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Textile Wastewater Treatment Using Polypyrrole/Polyphenol Oxidase Membranes

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Article Info Abstract Article history: Polypyrrole (PPy) is widely regarded as a useful electrode material because it has the advantages of low cost, high electrical conductivity, and thermal stability. Received: 24th November 2023 This study aimed to synthesize PPy membranes using polyphenol oxidase (PPO) Revised: 07th March 2024 isolated from white oyster mushrooms as a biocatalyst for processing textile Accepted: 15th March 2024 wastewater. The membranes were produced through the electropolymerization of Online: 20th March 2024 pyrrole (Py) using the electrodeposition method. The raw materials comprised Keywords: 0.05 M Py and crude PPO white oyster mushroom extract at 35% v/v in citrate Membrane; PPy; PPO; Textile; buffer pH = 6.8. The electrolysis process was performed at 6.00 V and 1.063-Wastewater 1.142 A using 16.57-48.97% immobilized PPO in PPy, PPO activity of 1.640-4.160 U, and 0.35 mM phenol as a substrate. The results showed that the use of the membrane in textile wastewater with a discontinuous flow caused a decrease of pH by 14.86%, phenol by 6.80%, Chemical Oxygen Demand (COD) by 81.30%, Biological Oxygen Demand (BOD) by 78.25%, and Total Suspended Solids (TSS) by 20.65%. Meanwhile, using the sample with a continuous flow caused a decrease of pH by 23.97%, phenol by 26.09%, COD by 88.50%, BOD by 78.00%, and TSS by 65.70%. The physical performance of membrane application to textile wastewater with discontinuous (flow rate = 48.19-51.50 L/h, flux = 3191.6-3387.5 $L.m^{-2}.h^{-1}$, and permeability = 319.2-338.7 $Lm^{-2}.h^{-1}.bar$) and continuous flow (flow rate = 48.19 L/h, flux = 3191.6 Lm^{-2} .h⁻¹, and permeability = 319.2 Lm^{-2} .h⁻¹.bar) was also assessed in this study. The Scanning Electron Microscopy (SEM) image was used to assess the morphology of the membrane before and after its application.

1. Introduction

The textile industry is an essential sector due to the versatile application of its products for various purposes. Several studies have reported the importance of electrochemical methods in both textile processes and wastewater treatment of synthetic dyes as hazardous materials. Electrochemical reduction reactions are also widely used in sulfur and vat dyeing, while oxidation processes are extensively applied to eliminate color from textile dyestuffs. Furthermore, the reuse of the discolored solution can lead to significant water and salt savings, reaching up to 70% and 60%, respectively [1]. As the

generation of hazardous dye wastewater increases across various industries, it poses a significant threat to public health and the environment, creating a major challenge for existing water treatment facilities [2]. The diverse associated processes contribute to pollutants, prompting the development of various wastewater treatment technologies [3, 4].

In recent years, membrane technology has attracted significant interest from various industries and research institutions, driven by the increasing need for versatile and cost-effective separation processes in biotechnology, water desalination, and wastewater treatment [5].



Membrane technologies, classified as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis based on molecular weight, offer versatile applications [6]. The membrane bioreactor has emerged as a simple, reliable, and cost-effective method with significant contaminant removal abilities for textile wastewater treatment. However, a significant drawback is fouling, leading to reduced permeate flux and necessitating cleaning, which decreases the lifespan of the material [7]. Although physicochemical methods, such as coagulationflocculation, absorption, and the advanced oxidation process, effectively handle micropollutants, these methods are often used when biological methods become less optimal. Biological treatment methods, including activated sludge, constructed wetlands, and membrane bioreactors, are known to be cost-effective and environmentally friendly [8].

