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Pengaruh Kinerja Membran Kitosan-TiO_2 Terhadap Degradasi Limbah Batik dengan Sistem Hybrid Fotokatalitik

Effect of Chitosan-TiO2 Membrane Performance for the Degradation of Batik Waste with a Photocatalytic Hybrid System

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ABSTRAK: Limbah industri telah mendapat perhatian besar dalam beberapa tahun terakhir karena dampak buruknya terhadap lingkungan dan kesehatan masyarakat. Penelitian ini bertujuan untuk mengetahui tingkat efektivitas sistem hybrid fotokatalitik dengan membrane kitosan-TiO_2 dengan mempelajari pengaruh penambahan TiO_2 terhadap tingkat performa penyisihan logam berat. Kinerja membran diselidiki melalui serangkaian percobaan, mengevaluasi kemampuannya dalam menghilangkan polutan organik dan meningkatkan efisiensi pengolahan secara keseluruhan. Parameter yang digunakan yaitu untuk mengevaluasi kinerja membrane pada parameter operasi kinerja yang digunakan dengan mengecek tingkat penyisihan logam berat. Morfologi dengan menggunakan analisa SEM menunjukkan permukaan kasar dimana permukaan tersebut mengindikasikan adanya TiO_2 yang dicangkokkan pada membran hal ini mengindikasikan peningkatkan efisiensi fotokatalitik yang dapat menyediakan area permukaan yang lebih besar untuk reaksi. Distribusi partikel TiO_2 yang seragam dalam matriks kitosan sangat penting untuk degradasi polutan yang stabil dan efisien selama fotokatalisis. Degradasi limbah sintesis dapat dilihat pada analisa FTIR. Selain itu, membran Kitosan-TiO_2 menawarkan solusi yang menjanjikan untuk pengolahan air limbah batik. Membran Kitosan- TiO_2 menggabungkan keunggulan permeabilitas kitosan dan penangkapan zat organik dengan kemampuan fotokatalitik TiO_2. Terakhir, analisis AAS menunjukkan bahwa penambahan TiO2 memperbaiki degradasi logam berat dalam limbah batik, dengan kinerja optimal yang diamati hingga tingkat penolakan 89,78%, setelah itu terjadi aglomerasi TiO_2.
Kata Kunci: membran; fotokatalitik; kitosan; TiO_2; limbah batik

ABSTRACT: Industrial waste has received great attention in recent years due to its adverse impact on the environment and public health. This research aims to determine the level of effectiveness of the photocatalytic hybrid system with chitosan-TiO_2 membranes by studying the effect of adding TiO_2 on the level of heavy metal removal performance. The performance of the membrane was investigated through a series of experiments, evaluating its ability to remove organic pollutants and improve overall processing efficiency. The parameters used are to evaluate the performance of the membrane on the operational performance parameters used by checking the level of heavy metal removal. Morphology using SEM analysis shows a rough surface where the surface indicates the presence of TiO_2 carried on the membrane. This indicates an increase in photocatalytic efficiency which can provide a larger surface area for the reaction. Uniform distribution of TiO_2 particles in the chitosan matrix is essential for stable and efficient degradation of pollutants during photocatalysis. Degradation of synthetic waste can be seen in FTIR analysis. In addition, Chitosan-TiO_2 membrane offers a promising solution for batik wastewater treatment. Chitosan- TiO_2 membrane combines the advantages of chitosan permeability and capture of organic substances with the photocatalytic capabilities of TiO_2. Finally, AAS analysis shows that the addition of TiO_2 improves the degradation of heavy metals in batik waste, with optimal performance observed up to a rejection rate of 89.78%, after which agglomeration occurs TiO_2.
Keywords: membrane; photocatalytic; chitosan; TiO_2; batik waste

