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Original Research Article

Enhancing Ibuprofen Degradation through Optimization of ZrCo Synthesis Catalyst in Membrane Distillation

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Abstract

This study will optimize ZrCo as a catalyst applied to the surface of porous membranes to remove micropollutants, specifically ibuprofen. This method improves the reaction rate and accelerates the chain degradation of Ibuprofen, thereby preventing blockage caused by impurities in the membrane pores. The catalyst synthesis was performed using a hydrothermal method with $ZrCl_4$ and $CoCl_2 \cdot 6H_2O$ as the primary materials. This method is employed to produce a high purity catalyst and yield a more stable catalyst. This research will measure the optimal catalyst through flux and removal efficiency during the membrane distillation process for 1 hour. Reaction conditions were adjusted using Air Gap Membrane Distillation at 80°C heating temperature, 4 L/min flow rate, and 1.5 mmol/L peroxymonosulfate as pre-oxidation. Experiments were conducted by comparing 9 types of catalysts, from which the best calcination temperature was selected for catalyst concentration optimization. Based on the flux and removal data tested statistically, the optimum catalyst type and calcination temperature were achieved at a 2:1 composition with a calcination temperature of 600°C, yielding flux and removal efficiency values of 7.0238 LMH and 98.53%. Meanwhile, the optimum catalyst concentration was obtained at 0.5 wt%, with flux and removal efficiency values of 8.05 LMH and 99.83%.

Keywords: ZrCo catalyst; catalyst optimization; hydrothermal method; air gap membrane distillation

1. Introduction

The use of chemicals in various activities such as industry, households, agriculture, and livestock farming results in pollution from hazardous chemical substances in the environment (El Hammoudani et al., 2024). Among these chemicals are substances known as micropollutants. This group of micropollutants includes pharmaceuticals, personal care products, micro and nano plastics, artificial sweeteners, and pesticides (Abbasi et al., 2022). One pharmaceutical product that has a significant impact is ibuprofen. Ibuprofen is a non-steroidal anti-inflammatory drug commonly used for pain relief, fever reduction, and anti-inflammatory purposes, making it one of the most frequently consumed medications by humans (Varrassi et al., 2020). It has a relatively low solubility in water, approximately 11 μg/mL at room temperature. Despite its low water solubility, ibuprofen has a high annual consumption rate of about 200 tons. The ingested ibuprofen is excreted or disposed of in expired forms, ultimately entering the environmental ecosystem. In Indonesia, the presence of ibuprofen in surface water is reported to be between <1 and 22 mg/L (Trianda et al., 2024).

Ibuprofen is also resistant to natural degradation in aquatic bodies and during wastewater treatment (Trianda et al., 2024). The presence of ibuprofen cannot be eliminated by conventional wastewater treatment methods (Farhadi et al., 2021). Several technologies can remove ibuprofen from contaminated water, including adsorption, photocatalysis, ion exchange, electrochemistry, membrane distillation, and biological treatment (Yakamercan and Aygun, 2020). However, membrane distillation technology has several advantages over other technologies, including low electrical energy consumption since the heat source can originate from industrial processes. It does not produce other pollutant by-products, thereby minimizing environmental impact (Johnson and Hilal, 2021). Most importantly, the purity level of waste treatment results using membrane distillation is exceptionally high, achieving over 99.97% purification (Bernardo et al., 2020). This study will utilize membrane distillation technology because it selectively rejects ibuprofen while producing pure water, with the concentrated ibuprofen remaining on the feed side. To degrade the concentrated ibuprofen on the feed side, a chemical oxidation process and a catalyst will be applied (Guo et al., 2023).

