ISSN 2355-8776

Rubber Industry Wastewater Treatment using A Combination of Ozonation and Modified PES-Nano ZnO Membranes

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ARTICLE INFO

Article history
Received August 28, 2022
Revised January 26, 2023
Accepted January 29, 2023

Keywords
Membrane
Ozonation
Polyethersulfone (PES)
Rubber Industry
Wastewater

ABSTRACT

The application of the combination of biological, physical, and chemical methods to eliminate contaminants from the rubber industry wastewater has not been reported. This study aimed to analyze the use of membrane techniques and the effect of pre-treatment of industrial rubber wastewater and ozonation on the performance of the modified PES-nano ZnO membrane. Modified PES-nano ZnO membranes were made with phase inversion techniques and membrane performance based on flux and rejection. The cross-flow filtration systems was used and ozonation time variations were 1, 2, 3 hours. The ozonation process influenced membrane rejection. The membrane rejection value increased to 89.6%, and ammonia decreased to 4.3 mg/L. The flux value increased to 10.2 $L.M^{-2}.h^{-1}$ in 1 hour-ozonation and decreased with the increasing of filtration time. Pre-treatment with ozonation can increase membrane selectivity and extend membrane life during the filtration process due to reduced fouling. The pre-treatment process time of 3 hours-ozonation gave the highest membrane rejection even though the flux value has decreased.

1. Introduction

Rubber industry produces a large amount of wastewater from several stages of processing. The processing is coagulation, grinding, centrifugation, washing, and other mechanical manufacturing that will be disposed of in the environment [1]. The addition of chemicals during the process, like ammonia (latex preservation) and sulfuric acid (skim latex coagulation), can cause the formation of various contaminants in the waste. Wastewater will harm the environmental ecosystem and human health if it is directly discharged [2]. It has been reported that the total dissolved solids (TDS) were 2240 mg/L, total suspended solids (TSS) were 3.512 mg/L, ammonia 94 mg/L, BOD 1340 mg/L and COD 2834 mg/L. This value indicates that wastewater has high contamination and must be treated before being discharged into the environment [3].

Rubber industrial wastewater treatment techniques have been carried out in several industries, but still, have limited and low efficiency. In general, the treatment of rubber industry wastewater in the Southeast region is based on biological processes, for example, lagoon systems, oxidation trenches, anaerobic digestion, and activated sludge [2]. However, this process requires a large area and still leaves an odour. This process is suitable for wastewater with less polluted and may not function near residential areas. Another method is the anaerobic method and treatment of activated sludge because of the low operating costs and efficient processing of organic material [4]. However, this process requires considerable maintenance time.

The main problem in rubber wastewater treatment in the southeast region, including in Indonesia, is the inefficiency of the technology applied [1]. Biologically based technologies, including Up-Flow Anaerobic Sludge Blanket (UASB), activated sludge, oxidation trenches do not have sufficient ability to remove contaminants that contain Nitrogen. Biological methods are also inefficient, maintenance of microorganisms is uneasy, and microorganisms generally die due to the high organic content of the rubber industry wastewater. To date, the application of a combination of biological, physical, and chemical methods for removing rubber industry wastewater contaminants has been unreported. As a result, many advanced technologies are being investigated to achieve better elimination of contaminants like coagulation-flocculation, flotation, membranes, ozonation. Sulaiman et al. (2010) have carried out rubber wastewater treatment using membrane bioreactors (MBR) that can overcome the weaknesses of biological systems. This technology has been investigated for wastewater treatment of latex rubber processing. The results revealed the optimal method flux was achieved at 0.009 $m^3.M^{-2}.h^{-1}$ and COD elimination efficiency 96.99%, BOD 96.78%, NH_3 61.35% [5].