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1. Introduction

The textile industry, a major contributor to global pollution, generates vast amounts of wastewater containing hazardous chemicals and organic dyes (Nasrollahi et al., 2021; Rashidi et al., 2012). The batik making process uses traditional textile coloring which is known for its complex patterns and bright colors. Behind this, batik waste has several impacts that are not good for the environment, because batik waste contains synthetic waste from the dyes produced. Batik synthesis waste contains various kinds of synthetic dyes which can harm the environment because it contains various kinds of heavy metal waste, the highest of which is Pb (II) copper content of 4.6 mg/l and Cd (II) of 0.724 mg/l (Mukimin et al., 2017). Conventional treatment methods often fall short in effectively degrading these complex organic compounds, necessitating the development of novel and efficient approaches (Dwi Nyamiati et al., 2023; Syamani, 2020).

Photocatalysis has emerged as a promising technology for the treatment of various wastewater streams, including those from textile industries (Mozia, 2010). In particular, titanium dioxide (TiO_2)-based photocatalysts have shown remarkable photocatalytic activity under ultraviolet (UV) light irradiation, leading to the degradation of organic contaminants through oxidative reactions. However, the immobilization of TiO_2 photocatalysts onto a suitable support material is essential to enhance their practical application (Mousa et al., 2023; Tung et al., 2018).

Chitosan, a naturally abundant biopolymer derived from crustacean shells, has garnered considerable attention as a potential support material for photocatalysts due to its unique properties. Chitosan possesses excellent biocompatibility, biodegradability, and mechanical strength, making it an ideal candidate for various environmental applications. Moreover, the incorporation of TiO_2 nanoparticles within the Chitosan matrix can enhance the photocatalytic activity and facilitate the separation of catalysts from the treated wastewater (El-Hefian et al., 2010; Kumar et al., 2013).

In the last few decades, the development of hybrid membrane composites has increased rapidly because they show several profitable applications, for photocatalysis processes, water treatment, and antimicrobial removal. Chitosan is a natural polymer made from organic material which is combined with the inorganic material Titanium Dioxide (TiO_2) to form a hybrid composite (Mozia, 2010; Wang, 2018).

The inorganic material TiO_2 is an inert material that has good applications in the world of food, pharmaceuticals, biomedicine, antimicrobials, and the environment. The use of TiO_2 has various advantages, namely because it has high levels of physicochemical, mechanical properties, photocatalytic, reactivity, thermal stability, low cost, and safe production, and can be combined with other materials, above some of the advantages TiO_2 has a disadvantage, namely the ability to coagulate TiO_2 nano if grafting with other compounds, several studies have reported that the interaction between nani-TiO_2 and biopolymers such as starch, gum and chitosan can help reduce the formation of agglomeration of TiO_2 so that it can increase the functional composite of the membrane Anaya-Esparza et al., 2020; Wang et al., 2016).

Chitosan-TiO_2 membrane represents the latest innovation in batik wastewater filtration technology, combining the advantages of Chitosan, a natural polymer extracted from chitin, with TiO_2, a photocatalytic semiconductor. This membrane has demonstrated highly promising performance results in the context of hybrid photocatalytic filtration for batik wastewater. Chitosan is utilized as the base material for the membrane due to its properties such as good permeability, sufficient mechanical strength, and the ability to capture organic substances in batik wastewater. Meanwhile, the addition of TiO_2 to the membrane enables a photocatalysis process that can break down the organic compounds trapped in the wastewater. When exposed to UV light or sunlight, TiO_2 catalyzes an oxidation reaction that transforms organic compounds into more environmentally friendly products, such as CO_2 and water. The result is a more efficient and sustainable purification of batik wastewater (Fu et al., 2019; Mozia, 2010).

The objective of this study is to investigate the performance of a Chitosan-TiO_2 membrane in a photocatalytic hybrid system for the degradation of batik waste. The hybrid system combines the advantages of Chitosan as a support material and TiO_2 as a photocatalyst to achieve efficient removal of organic pollutants. By immobilizing TiO_2 nanoparticles onto the Chitosan membrane, we aim to enhance the overall degradation efficiency and ensure the effective treatment of batik waste. To evaluate the performance of the Chitosan-TiO_2 membrane, we conducted a series of experimental tests, including the analysis of degradation efficiency, removal of specific pollutants, and assessment of membrane stability under various operating conditions. The obtained results will provide valuable insights into the potential of the Chitosan-TiO_2 membrane-based photocatalytic hybrid system for treating batik waste and highlight its suitability for broader applications in wastewater treatment.