Oxidative enzymes from bacteria, fungi, and plants are essential in various waste treatment applications. Peroxidase and PPO can act on certain stubborn pollutants by precipitating or converting them into more manageable forms [9]. Mushroom-derived PPOs are favored in studies due to their commercial availability, cost-effectiveness, and easy obtainability, leading to a wide range of clinical and industrial interests. Furthermore, enzyme immobilization is an essential aspect of biotechnology, and recent trends suggest its feasibility in industry for cost reduction through enzyme reuse [10]. Polypyrrole nanotubes (PPy-NTs) serve as an effective immobilization matrix for PPO on the electrode surface, using glutaraldehyde as a crosslinker in biosensor applications. This method provides efficient entrapment of the enzyme in the polymer film and reflects long-term stability [11]. PPO can be immobilized a matrix, such as PPO immobilized in in chitosan/montmorillonite (CTS/MMT, IPPO) and chitosan-gold nano-particles/montmorillonite (CTS-AuNPs/MMT, IPPO-Au) with the highest enzyme activity at 15.61 × 10³ and 29.01 × 10³ U/g, respectively [12].

In a previous study, PPO immobilized on chitosan/organic rectorite (CTS/OREC) by physical adsorption (APPO) had the highest activity and covalent binding of 16.37×10^3 U/g and 8.92×10^3 U/g, respectively, based on Taguchi method [13]. PPO activity in the poly(ethyleneoxide)/polypyrrole (PEO/PPy) matrix has been achieved at 65% for 20 days and constant 75% until 40 days. The amount of protein trapped in PPy was 2.9 \times 10⁻³ mg. The composition of the solution consists of 0.2 mg/mL PPO, 2 mg/mL PEO, 1.2 mg/mL sodium dodecyl sulfate (SDS) as a supporting electrolyte, 0.01 M pyrrole, and 10 mL citrate buffer pH = 6.5 [14]. PPy, as a conducting polymer, is widely used for various applications due to its thermal stability [15]. This material is also widely used as a membrane composite for industrial wastewater application purposes.

A new conception/strategy of in situ electroflotation driven by hydrogen evolution reaction (HER) combined with a PPy-modified fabric membrane was proposed for efficient oil/water separation [16]. Conducting polymers, such as polyaniline and PPy, are efficient materials for removing organic dyes from the environment due to their low production cost. These materials have also been reported to be able to remove noble metal ions, heavy metal cations, and various anions from aqueous media. The electrical properties, such as conductivity and redox electroactivity, are expected to be used to control the adsorption/desorption phenomena [17].

Organic dyes, which are widely used in dyeing processes across various industries, have similar features to conducting polymers. The coloration of these materials can be attributed to the presence of conjugated double bonds in the molecular structure and consequent selective absorption of light in the visible spectrum [18]. Organic dyes are also widely used in leather, textile, paper, plastic, and pharmaceutical industries. A previous study explored the synthesis of adsorbent poly(pyrrole methane) (PPm) with abundant -OH using facile and effective polymerization methods for the removal of anionic and cationic dyes [19].

In this study, a PPy membrane with PPO active ingredients from white oyster mushrooms was synthesized and used as a membrane filtration for phenol removal and textile wastewater parameters reduction (COD, BOD, and TSS). Phenolic compounds are designated as major pollutants by the US EPA due to their unpleasant taste and biological toxicity, even at low concentrations [12]. Our previous research has studied PPy membranes immobilizing PPO from apple fruit for the degradation of phenol-polluted wastewater [20]. Therefore, this study aimed to determine the performance of a PPO-based membrane as a catalyst in the degradation process of phenolic compounds and their derivatives. The material produced is expected to reduce the quality standard parameters of textile wastewater (pH, BOD, COD, and TSS). The performance of the membrane was assessed based on retention, flux, permeability, and thickness [21].

2. Experimental

2.1. Chemical, Laboratory Apparatus, and Instrumentations

White oyster mushrooms were obtained from a local supermarket in Cimahi (West Java–Indonesia). Furthermore, the isolation of crude PPO extract from white oyster mushrooms could be seen in the previous procedure [22]. All chemicals used were of analytical grade quality and were obtained from Sigma–Aldrich, including phenol (C_6H_5OH) as a substrate, citric acid ($C_6H_8O_7$), and sodium citrate ($C_6H_5O_7Na_3.2H_2O$). A textile wastewater sample was obtained at the inlet of the wastewater treatment plant in the textile industry.

