

Application of Membran Polyvinylidene fluoride (PVDF) Synthesis Blending TiO_2 -Serbuk Kelor (Moringa Oleifera) Seed on Coal Wastewater Treatment

Marhaini*, Legiso, Neny Rochyani

Department of Chemical Engineering, University Muhammadiyah Palembang, Palembang, Indonesia

Email address:

marhainiump@gmail.com (Marhaini), legiso_poniman@yahoo.com (Legiso), nenyrochyani@yahoo.com (N. Rochyani)

*Corresponding author

To cite this article:

Marhaini, Legiso, Neny Rochyani. Application of Membran Polyvinylidene fluoride (PVDF) Synthesis Blending TiO_2 -Serbuk Kelor (Moringa Oleifera) Seed on Coal Wastewater Treatment. *International Journal of Environmental Chemistry*.

Vol. 3, No. 1, 2019, pp. 1-6. doi: 10.11648/j.ijec.20190301.11

Received: December 10, 2018; **Accepted:** December 25, 2018; **Published:** January 24, 2018

Abstract: Membrane technology is the right choice with its ability as a highly selective separation process to produce high quality products. The technology research applied based on chemical technology of Advanced Oxidation Process (AOP), a technology of coal wastewater treatment using strong oxidizing agents with photocatalysts TiO_2 and moringa seed powder (Moringa oleifera). The research methodology used was preparation of Moringa seeds, synthesis of composite photocatalyst TiO_2 -Moringa seed powder and manufacture of membrane Polyvinylidene fluoride (PVDF)-Moringa seed powder with a total of 4 membranes (A, B, C, D). The results of the study produced membrane characteristics with a pore size of 0,1 μm - 6 μm , wet weight of 20% and an average tensile test value of 4.53 N/mm². Application of membrane PVDF-synthesis TiO_2 -Moringa seed powder (Moringa oleifera) in coal wastewater treatment resulted in a decrease of 89% in Fe and Mn pollutants in the composition of 5% TiO_2 and 5% Moringa seed powder in Membrane B.

Keywords: Coal Wastewater, Membrane PVDF, Moringa Oleifera, Synthesis TiO_2

1. Introduction

The technology applied is chemical-based technology called Advanced Oxidation Process (AOP) that is wastewater treatment technology using strong oxidizing agent through TiO_2 photocatalyst. This advanced oxidation process can be used as an alternative of coal wastewater treatment that is quite economical [1]. Commercially, TiO_2 powder is easy to obtain and produced in large quantity [2]. Moreover, TiO_2 is a semiconductor that has high melting point, photoactivity, thermal and chemical stability, has nontoxic property, and one of the best catalysts to be applied in the environment since it is biologically and chemically inert and has relatively cheap price [3-7]. Based on those properties, TiO_2 is the most effective photocatalyst to be used as one of semiconductor materials, and has been widely researched, mainly in the processing of solar energy source and hazardous waste treatment [8] as well as medical waste treatment from hospital [9]. TiO_2 photocatalyst is highly efficient in reducing

the concentration of heavy metals of Fe, Cr and Pb in wastewater by 96-98% and TiO_2 photocatalyst through the sunlight shows higher result in degrading dye waste compared to commercial TiO_2 [10].

Filtration performance of UF micro wettability membrane is particularly on the effect of porous structure [11] and surface property [12-15]. Several studies conducted included the use of UF membrane for the treatment of liquid waste, oil [6, 27]. This membrane is made of polymer materials like Cellulose Acetate (CA) and polysulfone (PSF) combined with organic matters such as Alumina and Titanium dioxide. Technology of polyvinylidene fluoride (PVDF) membrane is one of the best membranes to be applied in UF systems since the activity of PVDF membrane has antioxidant, high durability both in term of chemical and thermal stability, highly organic selectivity, and has good mechanical and membrane formation properties [16-20]. However, the

