Backwash pump running • Failure of the control valve system	Damage the membrane	• Emergency stop	Do checks on the pump and control system
Tekanan	High	• Valve retentate is closed • Membrane pore blocking	• Potentially damaging membrane materials • Very low flux	• Adjust valve retentate • Perform periodic backwash and CIP cleaning	There is no specific follow up
	Low	• Totally open retentate valve • Completely open by-pass valve • The pump is not working properly • There is a membrane leak	• Driving force trans-membrane pressure is not achieved • Very low flux • Quality of product water is decreasing	• Adjusting the retentate valve opening and by-pass valve • Checking the pump • Check product water quality	If the quality of the product water has decreased drastically, it is necessary to check for membrane leaks and then replace

Equipment Part	Multimedia pre-filter, cartridge microfilter				Activity:	Filtering large size contaminants such as TSS
Operating Condition Data	Pressure (atm-g)	Temp. (°C)	Flow (gal/day)	Vaccum	Material:	Natural Rubber Wastewater
	0.1 – 0.5	ambient	10.000	-	Source:	Feed tank of wastewater

Parameter	Keyword	Possibility Cause	Consequences	Safety guards	Action
					the membrane
General	General	• Feed conditions that have the potential to cause corrosion • There was a short circuit due to splashing water	• Damaging the pump components especially the impeller • Pump failure causing operation failure	• Using pumps with anti-corrosion materials • Installing a pump cover (pump cover) to prevent splashing air	There is no specific follow up
Head suction	High	• Level of feed liquid in full tank	• No significant effect		There is no specific follow up
	Low	• The liquid level in the feed tank is low	• avitation occurs • Low flow rate • Production capacity is not reached • Insufficient driving force	• Make sure the feed water level is at the required level	Installing level control on the tank
Flow	No Flow	• Closed valve on pipe flow • Spill from bucket elevator	• Pipe line overpressure and pump overheat	• The operator must be alert in adjusting the valve when the pump is started • Pipelines are designed to prevent shut off pressure	Immediately turn off the pump
	Back flow	Katup tidak ditutup saat dibutuhkan, kedua tangki menjadi terhubung	• No significant effect	• Installation of a back stop system in the event of a feed failure	There is no specific follow up
	Impurities	The booster pump seal is chipped or damaged	• Oil or lubricant leaks		Install a double seal booster pump
Rotor	Shaft failure	• Workload overload • The rotor is not completely submerged in water • The rotating part swipes the stationary part	• The pump vibrates • The pump is not working • Cavitation • No flow	Routinely replace the lubricant, avoid overload workload	Replaced the shaft with a stronger one
	Eroded shaft	• Vibration from the pump • Power absorbed due to excessive	• The pump vibrates and is noisy	Adjust the electric power to the needs of the pump	Routinely provide

Equipment Part	Multimedia pre-filter, cartridge microfilter				Activity:	Filtering large size contaminants such as TSS
Operating Condition Data	Pressure (atm-g)	Temp. (°C)	Flow (gal/day)	Vaccum	Material:	Natural Rubber Wastewater
	0.1 – 0.5	ambient	10.000	-	Source:	Feed tank of wastewater

Parameter	Keyword	Possibility Cause	Consequences	Safety guards	Action
		pump energy	• The pump is not working • Overheat and pump seizures	according to specifications	lubrication
	Bearing failure	• Lubricant failure • Improper installation • Abnormal load on rotor • Incompatible bearing type	• Small flow below normal • The pump vibrates and is noisy	Adding lubricant Adjust bearings	Replace the appropriate bearing
	Wheel failure	• Cavitation • Unlubricated bearings • The moving part swipes the stationary part	• Insufficient flow • Insufficient discharge pressure • The pump vibrates	Provide lubricant Make sure the suction head is sufficient	Replace the pump wheel
	Diffuser failure	• Cavitation, overheat, corrosion	• Insufficient flow • The pump vibrates • leaks	Make sure the suction head is sufficient Match the characteristics of the pump material to the material being handled	There is no specific follow up
	Corrosion	• Material characteristics and materials handled	• The pump is running abnormally • Pump noise	Match the characteristics of the pump material to the material being handled	Determine appropriate feed specifications
Housing	Erosion	• Cavitation, erosion, corrosion and vibration	• Big leak • Impaired pump performance	Ensure the pump has sufficient suction head	There is no specific follow up
General	General	• Feed conditions that have the potential to cause corrosion • There was a short circuit due to splashing water	• Damaging the pump components especially the impeller • Pump failure causing operation failure	• Using pumps with anti-corrosion materials • Installing a pump cover (pump cover) to prevent splashing air	There is no specific follow up
Head suction	High	• Level of feed liquid in full tank	• No significant effect		There is no specific follow up
	Low	• The liquid level in the feed tank is low	• avitation occurs • Low flow rate • Production capacity is not reached	• Make sure the feed water level is at the required level	Installing level control on the tank