2. Research Methods

2.1. Materials

Chitosan with a degree of deacetylation (DD) of 88.1% determined by UV method and TiO_2 were purchased from Sigma Aldrich. Dimethylformamide (DMF) was purchased from Merck and was used as the solvent. The other non-solvent is water, in here we used aquadest.

2.2. Membrane Preparation

Chitosan/TiO_2 membranes with a composition of 100/0; 90/10; 80/20; 70/30; 60/40 wt/wt were prepared by phase inversion method. Chitosan/TiO_2 were dissolved in DMF as solvent until the solution is homogeneous and casted on the glass plate by using a film applicator followed by immersion process into coagulation bath containing non-solvents water,

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for 15 minutes. Then, Chitosan/TiO_2 membranes were dried and analyzed the morphology of the membrane by using Scanning Electron Microscopy (SEM). Rejection and permeate flux were analyzed to determine performance of the membrane. For membrane's characterization and performance analysis, total polymer and solvent used are 2.5 g and 17 mL

2.3 Membrane Performance

Figure 1 provides a visual representation of the setup employed to evaluate the membrane's performance. The feed tank was loaded with water containing varying levels of Pb(II) and Cd(II). The membrane was affixed within the flux test apparatus, specifically positioned within the plate and frame module. By regulating the pump pressure via an intake valve and closely monitoring the pressure gauge, the feed water was compelled to traverse the membrane.

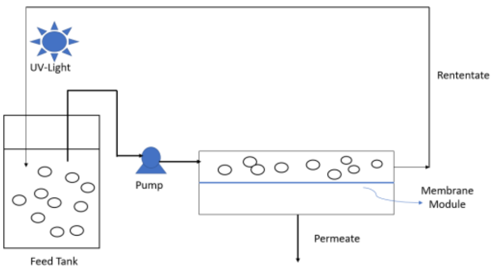

Fig. 1 Schematic of membrane performance test

The resulting liquid that passed through the membrane, known as the permeate, was collected in a measuring glass, and its rate of flow was documented. Subsequently, an analysis of the permeate was conducted to determine the concentrations of Pb(II) and Cd(II) using AAS. Moreover, parameters such as permeate flow, permeability, and the extent to which Pb and Cd ions were rejected were also calculated.

Calculation of Rejection of Pb (II) Metal Ions

The concentration of heavy metals were determined using an atomic absorption spectrophotometer, specifically the Shimadzu AA 6300 model, which is produced in Japan and the data was analyzed using the formula given in Equation (2.12) to determine the percentage rejection of Pb(II) and Cd(II) ions % Rejection of Pb(II and Cd(II)) Metal Ions

$$x = [\frac{X_{in}}{X_{im} - X_{out}} x100\%] \quad (1)$$

Where [X] in represents incoming Pb(II) and Cd(II) content ($mg \cdot L^{-1}$) and $[X]_{out}$ represents level of Pb (II) in permeate ($mg \cdot L^{-1}$)

3. Results and Discussion

The morphology of chitosan membranes is crucial in determining their performance in various applications. Chitosan membranes typically possess a highly porous structure, and pore size can be adjusted during the manufacturing process (Rahman & Rimu, 2020).