disadvantage of this PVDF membrane includes its membrane surface that has a tendency to be hydrophobic, thus filtration process that involves hydrophilic solution is lower than it should be [21]. To obtain membrane with excellent performance in the treatment of waste in which its biggest component is water, modification of membrane surface and internal pore is performed through the blending technic using moringa seed powder synthesized by using TiO₂. Based on the exploration study result on natural coagulant material from plants and its effect on Coli bacteria count, moringa (*Moringa oleifera*) seed was found to reduce Coli bacteria by 28% [22]. The use of moringa (*Moringa oleifera*) seed as biocoagulant showed that moringa (*Moringa oleifera*) seed was able to reduce turbidity, heavy metal concentration in coal mining wastewater [23]. Moringa (*Moringa oleifera*) seed powder also has effectivity of 99.529% to decrease Fe ion concentration and 99.355% for Mn, also 99.868% of turbidity in the water [15, 23]. The advantage of moringa (*Moringa oleifera*) seed includes its active compound of *rhamnosyloxy-benzil-isothiocyanate* which is able to adopt and neutralize particles of sludge and metals contained in wastewater. It is also easy to cultivate in the environment surrounding ex-coal mining industry since moringa plant (*Moringa oleifera*) is classified as plant that lives in area at altitude ranges from coastal area to highland.

2. Research Materials and Methods

Materials: Titanium Tetra Isopropoxide (TTIP), Polyvinylidene fluoride (PVDF), N-Methyl-2-Pyrrolidone (NMP), NH₄Cl, aquadest and acetic acid, moringa seed (*Moringa oleifera*), and coal mining wastewater. Preparation of Moringa Seed. Sample in the form of old moringa seeds (*Moringa oleifera*) were dried at temperature of 105°C for 24

hours, and further weighed for 1 kg. Later, dry moringa seeds were grinded to powder using mortar, sieved using a sieve of 100 nm. Moringa seed powder at size of 100 nm was added with acetic acid 10% at ratio of 1:2 (b/v) and stirred using magnetic stirrer for 5 hours at room temperature, resulted in solution of moringa seed powder. The solution was further filtered to remove the remaining undissolved particles. Synthesis of TiO₂ Composite Photocatalyst-Moringa (*Moringa oleifera*) Seed Powder. The solution of moringa seed powder was added with sol Titanium Tetra Isopropoxide (TTIP) of each composition, slowly stirred using stirrer for 24 hours at room temperature to form suspension of nanoparticle. The suspension was sonicated for 30 minutes and evaporated to remove the water. Calcination was further performed at temperature of 500°C for 2 hours. Production of Polyvinylidene fluoride (PVDF) Membrane – Moringa (*Moringa oleifera*) Seed Powder. PVDF was dissolved in N-methyl-2-pyrrolidone (NMP) and further added with additive NH₄Cl, blended with TiO₂ synthesis-moringa seed powder at ratio of 15/0/85/0(A); 13/1/85/1(B); 11/2/85/2(C); 9/3/85/3(D) % (b/b/b/b). The mix of membrane materials was stirred using magnetic stirrer to homogeneous at temperature of 40°C for 15 minutes. The solution was molded using petri dish and further dipped into coagulation tank contained mix of aquadest. Activity test of composite TiO₂- PVDF membrane Moringa seed powder showed in (Fig. 1). Two liters of wastewater was added TiO₂ photocatalyst at ratio 10:0, 10:1, 10:1.5, 10:2 and 10:2.5. It was put into reactor and stirred for 2 hours at 60 rpm. Radiation under the sun for 2 hours in between 9 a.m until 1 p.m. The mix of solution then flowed into the tube filled with PVDF membrane – TiO₂ synthesis of Moringa seed powder. Later, it was analyzed of water quality such as pH, Zn, Cu, Fe, Mn, Hg, Co, Ni and Cr