2.2. Laboratory Apparatus and Instrumentations

One unit of electrolysis cell was used in this study, consisting of a 1000 mL container cell, steel gauze with type ST-304 (surface area = 8.00×8.00 cm) as an anode, platinum (Pt) (surface area = 8.00×8.00 cm²) as the cathode, and a set of cables. Furthermore, the electrolysis unit was connected with a DC-power supply Atten APS-3005-DM30V/5A. Spectrophotometer UV-Vis double beam UV-3101PC Shimadzu. Scanning Electron Microscope, SEM Jeol JSM-6510 LA.

2.3. Preparation of the Membrane of PPy/PPO White Oyster Mushroom Extract

The electrolyte solution used had a composition of 0.05 M pyridine and 35% (v/v) crude Pleurotus ostreatus (white oyster mushroom) extract in a citrate buffer solution at pH 6.8. Furthermore, one electrolysis cell with a container volume of 1000 mL, 400 mesh of steel gauze as the anode $(8.00 \times 8.00 \text{ cm})$, and a Pt electrode were connected to the DC power supply [23]. The membrane used in this study was produced using electrodeposition (potential = 6.00 V, the distance between the two electrodes = 4.00 cm, and the electrolysis time = 900 s). The experiment was repeated three times for three membranes (mPPy/PPO-A, mPPy/PPO-B, and mPPy/ PPO-C). The immobilized PPO activity was then determined spectrophotometrically with PPO λ_{max} = 269.6 nm and phenol (0.50, 1.50, 2.50, 3.50, and 4.50 mM) as substrates.

2.4. Textile Wastewater Treatment Using the Membrane of PPy/PPO White Oyster Mushroom Extract

The removal of phenol and other waste parameters (COD, BOD, and TSS) was carried out with a filtration process using a membrane of PPy/PPO white oyster mushroom extract. The three membranes stored in the housing variant had a dead-end design. Furthermore, the design of the filtration unit consisted of the feed phase container, pump, manometer, membrane housing, and permeate container. The filtration process in this study was carried out with continuous (five repetitions) and discontinuous flow (five times). The solution from the process was stored in a permeate solution container, followed by testing the conversion of phenol to quinone, COD, BOD, and TSS [24].

2.5. Detection Method

The immobilized PPO activity in the membrane was determined spectrophotometrically using PPO λ_{max} = 269.6 nm and phenol (0.50, 1.50, 2.50, 3.50, and 4.50 mM) as substrates. The enzyme activity was calculated using methods proposed in a previous study [22, 25]. The membranes of PPy/PPO white oyster mushroom extract were observed before and after applying textile wastewater, followed by SEM characterization. The membrane parameters were assessed based on retention, flux, and permeability.

3. Results and Discussion

3.1. Characterization of PPy/PPO White Oyster Mushroom Extract by SEM

The initial pore size of the membrane film of PPy/PPO white oyster mushroom extract based on the surface morphology before it was applied to textile wastewater samples was $0.668 \pm 0.362 \mu$ m, as shown in Figure 1a, but increased to $2.106 \pm 0.631 \mu$ m after application (Figure 1b). Therefore, after using the PPy/PPO membrane on textile wastewater, the effect on the pore size increased by approximately 1.438 µm. The parameter became relatively smaller because the surface

of the sample had been used during the filtration process, and there was a cake build-up on the surface.

SEM images of membranes with cross-section were used to study the thickness (69.444 ± 4.492 µm) of PPy/PPO white oyster mushroom extract before it was applied (Figure 1c). The results based on the SEM image could be compared with the data obtained from measurements using the multimeter, as presented in Table 1 (73.670 ± 2.867 µm). The membrane thickness of PPy/PPO white oyster mushroom extract after being applied to the textile wastewater sample was 88.333 ± 19.552 µm (Figure 1d). Using the sample on textile wastewater also affected the increase in the parameter (18.889 ± 15.060 µm), which could be studied based on a 600× magnification SEM image.