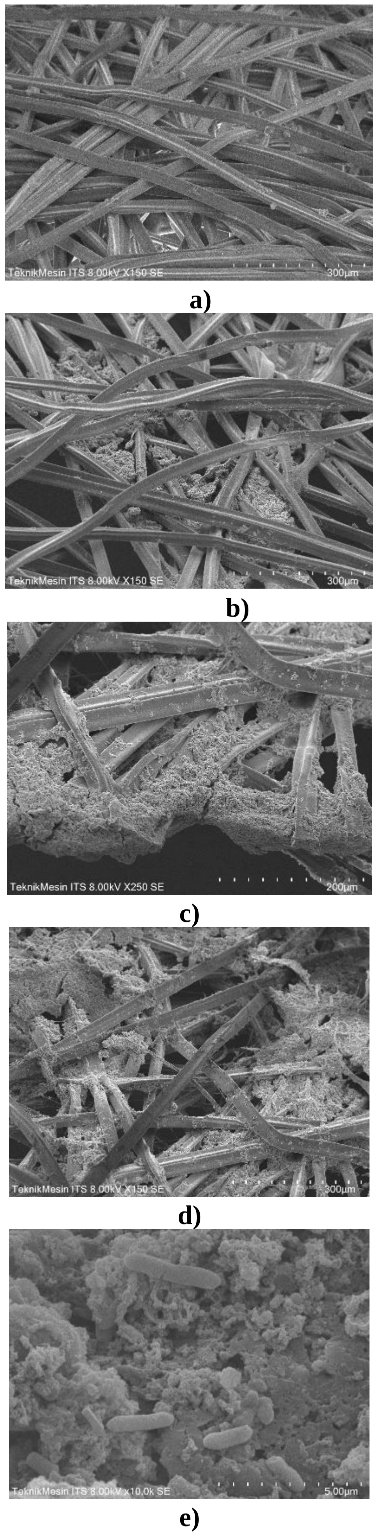

Figure 2. SEM Image for a) Chitosan-TiO2 100/0; b) Chitosan-TiO2 90/10; c) Chitosan-TiO2 80/20; d) Chitosan-TiO2 70:30; e) Chitosan-TiO2 60:40

These pores enable the deposition of desired particles or molecules and the removal of water, making them highly useful in filtration, separation, and purification processes. It is important to understand that the morphology of Chitosan-TiO_2 membranes plays a crucial role in their photocatalytic efficiency (Nurkhamidah et al., 2019). When observed using Scanning Electron Microscopy (SEM), the morphological structure of these membranes typically exhibits several significant characteristics. Firstly, the combination of chitosan and TiO2 often results in a rough membrane surface with cracks and varying levels of porosity. This rough surface can enhance the available surface area for photocatalytic reactions, which is essential for improving the efficiency of the process.

From Figure 2, it depicts the morphology of Chitosan-TiO_2 membranes with several variations in the addition of TiO_2 to the Chitosan membrane. Furthermore, the morphology of Chitosan-TiO_2 membranes can indicate the even distribution of TiO_2 particles within the chitosan matrix. These TiO_2 particles serve as the starting point for photocatalytic reactions, where they capture UV light energy and initiate the degradation of dissolved pollutants in the water environment. The uniform distribution of TiO_2 particles and strong bonding between TiO_2 and the chitosan matrix are crucial for maintaining membrane stability during the photocatalysis process and enhancing pollutant degradation efficiency.

Table 1. Performance rejected for Pb (II) and Cd (II)

Membrane Chitosan-TiO2	Performance Rejected of Pb (II) (%)	Performance Rejected of Cd(II) (%)
100/0	72.68	70.67
90/10	78.39	77.45
80/20	82.23	80.24
70/30	91.89	89.78
60/40	65.90	67.96

The advantage of the Chitosan-TiO_2 membrane in this hybrid photocatalytic process is its ability to integrate the filtration process with photocatalytic treatment (Hashemi & Lai, 2023), making batik wastewater treatment more efficient in a single step. This reduces the use of hazardous chemicals in the wastewater treatment process and produces wastewater that is safer for the environment. Furthermore, this membrane also has a relatively long lifespan due to TiO_2 resistance to corrosion and degradation. Therefore, the performance of the Chitosan-TiO_2 membrane for hybrid photocatalytic batik wastewater filtration becomes an attractive alternative to addressing environmental pollution issues caused by the textile industry's wastewater while contributing to sustainability efforts in this sector.