Equipment Part	Multimedia pre-filter, cartridge microfilter				Activity:	Filtering large size contaminants such as TSS
Operating Condition Data	Pressure (atm-g)	Temp. (°C)	Flow (gal/day)	Vaccum	Material:	Natural Rubber Wastewater
	0.1 – 0.5	ambient	10.000	-	Source:	Feed tank of wastewater

Parameter	Keyword	Possibility Cause	Consequences	Safety guards	Action
			• Insufficient driving force		
Flow	No Flow	• Closed valve on pipe flow • Spill from bucket elevator	• Pipe line overpressure and pump overheat	• The operator must be alert in adjusting the valve when the pump is started • Pipelines are designed to prevent shut off pressure	Immediately turn off the pump
	Back flow	Katup tidak ditutup saat dibutuhkan, kedua tangki menjadi terhubung	• No significant effect	• Installation of a back stop system in the event of a feed failure	There is no specific follow up
	Impurities	The booster pump seal is chipped or damaged	• Oil or lubricant leaks		Install a double seal booster pump
Rotor	Shaft failure	• Workload overload • The rotor is not completely submerged in water • The rotating part swipes the stationary part	• The pump vibrates • The pump is not working • Cavitation • No flow	Routinely replace the lubricant, avoid overload workload	Replaced the shaft with a stronger one
	Eroded shaft	• Vibration from the pump • Power absorbed due to excessive pump energy	• The pump vibrates and is noisy • The pump is not working • Overheat and pump seizures	Adjust the electric power to the needs of the pump according to specifications	Routinely provide lubrication
	Bearing failure	• Lubricant failure • Improper installation • Abnormal load on rotor • Incompatible bearing type	• Small flow below normal • The pump vibrates and is noisy	Adding lubricant Adjust bearings	Replace the appropriate bearing
	Wheel failure	• Cavitation • Unlubricated bearings • The moving part swipes the stationary part	• Insufficient flow • Insufficient discharge pressure • The pump vibrates	Provide lubricant Make sure the suction head is sufficient	Replace the pump wheel
	Diffuser failure	• Cavitation, overheat, corrosion	• Insufficient flow • The pump vibrates • leaks	Make sure the suction head is sufficient Match the characteristics of	There is no specific follow up

Equipment Part	Multimedia pre-filter, cartridge microfilter				Activity:	Filtering large size contaminants such as TSS
Operating Condition Data	Pressure (atm-g)	Temp. (°C)	Flow (gal/day)	Vaccum	Material:	Natural Rubber Wastewater
	0.1 – 0.5	ambient	10.000	-	Source:	Feed tank of wastewater

Parameter	Keyword	Possibility Cause	Consequences	Safety guards	Action
				the pump material to the material being handled	
	Corrosion	• Material characteristics and materials handled	• The pump is running abnormally • Pump noise	Match the characteristics of the pump material to the material being handled	Determine appropriate feed specifications
Housing	Erosion	• Cavitation, erosion, corrosion and vibration	• Big leak • Impaired pump performance	Ensure the pump has sufficient suction head	There is no specific follow up

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3.6 Policy of Health, Safety, and Environmental Protection

Basically, membrane filtration systems are included in process systems with a low level of hazard because they operate in mild conditions. However, in the operation of membrane filtration equipment there is the possibility of an accident/injury to the operator either due to operator negligence or process equipment failure. Due to safety hazards associated with handling machinery such as booster pumps and electrical systems. Every personnel must be properly trained before operating the equipment. If there is severe fouling or deadlock so that a pressure rise in the membrane system can occur this can cause pump damage, membrane material damage, and the piping system to leak or explode due to high pressure.

The membrane filtration process for treating rubber waste water will produce clean water as a product that can be reused in the production process. Meanwhile, the retentate which contains pollutant in high concentration will be collected for further biological processing to reduce the pollutant load. While the results of the cleaning process that contain washing chemicals will be handled by procedures for handling hazardous and toxic materials (B3).

5. Conclusion

PSf-sZnO composite membranes have been successfully prepared using the dry-wet phase inversion method. SEM images reveal that the sZnO nanoparticles have good compatibility with the indicated PSf polymer with no observable non-selective gaps. The FTIR spectrum also confirmed the successful sulfonation of ZnO nanoparticles with the appearance of absorption as a result of the vibration of the sulfonic acid groups. Combining sZnO also increases the PWF value but excess sZnO causes a decrease in PWF. The surface hydrophilicity of the membrane was increased by the addition of sZnO by decreasing the water contact angle from 79.33° to 56.33°. PSf membrane performance was significantly improved by incorporation of sZnO nanoparticles in which the permeate flux was increased from 9.0 to 14.5 $L.m^{-2}.h^{-1}$ and the rejection efficiency was also improved. PSf membrane with sZnO filler selectively rejects positively charged ions such as NH_4^+ up to 87%. This study suggests the application of PSf-sZnO composite membranes for cationic selective membranes. The results of the HAZOP study indicate that the potential hazard in the operation of membrane filtration is the formation of high pressure in the pipeline due to blockage and equipment corrosion which can cause equipment damage.

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