The membrane separation process offers various advantages such as its operation can be controlled, easy maintenance, and low demands for chemicals. However, despite its benefits, membranes have a limitation that is the decrease in flux caused by membrane impurities. This problem may be caused by the obstruction of organic and inorganic material in the pores of the membrane [6]. Then, the Advanced Oxidation Process (AOP) method shows great potential in various fields of wastewater treatment applications. The technique reduces organic contaminants, destroys specific pollutants, and reduces color and odor [7]. Ozonation, as one of the AOPs technologies, can break down non-biological natural substances that have large molecular weights into smaller organic materials. Also, the ozonation method can reduce oxygen-binding elements, eliminate odors, turbidity, increase dissolved oxygen and increase the reduction of suspended solids. Ozonation is deemed to be one of the most exciting methods for controlling the levels of organic contaminants in water. It can be used to remove inorganic species, as an aid to the coagulation-flocculation process. In a study conducted by [8], the effects of pre-ozonation can increase membrane rejection. Subsequently, it has been reported that adding ozone was able to reduce organic pollutants because it can endorse phenolic and humic. Therefore the focus of this research is the effect of ozonation for the pre-treatment of rubber industry wastewater in combination with modified ZnO-polyethersulfone membranes (PES) [9].

2. Research Methodology

2.1. Materials

In this study, Polyethersulfone (Veradel® PESU) from Solvay Advanced Material (USA) was used for membrane material, N-methyl-2-pyrrolidine (NMP) and Polyethylene glycol (PEG) 12000 $g.mol^{-1}$ from Merck (Germany), ZnO nanoparticles were bought from Nano Center Indonesia (Tangerang, Indonesia) with an average size of 341.7 nm. Additional and polyvinyl alcohol (PVA) was obtained from Brataco Chemica. The liquid waste rubber samples used were taken from Bengkulu PTPN VII waste pool with Characterization BOD of 85 mg/L, COD of 262 mg/L, TDS of 208 mg/L, Ammonia Total of 25.6 mg/L.

2.2. Procedures

1) Membrane Preparation

PES-nano ZnO dope solutions were first prepared by dispersing of nano ZnO 1.0 wt%, and PEG 5 wt% in NMP solvents. The solution was sonicated for 3 hours to avoid nanoparticle aggregation [10]. The solution was subsequently put into a 17 wt% PES dope solution and stirred 12 hours to obtain a sustainable and homogeneous solution. Next, the solution was left for 24 hours to remove the air bubbles trapped in the solution. Furthermore, the casting process used the dry-wet phase inversion technique. Subsequently, the solution was cast the dope solution on a glass plate, then directly exposed under UV light; the type C UV lamp used was a wavenumber of 254 nm and a power of 10 watts. The membranes were exposed under UV light for 2 minutes to modify the membrane surfaces.

An appropriate amount PVA polymer 3 wt% was dissolved in distilled water at 90 °C until it was homogeneous by stirring for 8 hours at constant mixing speed. After that, the PVA solution was used to coat the PES-nano ZnO membrane using the dip-coating technique [1] and dried at 60ºC [11]. The last thermal annealing modification used a temperature of 180 ºC for 0.5 minutes. After heating, a natural convection process cooled the membrane sheet at room temperature. The resulting ZnO PES-nano membrane was stored in the desiccator before it was tested for performance.

2) Membrane Performance

Pre-treatment process was carried out before the rubber industry wastewater is passed through the membrane. The first process of sewage pre-treatment was the addition of activated charcoal then continued with the ozonation process. The ozonation process was carried out with time variations of 1, 2, 3 hours. After that, the liquid waste is diverted to the flow process filtration tank to be passed to the membrane. Performance tests of the PES-nano ZnO membrane were carried out in a cross-flow filtration system with a pressure of 6 bar. Membranes with an active surface area of 12.57 cm^2 were placed on the filtration module. The valuation of water flux was conducted by measuring permeate every 30 minutes and the filtration process for 2.5 hours. The operation process scheme was displayed in Figure 1.