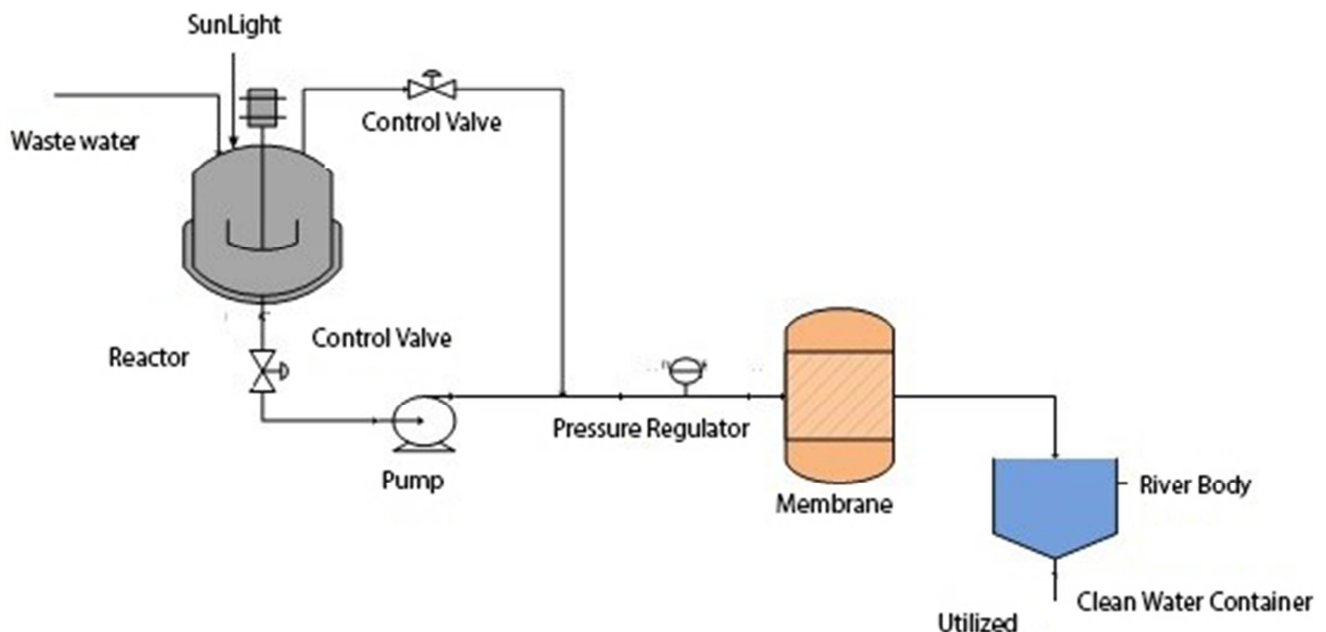


Figure 1. Flow Chart Scheme of Tools Used in Coal Mining Wastewater Treatment.

3. Research Results and Discussion

3.1. Environmental Scanning Electron Microscope (ESEM)

Morphology of SEM image on PVDF membrane– deris presented in (Figure. 2). Result showed that the membrane had a typical asymmetrical structure with outer solid skin layer, perfect pores on membrane surface with support layer in the form of more open micropore. According to [24-26] the size of membrane surfac pore decreases along with the increasing molecular mass of PVDF.

SEM cross section morphology on membrane PVDF-synthesis TiO_2 -moringa seed powder (*Moringa oleifera*) is shown in Figure 2. The results show that the membrane has a typical asymmetrical structure with a dense outer skin layer, has a perfect pore on the membrane surface with supporting layer of more open micropore. According to (Cardoso et al, 2015; Hassankiadeh et al, 2014; Matsuyana et al, 2002), the pore size of the membrane surface decreases with increasing molecular weight of PVDF.

From the results of Scanning Electron Miscroscopy (SEM) with a 1000x magnification, it can be seen that the pore size of each sample is different. Based on the images obtained from Scanning Electron Miscroscopy (SEM), the membrane pore size can be seen as follows:

a). Membrane A with a ratio of 66,67% NMP and 33,3% PVDF had a pore size between 0,1 μm - 2 μm .

b). Membrane E with a ratio of 66,67% NMP ; PVDF 16,67%; 13,3% Moringa Seed Powder; 3,3% TiO_2 had a pore size between 0,8 μm - 4 μm .