Catalysts are substances that enhance the rate of chemical reactions without altering the composition of the reacting substances or undergoing any permanent change themselves. (Dev, Srivastava and Karmakar, 2018). Catalysts accelerate the breakdown of the ibuprofen chain, thereby preventing blockages caused by impurities in the membrane pores (Hussain et al., 2020). Zirconium (Zr) is chosen as the catalyst due to its low toxicity, ease of synthesis, stability, and the extensive research supporting its effectiveness (Scotti et al., 2020). Zirconia will be synthesized with cobalt (Co) to produce the ZrO2Co catalyst. Cobalt (Co) also exhibits low toxicity, stability, and catalytic properties and reacts well with oxygen. The synthesis of the zirconium-cobalt catalyst is derived from zirconium tetrachloride (ZrCl4) and cobalt(II) chloride hexahydrate (CoCl2·6H2O) using a hydrothermal method (Sonawane, Patil and Sonawane, 2018).

Membrane distillation is a technology that employs hydrophobic membranes to separate solutions at different temperatures. The temperature difference creates a difference in vapour pressure, which leads to vapour transport from the side of the membrane with high vapour pressure to the side with low vapour pressure (Kujawska et al., 2015). Membrane distillation processes can be classified into four configurations based on their methods: Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Sweeping Gas Membrane Distillation (SGMD), and Vacuum Membrane Distillation (VMD) (Parani and Oluwafemi, 2021). In this study, the Air Gap Membrane Distillation (AGMD) configuration will be utilized, where an air gap serves as a thermal insulation layer between the hot feed and the cooling surface, thereby reducing significant heat loss (Rahimpour, Kazerooni and Parhoudeh, 2018).

The performance of both methods, namely catalysis and membrane distillation, will be combined by applying the catalyst to the surface of a porous membrane. This catalyst will be applied to the porous membrane surface by coating (Eykens et al., 2018). The membrane coating will involve an immersion process, where the pre-fabricated membrane substrate is submerged in a solution containing the materials to be deposited. In this study, the catalyst will be applied to the surface of the porous membrane using a dip-coating method, where the membrane is immersed in the solution and then withdrawn, forming a uniform layer (Yang et al., 2021). This method will be applied because it improves the reaction rate and accelerates the chain degradation of Ibuprofen, thereby preventing blockage caused by impurities in the membrane pores (Krishna and Prasanna, 2024).

Additionally, Advanced Oxidation Processes (AOPs) utilize added oxidants to oxidize pollutants in wastewater (Kaur et al., 2020). The AOP to be used is a sulphate radical-based AOP, which involves using sulphate-containing compounds such as $S_2O_8^{2-}$, a strong oxidant. This compound must be activated using heat, UV irradiation, transition metals, or increased pH to generate sulphate radicals that initiate oxidation (Palit and Hussain, 2021). In the upcoming research, the Advanced Oxidation Process (AOPs) will employ peroxymonosulfate ($KHSO_5$) as the oxidant for the degradation of ibuprofen ($C_{13}H_{18}O_2$). Peroxymonosulfate is a source of SO_4 (Yuan et al., 2017).

In the previous study has been conducted on applying SiO_2 as a catalyst on the surface of a porous membrane with a sandwich structure, where polyvinylidene flouride (PVDF) is used as the primary membrane material. This research focuses on enhancing the efficiency of surfactant removal from wastewater. The membrane configuration employed in this study is the Direct Contact Membrane Distillation (DCMD) configuration (Guo et al., 2023). In the study, ZrCo catalyst will be utilized, as it has not yet been applied in membrane distillation processes using AGMD. The use of the ZrCo catalyst on the surface of this porous membrane aims to treat ibuprofen, a type of micropollutant commonly found in wastewater. AGMD configuration will also be utilized. Analysis will be conducted by measuring flux values and removal efficiency, followed by statistical testing to determine the effect of variables on this process.

2. Methods

2.1. Materials

The catalyst ZrCo was prepared using the primary materials of zirconium tetrachloride ($ZrCl_4$) and cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$). Ammonia (NH_3) was used to adjust the pH of the catalyst (Rakngam et al., 2024). The entire solution was prepared using distilled water. Ethyl alcohol was utilized for the washing process. Subsequently, the synthesis resulted in wastewater containing ibuprofen at a 5 mg/L concentration. 5 mg/L Ibuprofen is intended to ensure that the experiments are more controlled and optimize the membrane properties, specifically to determine whether it can perform effectively with a high contaminant concentration (Hussain et al., 2022). Ethyl alcohol was also used to synthesize wastewater containing ibuprofen to aid in the solubilization of ibuprofen. Polysulfone (PSF) employs the membrane distillation process as a based membrane. For the membrane coating solution, polydimethylsiloxane (PDMS), tetraethylorthosilicate (TEOS), dibutyltin dilaurate (DBTDL), and n-hexane were used as solvents (Guo et al., 2023).