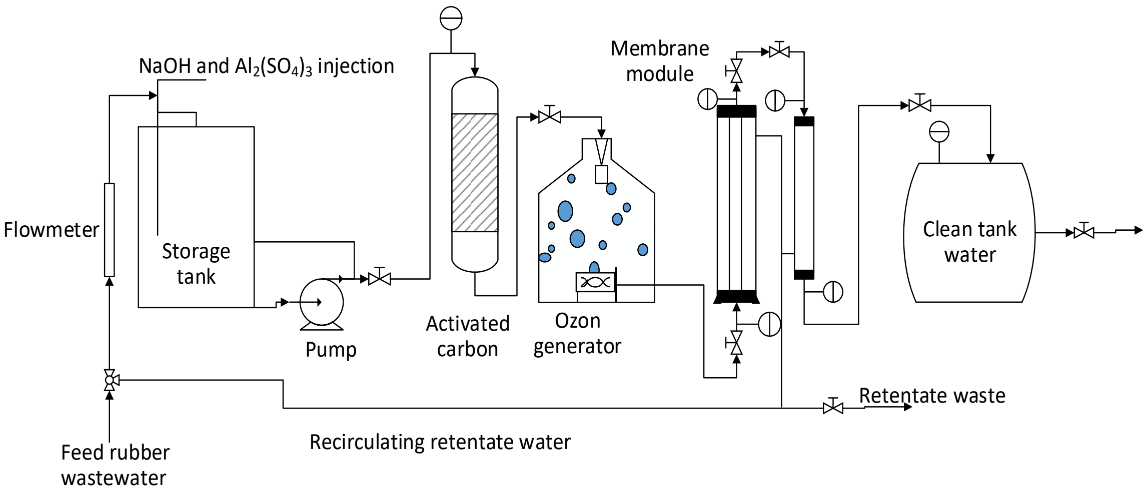

Fig. 1. Applied technology flow diagrams for rubber wastewater treatment

3. Results and Discussion

3.1. Characterization of the membrane

Membrane characterization will be related to membrane performance between porosity and water contact angle values. The modified PES-nano ZnO membrane porosity value was 76.25% reported by [12]. PEG additives are known as pore-forming agents in polymer membranes and increase permeation properties in polymer membranes. UV irradiation leads to degradation of the polymer chain for 2 minutes. As a result, the pores of the membrane are becoming more substantial, as reported by [13]. Modification with the addition of PEG additives and UV irradiation increases membrane permeability so that the flux value can increase. The concentration of PVA 3% decreases porosity value. This is because the presence of PVA additives on the membrane surface can make the membrane matrix undergo cross-linking. Significant concentrations of PVA additives results in thicker membrane surface layers [14]. Then, the presence of thermal annealing causes the solvent to evaporate from within the polymer, thereby increasing the adhesion of the membrane matrix bond [15]. Modification by adding PVA to the surface of the thermal annealing membrane can increase the selectivity of the membrane. Increased permeability is confirmed by the contact angle value which decreases to 29 ºC. This value states that the hydrophilic nature of the membrane increases. Therefore, it can increase the flux value of membrane. The hydrophilic membrane is equally related to the number of functional groups in the matrix PES-nano ZnO modified membrane. The results of FTIR characterization can be seen in Figure 2:

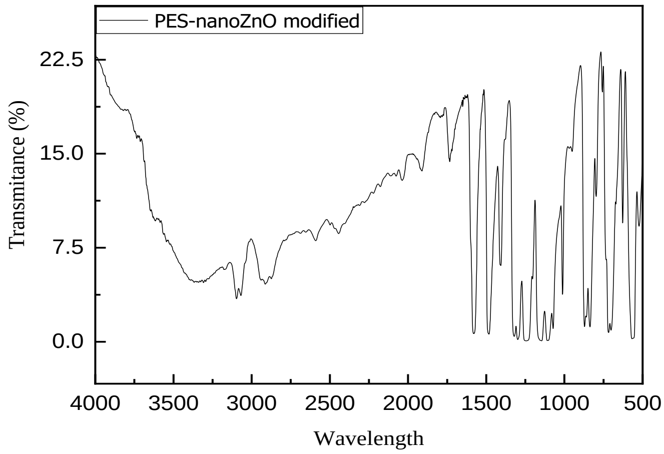

Fig. 2. The FT-IR spectrum of PES-nano ZnO membrane

Based on Figure 2, the spectrum of the sulfonate groups (Ar-SO_2-Ar) and ether groups (Ar-O-Ar) were shown by deep bonds in the 1130 cm^{-1} region and 1242 cm^{-1}. Then, absorbance were at 836 cm^{-1} and 871 cm^{-1} as stretching of aromatic C-H from PES. The absorption of 1298 cm^{-1} and 1320 cm^{-1} were the vibration of C=C by the PES molecule, which was a chain on the membrane matrix. Besides, peak changes in the wavelength region of 1733-1679 cm^{-1} occur because of the vibration of -C=O- aldehyde from PVA. Spectrum images also experienced changes in the area 2000-2500 cm^{-1} due to the wave of the hydrogen stretching on the carbonyl group to become radical. Radical sites found on the membrane surface will affect the membrane performance because it can increase the flux value.