The formation of cake due to the fouling process on the surface of the sample had an impact on increasing the size of the membrane thickness or pore size. PPy is a relatively hydrophobic membrane-forming polymer arranged in a steel mesh network obtained from an electrodeposition method. The hydrophobicity of the PPy polymer that immobilizes PPO can give the membrane properties that tend to be hydrophilic with PPO activity = 4160 U. The Cu active site of PPO acts as a biocatalyst that plays a role in redox chemical reactions, which is the oxidation of phenol in textile waste to quinones (Figure 2).

The adsorption and chemical redox reaction of phenol by copper ions in the presence of pollutants COD, BOD, TSS, and a PPO/PPy membrane. (i). Adsorption: Phenol and other pollutants such as COD, BOD, and TSS are adsorbed onto the surface of the PPO/PPy membrane. This adsorption process concentrates the pollutants near the membrane surface, facilitating their interaction with the immobilized PPO. (ii). Redox Reaction: Copper ions (Cu) present in the PPO/PPy membrane catalyze the oxidation of phenol. In this reaction, Cu(II) represents copper ions in the oxidized state, and Cu(I) represents copper ions in the reduced state. Phenol is oxidized to quinone, a less toxic and more easily removable form, while Cu(II) is reduced to Cu(I). The hydroquinone (H₂Q) is oxidised to the semiquinone (HQ). In the second oxidation step, the semiquinone (HQ) is oxidized to the quinone (Q) by Cu(II) [26].

$$Cu (II) + H_2Q \rightarrow Cu (I) + HQ$$
(1)

$$Cu(II) + HQ \rightarrow Cu(I) + Q$$
 (2)

Overall, the adsorption of pollutants onto the PPO/PPy membrane enhances their interaction with the immobilized PPO, leading to the efficient oxidation of phenol by copper ions. This redox reaction contributes to the degradation of pollutants and improved water quality in the dye sample. The adsorption mechanism during the fouling process may cause attraction between the foulant and the PPy/PPO membrane. The accumulation of several foulants (inorganic, biological, or organic particles) leads to forming a cake layer on the membrane's surface. This layer impedes the mass or volume transfer rate through the membrane, as depicted in Table 3, due to the foulants obstructing the membrane pores either partially or completely [27]. Modification of PPO from white oyster mushrooms immobilized on the PPy membrane can help increase the repulsive interaction between foulant and modified membrane [28]. In this study, the durability of PPy/PPO membrane performance was achieved in up to five applications (Table 5).

Filtration membranes that could separate suspended solids from water with pore sizes above 0.10 μ m were microfiltrated. The analysis with SEM images showed that the pore size was above 0.10 μ m, and the PPy filtration system was classified as microfiltration. Previous studies have developed a monovalent ion-selective membrane by modifying the surface of the cation, and an anion-exchange sample was synthesized by polymerization of pyrrole. Furthermore, the wet thickness of the sample was measured using a micrometer with an accuracy of 0.10 μ m [5]. In the filtration process with a pressure of 0.50 Bar, a pore size of 10 μ m, and a thickness of this study were still close to the microfiltration group based on their function [21].

3.2. The Membrane of PPy/PPO White Oyster Mushroom Extract

A total of three membranes of PPy/PPO white oyster mushroom extract (mPPy/PPO-A; mPPy/PPO-B and mPPy/PPO-C) with the composition of PPy 0.05 M and 35% (v/v) PPO are presented in Table 1. The electrolysis method was successfully used for the synthesis of the membrane. Furthermore, the platinum cathode had good conductivity as a conductor of electric current to contribute to driving the current during the deposition process on the surface of the steel screen. The phenomenon of PPy/PPO membrane deposition on the surface of steel gauze in the electrolyte solution began with the oxidation of 0.05 M Py, continuously forming PPy polymer growth and simultaneously causing PPO immobilization. The results showed that physical and chemical interaction was stable in a buffered citrate solution pH = 6.8. Other studies had reported that PPO was active at optimal SDS concentrations and pH > 5, while SDS with higher concentrations caused further protein denaturation. At optimal SDS concentrations and pH < 5, the active form of the enzyme was converted to inactive [10].