2.2. Catalyst Preparation

ZrCo catalyst was prepared by mixing $ZrCl_4$ with $CoCl_2{\cdot}6H_2O$ by the predetermined mole ratio in 100 mL of distilled water. The mixture was stirred using a stirrer until a homogeneous solution was obtained. The pH was adjusted to 10 using ammonia (NH_3) (Wang et al., 2015). The solution was then transferred to an autoclave. The autoclave containing the solution was placed in an oven at 220°C for 10 hours. Subsequently, the solution was washed using ethyl alcohol and distilled water, followed by a centrifuge. The washed product was then placed in an oven at 110°C for approximately 24 hours to dry. The dried catalyst was ground using a ball mill or grinder for 20 minutes at a speed of 250 rpm. After grinding to a fine powder, the catalyst was calcinated to ensure its stability according to the variations in (Table 1) (Lee, Lee and Yoon, 2020). The hydrothermal method is used in catalyst synthesis, which utilizes high temperature and pressure. The hydrothermal method produces materials with a high surface area, thereby maximizing catalytic activity (Araujo et al., 2021).

Table 1. Variations of the synthesized catalyst

No	Catalyst Variants	
	Mole Ratio	**Calcination Temperature (°C)**
1.	1:1	400
		500
		600
2.	1:2	400
		500
		600

3.	2:1	400
		500
		600

2.3. Experiment Procedures

The ZrCo catalyst was applied to the membrane using a dip-coating method with PDMS. The study will begin with optimizing all catalysts listed in (Table 1). Subsequently, the catalyst with the optimum calcination temperature will be obtained for further research, specifically the optimization of catalyst concentration. The catalyst concentration applied to the membrane corresponds to the concentration variations in (Table 2). The catalyst-coated membrane will be installed in a membrane module within the air gap membrane distillation (AGMD) reactor (Leaper *et al.*, 2019). To prepare the wastewater containing ibuprofen, 20 mg of ibuprofen was dissolved in 30 mL of ethanol, and then distilled water was added to reach a final volume of 1000 mL, stirring until fully dissolved. The ibuprofen concentration of 20 mg/L was then diluted to 5 mg/L using distilled water (Sahin, Saygi-Yalcin and Saloglu, 2020). The preparation of ibuprofen with a primary concentration of 20 mg/L, which is then diluted to 5 mg/L, is carried out to ensure that the ibuprofen solution occurs significantly and that the ibuprofen compound is evenly distributed, resulting in a uniform concentration (Chopra and Kumar, 2020). The feed temperature or wastewater is maintained at 80°C controlled by a heating bath controller. Based on previous research, an increase in temperature from 40°C to 80°C can significantly enhance the flux. Therefore, the highest temperature was chosen (Luo and Lior, 2017). A pump controller regulates the flow rate of 4 L/min. It helps maintain a more uniform temperature across the entire membrane surface (Qi et al., 2021). The PMS molarity is set at 1.5 mmol/L and mixed before being heated for 10 minutes for the pre-oxidation process before membrane distillation. The membrane distillation process will last for 1 hour, since the flux calculation is expressed in units per hour (Boubakri, Hafiane and Bouguecha, 2017). After 1 hour, the amount of water that has passed through the membrane will be measured using an analytical balance. This measurement will be used to calculate the flux of the catalyst membrane. Additionally, the concentration of ibuprofen will be determined before and after the membrane distillation to assess the efficiency of ibuprofen removal. The concentration of ibuprofen will be measured using a spectrophotometric method at a wavelength of 240 nm with a spectrophotometric instrument following equation (1) and (2) (El-Maraghy and Lamie, 2019).