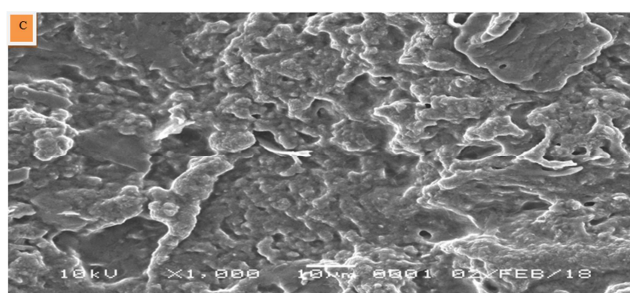
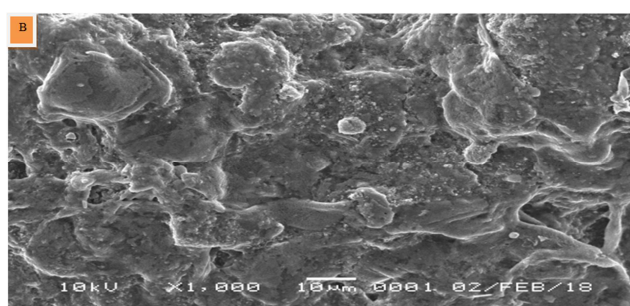
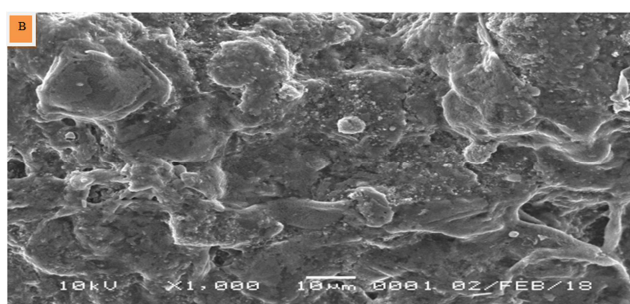
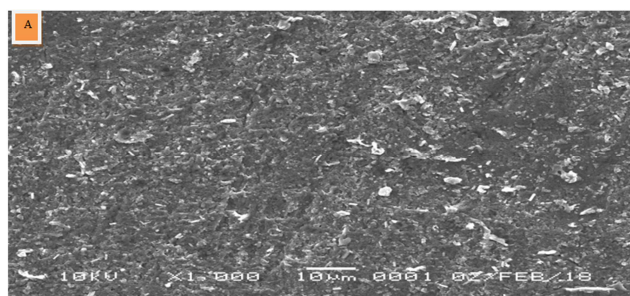
v). Membrane F with a ratio of 66,67% NMP; 16,67% PVDF; 10% Moringa Seed Powder; 6,67% TiO_2 had a pore size between 1 μm - 6 μm .

d). Membrane G with a ratio of 66,67% NMP; 26,67% PVDF; 3,3% Moringa Seed Powder; 3,3% TiO_2 had a pore size between 0,3 μm - 3 μm .

From the SEM results, the best membrane composition is in the composition of Membrane A. According to the picture result obtained from Membrane A, it is known that the membrane has an asymmetrical structure. Membrane with asymmetric structure will have better performance than membrane with symmetry structure. Judging from the pore size, the resulting membrane can be categorized as a microfiltration membrane, because it has a pore with a size between 0,1 μm - 6 μm . Microfiltration membranes are membranes with asymmetrical structures, which are made with the Loeb-Sourirajan process and have a perfect pore on the membrane surface with supporting layer of more open micropore. Perfect pores on the surface show a separation process, while supporting micropores provide mechanical strength (Baker, 2004).