Table 2 shows the PPO activity and the number of active PPOs immobilized in the PPy matrix of three membranes (mPPy/PPO-A, mPPy/PPO-B, and mPPy/PPO-C). The second mPPy/PO-B membrane was more effective due to its high activity (PPO activity = 4160 U; the amount of PPO immobilized on the PPy membrane = 48.97%, w/w) compared to the other two samples. Furthermore, PPO activity based on the calibration curve is presented as PPO λ_{max} = 269.6 nm, y = 1.537x + 0.0057, R² = 0.995, and phenol 0.35 mM. Table 1 showed that the membrane density PPy/PPO was high (0.0043 g/mm³, thickness = 77 µm).



Figure 1. SEM images of the membrane of PPy/PPO white oyster extract with a magnification of 600×: a) surface morphology of the membrane of PPy/PPO white oyster extract before being applied to the textile wastewater sample; b) cross-sectional morphology of the membrane PPy/PPO white oyster extract after application to the textile wastewater sample; c) surface morphology of the membrane of PPy/PPO-white oyster extract before applying to the textile wastewater sample; d) crosssectional morphology of the membrane of PPy/PPOwhite oyster extract after application to the textile wastewater sample

Table 1 . The membranes of PPy/PPO characteristic with a composition of 0.05 M Py and 35% (v/v) of PPO oyster –
mushrooms extract by the electrodeposition method (steel gauze anode, the surface area = 8.00 × 8.00 cm, and Pt
cathode, the surface area = 8.00 × 8.00 cm; the potential of 6.00 V; the distance between the two electrodes = 4.00 cm,
and the electrolysis time = 900 seconds)

PPy/PPO- oyster mushroom-extract membrane	Weight (g) —	The amount of PPO immobilized on the PPy membrane		Electric current	Electric charge	Thickness	Volume	Density
		Weight (g)	% (b/b)	(A)	(C)	(mm)	(mm ³)	(g/mm³)
mPPy/PPO-A	1.6189	0.254	28.49	1.063	956.34	0.074	14.08	0.0180
mPPy/PPO-B	1.6482	0.400	48.97	1.142	1027.98	0.077	91.52	0.0043
mPPy/PPO-C	1.6391	0.342	16.57	1.067	1003.86	0.070	77.06	0.0044

Table 2. The immobilized PPO activity in the PPy membrane was obtained based on the calibration curve (PPO λ_{max} =269.6 nm, y = 1.537x + 0.0057, R² = 0.995, phenol 0.35 mM)

		PPO	pH of electrolyte			
PPy/PPO-oyster mushroom- extract membrane	Before the electrolysis process (U/mL)	After the electrolysis process (U/mL)	The amount of PPO immobilized on PPy membrane (U/mL)	The amount of PPO immobilized on PPy membrane (U)	Before the electrolysis process	After the electrolysis process
mPPy/PPO-A	10.89	7.79	3.10	3100	6.69	7.33
mPPy/PPO-B	8.49	4.43	4.16	4160	6.58	6.84
mPPy/PPO-C	9.90	8.26	1.64	1640	6.22	6.64



Figure 2. Cresolase activity and catechol activity of tyrosinase and catechol oxidase [29]

The study showed that the thickness of the membranes included a porous sublayer with a range of $50-200 \mu m$, which primarily functioned as a supportive structure within the overall membrane composition. The permeation rate was inversely proportional to the actual thickness of the barrier layer, and an asymmetric sample showed a higher permeation rate (water flux) than a symmetric (homogeneous) variant of comparable thickness [22]. Table 2 shows the change in the pH of the electrolyte solution before and after electrodeposition. During the electrolysis process, it comprised a redox reaction, which caused a charge transfer of H⁺ and OH⁻ ions at the anode and cathode of H₂O in the electrolyte solution [20].