The performance of Chitosan-TiO_2 membranes was analyzed using AAS Analysis to reduce heavy metal degradation in batik waste it should be mention in the Table 1. The addition of TiO_2 resulted in an increased performance value of the rejection, with an optimal level observed up to 40%, beyond which agglomeration of TiO_2 occurred.

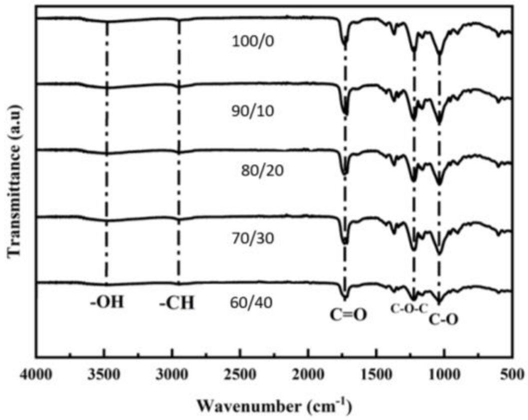

Figure 3. FTIR Analysis Chitosan-TiO_2 Membranes

FTIR analysis was used to see the degradation of synthetic dyes which was indicated to decrease with the addition of TiO_2 nanoparticles. Can bee seen at Figure 3 this is the result of FTIR analysis which illustrates that the degradation of synthetic dyes decreases with the addition of TiO_2 nanoparticles. The more TiO_2 added to the membrane, the more -OH groups there are on the membrane, this can be seen at a wavelength of 3500 cm^{-1}.

4. Conclusion

The morphology of chitosan membranes, particularly Chitosan-TiO_2 membranes, plays a critical role in their performance across various applications. These membranes possess a porous structure that can be tailored during manufacturing, making them valuable in filtration, separation, and purification processes. The morphology, as seen through SEM images, shows a rough surface that enhances photocatalytic efficiency by providing a larger surface area for reactions. The uniform distribution of TiO_2 particles within the chitosan matrix is crucial for stable and efficient pollutant degradation during photocatalysis. Furthermore, Chitosan-TiO2 membranes offer a promising solution for batik wastewater treatment. They combine the benefits of chitosan permeability and organic substance capture with TiO_2 photocatalytic capabilities. This integration allows for efficient, one-step hybrid photocatalytic filtration, reducing the use of harmful chemicals and producing environmentally friendlier byproducts. Additionally, the membranes have a relatively long lifespan, contributing to sustainability efforts in textile wastewater treatment. The result of FTIR analysis which illustrates that the degradation of synthetic dyes decreases as TiO_2 nanoparticles increase. Finally, AAS analysis demonstrated that the addition of TiO_2 improved heavy metal degradation in batik waste, with optimal performance observed up to a 91.89% rejection rate, beyond which TiO_2 agglomeration occurred.

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References

Dwi Nyamiati, R., Nurkhamidah, S., Rahmawati, Y., & Meka, W. (2023). Kinetic and Thermodynamic Studies in Cellulose Acetate-Polybutylene Succinate (CA- PBS)/ Single Solvent / Water. Eksergi, *20*(1), 9–15.

El-Hefian, E. A., Nasef, M. M., & Yahaya, A. H. (2010). The preparation and characterization of Chitosan / Poly (Vinyl Alcohol) blended films. *E-Journal of Chemistry*, *7*(4), 1212–1219. https://doi.org/10.1155/2010/626235

Fu, J., Wang, X., Ma, Z., Wenming, H., & Li, J. (2019). Photocatalytic ultrafiltration membranes based on visible light responsive photocatalyst : a review. *Chemical Engineering and Processing-Process Intensification. 168*, 42–55. https://doi.org/10.5004/dwt.2019.24403

Binazadeh, M., Rasouli, J., Sabbaghi, S., Mousavi, S. M., Hashemi, S. A., & Lai, C. W. (2023). An Overview of Photocatalytic Membrane Degradation Development. *Materials*, 16(9), 1-30.