Referring to the results of the tensile test in Figure 2. Membrane A had a large tensile strength reaching 5,33 N/mm^2 , strain of 0,60% and maximum load of 160 N. But on the contrary, if the composition of PVDF was less than tensile strength and strain abilities possessed by the membrane would decrease, and cause the particles

arrangement to be scattered in the print medium becoming uneven and had an unfavorable density. This can be seen in Membrane E with a ratio of 66,67% NMP; PVDF 16,67%; 13,3% Moringa Seed Powder; 3,3% TiO_2 with tensile strength ability only reached 4,27 N/mm^2 , strain of 0,37% and maximum load of 139 N. Significant differences in the strain magnitude can be influenced by composition, area, and magnitude of force or pressure given when a tensile test is carried out. The magnitude of the strain on the membrane shows the elasticity ability of the membrane when given the force during tensile test. Thus, the membrane produced in this study has a relatively small strain. Water uptake test results of membrane PVDF-Moringa Oleifera seed powder with the synthesis TiO_2 in each membrane by 20% for each membrane, indicating that the membrane has a good ability to absorb water (experiencing swelling).



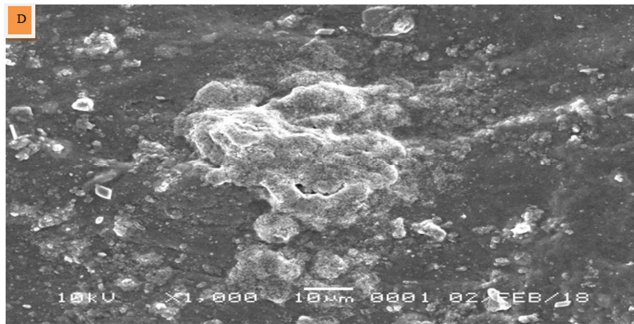


Figure 2. SEM Test Result of PVDF Membrane-TiO₂ Synthesis-Moringa (*Moringa oleifera*) Seed Powder.

However, in this study, as seen from the composition of PVDF- TiO₂ synthesis-Moringa (*Moringa oleifera*) seed powder and the result of water uptake (W_{wet}) test with average of 20%, there was no effect on membrane, both with and without TiO₂ synthesis-moringa seed powder. It indicates that membrane has excellent ability to absorb water [29]. Moreover, the result of membrane tensile test, namely the strength of membrane against external force which may result in membrane damage and how long the membrane strength remain undamaged after being used, which reached an average of 4.53 N/mm², strain of 0.60%, and maximum load of 160 N showed that PVDF membrane-TiO₂ synthesis-moringa (*Moringa oleifera*) seed powder was extremely strong.

3.2. The Use of PVDF Membrane TiO₂ Synthesis-Moringa (*Moringa oleifera*) Seed Powder on Coal Wastewater

As photocatalyst in wastewater treatment, TiO₂, due to its ability in the process of electron-hole generation on its surface, will react to hydrosol ion and oxide in organic compound (pollutant) and change both into O₂ and H₂ [37]. This method was selected as effective method since it

required less time to degrade pollutant, low risk of ne toxicant produced and abundant availability of materials. In this study, application of moringa (*Moringa oleifera*) seed powder synthesized using TiO₂ as *blending* of PVDF membrane, as wastewater treatment from coal mining, is shown in (Table 1)

The use of PVDF membrane-TiO₂ synthesis-moringa seed powder in coal wastewater treatment resulted in a decrease along with the effect of TiO₂ concentration within the membrane, in which the highest decline was found in concentration of TiO₂ 5 % and moringa seed powder 5%, namely in membrane D, while in membrane A that was without TiO₂ synthesis-moringa seed powder, the degradation of coal wastewater water quality was higher compared to that in membrane B, C and D. It is due to the effect of TiO₂ synthesis on moringa seed powder. Decline in membrane structure symmetry increase with low molecular mass was also possible, which further decreased the pore size, thus resulted in decreasing adsorption on pollutant [24-25]. Different from the study conducted by Marhaini *et al.*, 2018, coal wastewater treatment using TiO₂ synthesis-moringa seed powder with effect of stirring period of 250 minutes, was able to degrade coal wastewater up to 88%. Similar researches were conducted by [15, 28-29], while others only observed a slight increase [31-34] referred to reviews of polymer composite membrane/TiO₂ in some literatures (F: flatsheet membrane and H: porous membrane), yet several findings were opposed to the study result observed. However, membrane is used as binding agent of TiO₂ to form covalent bound between nanoparticle and membrane, hence removal of catalyst nanoparticle and its high durability against degradation activity of UV can be observed [19, 25] as well as to increase the permeability and membrane flux at concentration of 25% wt TiO₂ with permeability higher than 150 L h⁻¹/m² [35].