SEM results of post-treatment of thermal annealing of the membrane PES-nano ZnO are shown in Figure 3A (membrane surface). Based on these results, the membrane had a durable surface and several pores that can be observed. There are some nano submerged in the pores of the membrane matrix and spread without agglomeration. The high-temperature thermal annealing process induces the growth of polymer core crystal chains [16]. As explained in Figure 3B. The method of crystal formation occurs because of the mobility of polymer chains [13]. This phenomenon indicates that thermal annealing has a significant effect on the structure of the layer becoming denser. This found will increase membrane reflection performance.

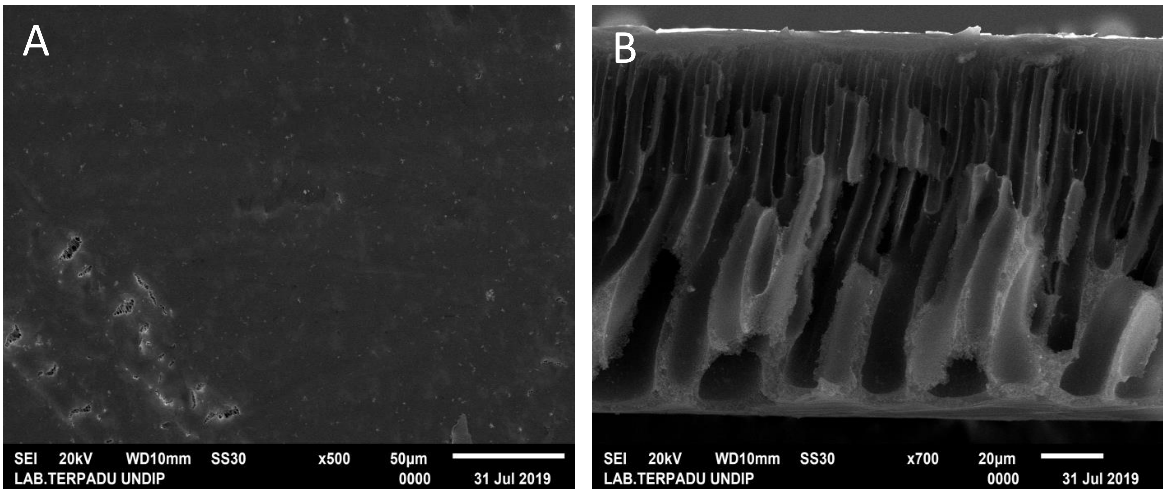

Fig. 3. SEM results of the PES-nano ZnO membrane

3.2. Effect of activated carbon

The process of activated carbon adsorption is the most efficient and promising fundamental approach to wastewater treatment [17]. Activated carbon is also used as a primary treatment, as an ensures of enabling other purifying processes and as a tertiary stage of waste purification. The effect of activated carbon on rubber industry wastewater can be seen in Table 1:

Table 1. The effect of activated carbon on contaminants of rubber industry wastewater

Parameter	Value (mg/L)	
	Wastewater	*Wastewater with Activated carbon*
TDS	250	195
COD	262.9	121
BOD	85	80
Ammonia	25.6	21.53

The concentration of contaminants in the rubber industry liquid waste decreased, especially in COD. COD concentration decreased to 121 mg/L, which was lower than without activated carbon, 262 mg/L, indicated that it can reduce 53.9% of contaminant. The value of other parameters were also decreased although not as significant as the TDS, which was initially 250 mg/L to 195 mg/L. Activated carbon can equally be used in water treatment to eliminate or control unpleasant flavors and odors.

3.3. Effects of ozonation

The ozonation process uses an ozone generator (model TSH-278) ozone output of 400 mg/hour. The effect of ozone can be seen in Figure 4:

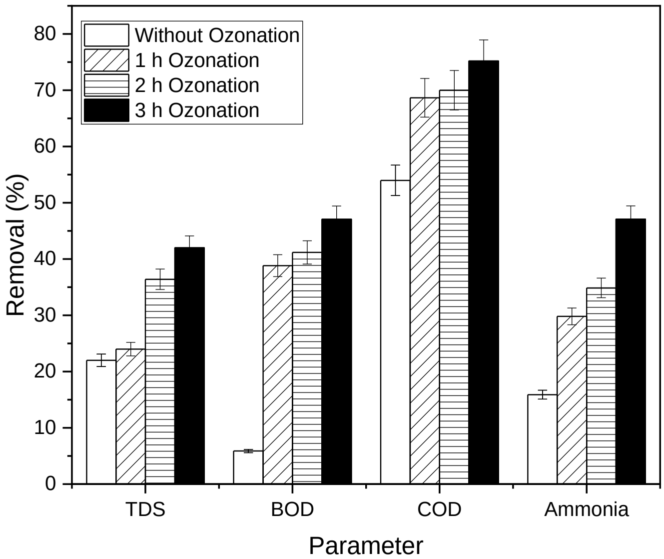

Fig. 4. Impact of ozonation time on waste parameters

Based on Figure 4, ozonation influences reducing contaminants in rubber liquid waste. Ozonation for 3 hours can reduce TDS contaminants up to 42%, BOD 47%, and COD 75%. This is because the ozone effect reacts with long-chain hydrocarbons that produce amphiphilic molecules. Ozonation is considered as one of the most promising processes for controlling the levels of organic contaminants in water. It can also be used to remove inorganic species, as an aid to the membrane filtration process. Pre-treatment with ozonation affects the removal of ammonia content from the rubber industry wastewater. Ammonia removal reached 47% higher than without ozonation, which was only 15.8%. It is related to the ability of ozonation to oxidize organic and inorganic compounds as reported by [18]. Formation of active species like OH•, H•, and H_2O_2 will merely increase with increasing contact time. The active species causes ammonia to be oxidized, thus its presence decreases to wastewater.

3.4. Effect of PES-nano ZnO Ozonation-membrane combination

PES-nano ZnO membrane performance evaluation was based on membrane permeability with flux and membrane selectivity was based on rejection values. The performance of the PES-nano ZnO membrane with ozone pre-treatment variations can be seen in Figure 5:

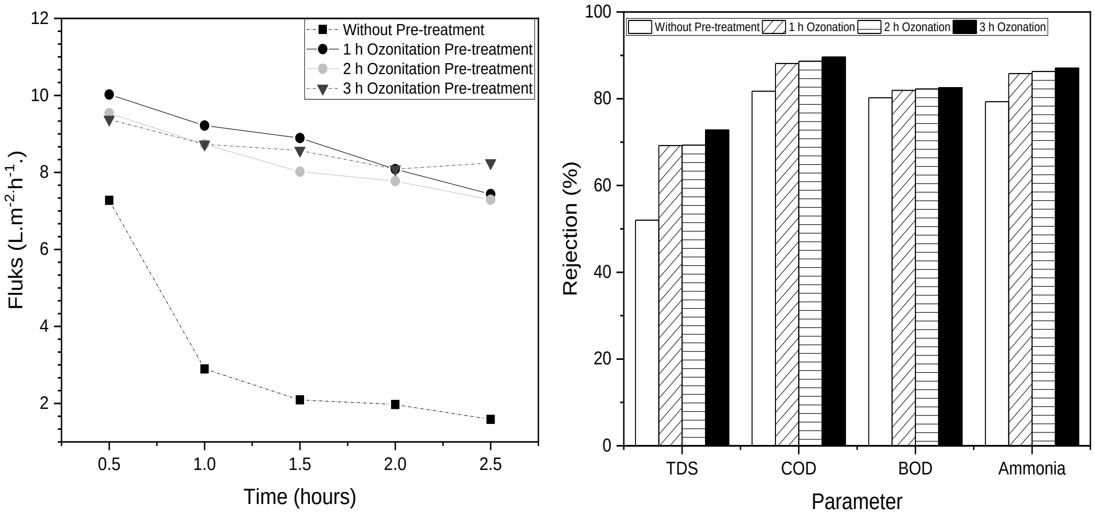

Fig. 5. PES-nano ZnO membrane performance: a). Flux b). Rejection

Based on Figure 5a, ozonation affected the flux value when filtration uses a PES-nano ZnO membrane. The amount of flux with pre-treatment 10.2 $L.M^{-2}.h^{-1}$ was higher than rubber liquid waste without pre-treatment, only 7.27 $L.M^{-2}.h^{-1}$. This phenomenon is related to the decomposition of pollutants present in wastes, especially organic compounds. Ozonation causes the degradation of organic matter, thereby reducing the molecular weight of compounds in water [19]. Flux values had stability during the activation process, up to 2.5 hours of filtration. This result confirms that the fouling occurs slowly on the surface of the membrane. Flux can be maintained at a constant level in the presence of ozonation pre-treatment [18]. It has been reported that ozonation reduced impurity of membrane pores and resistance of parallel polarization layers increased by the effect of ozone formation of the micelle [20]. It has been reported that ozonation of the water produced might also produce new compounds, such as acids, amines, and aldehydes, which affect membrane impurity levels during filtering [21]. This result causes the flux value to decrease with an increase in ozone time, as shown in Figure 5a. The speed of fouling destruction and fouling formation is managed under the same or balanced conditions.

The combination of ozonation and modified PES-nano ZnO membranes combination rejection value was higher than without ozonation (5b). Ammonia rejection value with ozonation pre-treatment reached 88% higher than the rejection value without ozonation, as well as the TDS, BOD, and COD values. In this case, the presence of ozone resulted in an increase in the concentration of radicals that are incredibly reactive on the membrane surface, which then decomposes organic foulant on the surface from superior molecular weight to reduced molecular weight. It has been reported that most organic compounds (approximately 35%) can be oxidized by ozone in water produced in smaller intermediate products, which are then decomposed into water-soluble CO and HO [22]. Therefore, the pretreatment ozonation affects the performance of the membrane, which can increase the value of flux and rejection. Low contaminants in liquid rubber waste can increase membrane life and avoid fouling. This phenomenon causes the BOD and COD rejection values to increase, and the concentration decreases, as shown in Table 2:

Table 2. The concentration of rubber liquid waste with various treatments

Parameter	Value (mg/L)								
	Standard Limits	Rubber wastewater (feed)	Ozonation			Membrane	Ozone - PES-nano ZnO membrane		
			1 h	***2 h***	***3 h***		***1 h***	***2 h***	***3 h***
TDS	100	250	190	159	145	110	77	76.7	68
BOD	60	85	52	50	45	15.8	15.36	15.08	14.84
COD	200	262.91	82.41	78.87	65.2	32.8	31.24	29.83	27.30
Ammonia	5	25.61	17.97	16.68	13.55	4.64	3.6	3.51	3.3

Based on Table 2, pre-treatment with ozone had a relatively high impact on the removal of rubber liquid waste contaminants. COD decreased to 65.2 mg/L with ozone for 3 hours, and the same thing also happened in TDS, BOD, and ammonia. According to The Regulation of Ministry of Environment No 5 2014, the standard limit of concentration (mg/L) for BOD, COD, TSS, and ammonia were 60, 200, 100, and 5 mg/L respectively. Therefore, the results for each parameters have met the standard limit of concentration for environment protection. This phenomenon is because the use of ozone will introduce oxygen atoms into the pollutants. Small molecules are designed to contain a higher percentage of oxygen in the chemical structure and to form groups of hydroxyl, carbonyl, and aldehyde that function for biodegradation [23]. After pre-treatment and filtration, the COD concentration decreased to 27.3 mg/L using the modified PES-nano ZnO membrane. This value indicates that the amount of organic compounds decreased when the water produced is subjected to ultrafiltration combined with ozone before or after treatment [21]. Other concentrations of contaminants also decreased with the combination of ozone/PES. This value was lower than the standard amount for rubber liquid waste. Therefore, it can be said that the permeate produced is quite safe.

4. Conclusion

The combination of ozonation and modified PES-nano ZnO membranes imparts a beneficial synergistic effect during the filtration process. Ozonation pre-treatment increased the flux value to 10.2 $L.M^{-2}.h^{-1}$ and increased the rejection value, especially ammonia, to reach 88%. This phenomenon is outstanding to the pre-treatment with ozonation, which causes the degradation of organic material, which in turn reduces the molecular weight of compounds in water. Ozonation of organics can also produce oxygenated functional groups that can be combined with ammonia, thus they can dissolve in water and reduce the concentration of ammonia. Pre-treatment ozone affects the performance of the membrane, which can increase the value of flux and rejection. Low contaminants in liquid rubber waste can increase membrane life and prevent fouling.

Acknowledgment

Authors thank Prof Tutuk D. Kusworo for all his help in this research and to all parties involved in this article.

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