Kumar, R., Isloor, A. M., Ismail, A. F., Rashid, S. A., & Ahmed, A. Al. (2013). Permeation, Antifouling and desalination performance of TiO2nanotube incorporated PSf/CS blend membranes. *Desalination*, *316*, 76–84. https://doi.org/10.1016/j.desal.2013.01.032

Anaya-Esparza, L. M., Ruvalcaba-Gómez, J. M., Maytorena-Verdugo, C. I., González-Silva, N., Romero-Toledo, R., Aguilera-Aguirre, S., ... & Montalvo-González, E. (2020). Chitosan-TiO2: A versatile hybrid composite. *Materials*, 13(4), 1-27.

Mousa, S. A., Abdallah, H., & Khairy, S. A. (2023). Low - cost photocatalytic membrane modified with green heterojunction TiO 2 / ZnO nanoparticles prepared from waste. *Scientific Reports*, 1–19. https://doi.org/10.1038/s41598-023-49516-0

Mozia, S. (2010). Photocatalytic membrane reactors (PMRs) in water and wastewater treatment. A review. *Separation and Purification Technology*, *73*(2), 71–91. https://doi.org/10.1016/j.seppur.2010.03.021

Mukimin, A., Zen, N., Purwanto, A., Wicaksono, K. A., Vistanty, H., & Alfauzi, A. S. (2017). Application of a full-scale electrocatalytic reactor as real batik printing wastewater treatment by indirect oxidation process. *Journal of Environmental Chemical Engineering*, *5*(5), 5222–5232. https://doi.org/10.1016/j.jece.2017.09.053

Nasrollahi, N., Ghalamchi, L., Vatanpour, V., & Khataee, A. (2021). Journal of Industrial and Engineering Chemistry Photocatalytic-membrane technology : a critical review for membrane fouling mitigation. *Journal of Industrial and Engineering Chemistry*, *93*, 101–116. https://doi.org/10.1016/j.jiec.2020.09.031

Nurkhamidah, S., Ramadhani, A., Cintya, B., Arief, B., & Nyamiati, R. D. (2019). Modified of Cellulose Acetate / Polyethylene Glycol Membrane by the Addition of Graphene Oxide. *Indonesian Polymer Journal 22*(2), 16–20. https://doi.org/10.37889/mpi.2019.22.2.4

Rahman, M. M., & Rimu, S. H. (2022). Recent development in cellulose nanocrystal-based hydrogel for decolouration of methylene blue from aqueous solution: a review. *International Journal of Environmental Analytical Chemistry*, 102(18), 6766-6783.

Rashidi, H. R., Sulaiman, N. M. N., & Hashim, N. A. (2012). Batik Industry Synthetic Wastewater Treatment Using Nanofiltration Membrane. *Procedia Engineering*, *44*, 2010–2012. https://doi.org/10.1016/j.proeng.2012.09.025

Syamani, F. A. (2020). Cellulose-based membrane for adsorption of dye in batik industry wastewater. *J. Hydrol*, 4, 281-283.

Tung, T. V., Ananpattarachai, J., & Kajitvichyanukul, P. (2018). Photocatalytic membrane reactors for wa ter and wastewater treatment applications: Process factors and operating conditions review. *Lowland Technology International*, *20*(3), 413–424.

Wang, L. (2018). Configurations and Membranes of Photocatalytic Membrane Reactors for Water and Wastewater Treatment Configurations and Membranes of Photocatalytic Membrane Reactors for Water and Wastewater Treatment. *IOP Conference Series: Earth and Environmental Science*, *208*(012078). https://doi.org/10.1088/1755-1315/208/1/012078

Wang, L., Xiong, W., Yao, L., & Wang, Z. (2016). *Novel Photocatalytic Membrane Reactor with TiO2 Nanotubes for Azo Dye Wastewater Treatment*. *06020*, 0–5.