Table 1. Analysis Result of Membrane Application on Coal Wastewater.

Parameter	Initial Analysis (ppm)	Membrane A (ppm)	Membrane B (ppm)	Membrane C (ppm)	Membrane D (ppm)
pH	2.6	4.5	4.7	5.1	5.5
Zn	0.94	0.29	0.38	0.35	0.34
Cu	0.07	0.07	0.07	0.07	0.07
Fe	18.3	1.75	2.40	2.32	2.01
Mn	6.59	0.33	0.31	0.30	0.29
Hg	0.001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Co	0.11	0.09	0.10	0.10	0.10
Ni	0.31	0.18	0.32	0.23	0.16
Cr	0.72	0.42	0.51	0.43	0.36

3.3. Effect of Sunlight on Coal Wastewater Using PVDF Membrane-Synthesis of Moringa (*Moringa Oleifera*) Seed

Test on the effect of TiO₂ concentration on membrane with sunlight irradiation showed that higher TiO₂ concentration will foster the declining concentration of coal wastewater. The decreasing quality of coal wastewater caused by photon energy being absorbed by photocatalyst is shown in (Table 2).

Table 2. Analysis result of coal wastewater using pvdF membrane-TiO₂ synthesis-moringa (*Moringa oleifera*) seed powder with sunlight.

Parameter	Initial Analysis (ppm)	Membrane A (ppm)	Membrane B (ppm)	Membrane C (ppm)	Membrane D (ppm)
pH	2.6	5	5.5	5.5	6
Zn	0.94	0.23	0.39	0.37	0.33
Cu	0.07	0.07	0.07	0.07	0.07

Parameter	Initial Analysis (ppm)	Membrane A (ppm)	Membrane B (ppm)	Membrane C (ppm)	Membrane D (ppm)
Fe	18.3	2.73	2.83	2.51	2.39
Mn	6.59	0.31	0.37	0.32	0.31
Hg	0.001	< 0.0001	< 0.0001	< 0.0001	< 0.001
Co	0.11	0.10	0.10	0.10	0.08
Ni	0.31	0.15	0.27	0.18	0.15
Cr	0.72	0.32	0.57	0.39	0.31

As seen in Table 2. higher concentration of TiO₂ on membrane resulted in higher photo degradation of wastewater. Therefore, there are more sunlight irradiation which radiates TiO₂, and led to more hole to further react to wastewater to form *OH radical. As presented in Table 2, result of wastewater degradation using PVDF membrane-moringa seed powder was not as high as the result of study performed by [36] about the effect of wastewater quality through TiO₂ synthesis-moringa seed powder with sunlight, in which coal wastewater quality degradation with stirring period of 200 minutes resulted in negative value of wastewater pollutant at concentration of Fe 15 ppm. It was due to the effect of TiO₂ synthesis on moringa seed powder, there was possibility that increase in structural symmetry of membrane with low molecular mass may decline the size of pore, reducing adsorption on pollutant [24-25].

4. Conclusion

Synthesis of TiO₂-moringa (*Moringa oleifera*) seed powder can be used as *blending* in PVDF membrane with result of having typical asymmetrical structure with outer solid skin layer, perfect pores at size of 0.1 µm – 6 µm on membrane surface with support layer in the form of more open micropore. Membrane characteristics included Wwet of 20% and average tensile test value of 4.53 N/mm², strain of 0.60%, and maximum load of 160 N. The use of PVDF membrane- TiO₂ synthesis-moringa (*Moringa oleifera*) seed powder on the quality of coal wastewater did not have significant effect compared to PVDF membrane without TiO₂ synthesis-moringa (*Moringa oleifera*) seed powder, due to the effect of molecular mass of PVDF compound, moringa seed, and TiO₂.

Acknowledgements

A big thank you to the honorable people, to the Ministry of Research, Technology and Higher Education of the Republic of Indonesia for the funds given for this research activity

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