Anode:
$$2Py_{(aq)} + 2A^{-}_{(aq)} \rightarrow 2Py^{+}A^{-}_{(s)} + 2e^{-}$$
 (3)

Cathode:
$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$
 (4)

overall:
$$2Py_{(aq)} + 2A^{-}_{(aq)} + 2H_{2}O_{(l)} \rightarrow 2Py^{+}A^{-}_{(s)} + H_{2(g)} + 2OH^{-}_{(aq)}$$
 (5)

The textile wastewater sample underwent no preliminary treatment involving acid addition to pH adjustment. Instead, it was directly streamed into the membrane system to ensure that the permeate solution experienced only a marginal pH reduction following filtration. This article was a preliminary study in measuring the performance capacity of PPy membranes based on PPO. Therefore, it was necessary to study continuous pH regulation with acid in a waterneutralizing container before using membrane filtration. Table 3 shows that the electrolysis efficiency measured using a digital multimeter was 50.10%. Based on Faraday's Law, further investigations could be carried out concerning current efficiency and electric power, predicting the one-time PPy/PPO membrane synthesis cost.

3.3. Application of Membrane of PPy/PPO White Oyster Mushrooms Extract in Liquid Waste Textiles

The results of the analysis of textile waste liquid samples before and after membrane filtration are presented in Table 3. The parameters measured included pH, phenol BOD, COD, and TSS. Furthermore, the membrane filtration design was installed with a deadend model, while 1000 mL of textile wastewater in the feed phase was given a pressure of 1 bar. Conventional pressure-based membrane processes with liquid permeation often operate in a dead-end manner. The resistance increased along with the thickness of the cake formed on the sample, which was expected to be roughly proportional to the total volume of the filtrate passed. Organic fouling in the bioreactor refers to the organic molecules' deposition to the membrane, which generally forms a colloidal layer on the surface [7]. This showed that packaging was needed for PPO before the immobilization process of PPy was carried out.

Several studies had reported a membrane bioreactor for investigating phenol degradation at high concentrations using Pseudomonas putida American Type Culture Collection 49451 immobilized in 25% (w/w) polysulfone. At an initial phenol of 1200 mg/L, the solution degraded completely under 95 h in the immobilized system. Meanwhile, no cell growth and phenol degradation were observed in the free suspension system at 1000 mg/L. Further biodegradation studies using 2000 and 3500 mg/L showed complete degradation at both high concentrations [30]. Preparation and modification of Cu²⁺ in PPO extract from purple eggplant for phenol degradation in coal wastewater have also been studied. The phenol response had a higher affinity for PPO-Cu²⁺ as a biocatalyst. The application of PPO-Cu²⁺ on purple eggplant extract was effective at 46.7% for artificial coal wastewater containing the compound [25].

The process of solution flow from the feed phase to the membrane of PPy/PPO white oyster mushroom extract carried out with a discontinuous and continuous flow is shown in Table 3. The rejection was achieved at 100% (complete retention solute, as an ideal semipermeable membrane) and 0% (solute and solvent pass through the membrane freely) [21]. The correlation with the membrane of PPy/PPO white oyster mushroom extract could hold solutes, where PPO as a catalyst played an active role in the oxidation process of phenol to a quinone.

Waste parameter							
	nЦ	Phenol	BOD	COD	TSS		
	рп	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
	Before filtration						
Initial condition	10.63	3.68	286	662.3	46		
After filtration: Discontinuous flow							
1	9.06	3.35	48	150.15	38.00		
2	9.02	3.13	45	145.63	34.7		
3	9.04	3.6	61	143.9	35		
4	9.06	3.6	58	140.2	37.8		
5	9.07	3.47	54.00	140.20	35.70		
$\overline{x} \pm \sigma$	9.05 ± 0.02	3.43 ± 0.18	53.20 ± 5.98	144.02 ± 3.72	35.80 ± 1.21		
Parameters decreased	14.86%	6.80%	81.30%	78.25%	20.65%		
After filtration: continuous flow							
	8.06	2.72	33	146	15.8		
Parameters decreased	24.20%	26.09%	88.50%	78.00%	65.70%		

Table 3. Wastewater parameters measured of pH, phenol, BOD, COD, and TSS before and after filtration using themembrane of PPy/PPO white oyster mushroom extract

The continuous flow membrane filtration obtained an average decrease in phenol content of 0.25 mg/L or 6.8%. Meanwhile, with continuous flow membrane filtration, the levels of the compound were reduced by 26.09%. Table 3 shows the discontinuous flow membrane filtration results from the first to the fifth use, with an average decrease in COD levels of 78.25%. Continuous membrane filtration could reduce COD levels by 78%. Furthermore, the measurement of the BOD was the amount of easily biodegradable organic matter in textile wastewater. Discontinuous flow membrane filtration achieved an average decrease in BOD levels of 81.30%. Meanwhile, a continuous flow membrane could reduce BOD levels by 88.50%. This showed that the decrease in the levels was greater than the wastewater sample, which was only passed once to the membrane.

TSS was an insoluble material that floated in textile wastewater, making the water cloudy and causing the proliferation of harmful bacteria. Discontinuous and continuous flow membrane filtration still showed precise results with an average decrease in TSS levels of 20.62% and 30.40%, respectively. Therefore, the reduction of phenol, BOD, COD, and TSS levels through continuous and discontinuous flow membrane filtration could be achieved compared to wastewater samples, which were only passed once through the membrane. This was because the contact time between the feed phase and the membrane was longer. Studies on polyaniline/rice husk ash and polypyrrole/rice husk ash nanocomposites had succeeded in removing heavy metals, COD, color, and anions from cotton textile wastewater with COD removal efficiency PAn/RHA = 92.50% and PPy/RHA = 97.15% [31].

The performance of membrane application to textile wastewater was studied with discontinuous and

continuous flow, as shown in Table 4. The results showed a decrease in flux and permeability by the discontinuous method. Furthermore, it was possible that fouling occurred during operation due to the deposition or adhesion of material on the surface of the sample. Membrane fouling could be defined as the irreversible deposition of particles, colloids, emulsions, suspensions, macromolecules, and salts on the surface or within the membrane [5]. The pre-treatment stage was the initial treatment phase, which generally consisted of an equalization process, pH adjustment, and a screening process. Equalization aimed to reduce fluctuations in wastewater discharge to ensure stability in the next stage. The pH adjustment was needed because the textile wastewater had a pH of approximately 10 and could be neutralized by lowering the pH by adding acid.

The primary treatment stage comprised removing suspended solids from the waste. The process of removing suspended solids was an integration of chemical-physical processes. Furthermore, the chemical process involved adding chemical substances, such as coagulants or flocculants. The physical process comprised separating suspended solids from the water, which could be facilitated by a sedimentation system. The wastewater sample used in this study was derived from the inlet of the Wastewater Treatment Plant (WWTP), showing that it had not undergone several crucial treatment stages. Consequently, the observed suboptimal results, such as decreased pH, phenol, BOD, COD, and TTS, could be attributed to the absence of comprehensive treatment. A combination of these processing stages was recommended to optimize the quality of the treated wastewater.

	Flow rate (L. h ⁻¹)	Flux (L.m ⁻² .h ⁻¹)	Permeability				
The discontinues membrane filtration method							
1	51.50	3387.5	338.7				
2	49.50	3378.5	327.8				
3	49.50	3378.5	327.8				
4	48.90	3238.5	323.8				
5	48.19	3191.6	319.2				
The continuous membrane filtration method							
	48.19	3191.6	319.2				

Table 4. Filtration process membrane of PPy/PPO white oyster mushroom extract with measured parameters, including flow rate, flux, and permeability. The filtration method was carried out with discontinuous and continuous flow

4. Conclusion

The membrane of PPy/PPO white oyster mushroom extract was synthesized successfully with a composition of 0.05 M Py and 35% (v/v) of stable PPO oyster mushroom extract in citrate buffer (pH = 7.0) using the electrodeposition method (potential of 6.00 V, the distance between the two electrodes = 4.00 cm, and the electrolysis time = 900 seconds). Furthermore, the immobilized PPO activity in the PPy membrane was 28.49% with 0.35 mM phenol as a substrate. PPy/PPO membranes were applied to textile wastewater using a filtration device with a dead-end flow model. Analysis of the physical parameters of the membrane showed a decrease in the flow rate, flux, and permeability of the membrane. This was possibly due to the formation of cake on the surface of the sample after its utilization. Based on the characterization results obtained from SEM images, which showed a pore size of 0.10 µm and a membrane thickness of 69.444 \pm 4.492 µm, the filtration system using the PPy/PPO membrane could be categorized as microfiltration.

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