$$\text{Permeate Flux} = \frac{M}{A \times \Delta t} \quad (1)$$

$$\text{Removal Efficiency (\%)} = (1-\frac{Cp}{Cf}) \times 100\% \quad (2)$$

Where M is the mass of pure water produced from the membrane distillation (MD) process, A is the effective membrane area, and Δt is the distillation time. Cp is the pollutant concentration in the permeate, and Cf is the pollutant concentration in the feed solution (Al-Sairfi, Koshuriyan and Ahmed, 2024).

Table 2. Variability in catalyst concentration with optimum calcination temperature

No	Catalyst Variants	
	Mole Ratio	**Catalyst Concentration (wt%)**
1.	1:1	0
		0.1
		0.25
		0.5
2.	1:2	0
		0.1

No	Catalyst Variants	
	Mole Ratio	Catalyst Concentration (wt%)
		0.25
		0.5
3.	2:1	0
		0.1
		0.25
		0.5

3. Result and Discussion

3.1. Optimum Conditions for the Composition and Calcination Temperature ff ZrCo Catalyst for Ibuprofen Degradation in Membrane Distillation

The study was conducted to determine the optimum catalyst conditions for ibuprofen degradation based on the values of flux and removal efficiency using the membrane distillation process. Initial waste data, such as the concentration of ibuprofen in wastewater, was required. There were nine types of catalysts, specifically with Zr and Co composition ratios of 1:1, 1:2, and 2:1, with calcination temperatures of 400°C, 500°C, and 600°C for each composition to compare the composition and calcination temperature that are suitable or effective in the ibuprofen degradation process. The calcination temperature was selected based on several studies conducted on the CuO-ZrO2 catalyst, with a temperature range of 400°C to 700°C (Wang et al., 2020). The catalyst concentration used was 0.5 wt% of the total mass of the membrane coating composition. The initial concentration of ibuprofen in the synthesized wastewater was measured at 7.26 mg/L. The results obtained from this optimization process consisted of two stages: selecting the optimum catalyst composition and the optimum calcination temperature for the catalyst. The results can be seen in (Figure 1) and (Figure 2).

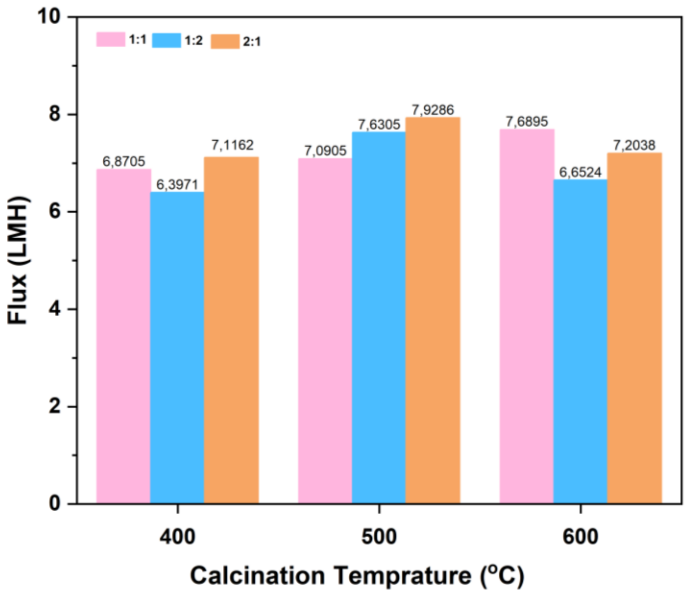

Figure 1. Flux efficiency catalyst composition and calcination temperature

Based on the optimization results of the catalyst, as shown in (Figure 1), the graph displays the flux values for the catalyst with a calcination temperature of 400°C, where the highest flux value was achieved with a catalyst composition of 2:1. For the catalyst with a calcination temperature of 500°C, the highest flux was also observed with the same catalyst composition of 2:1. In contrast, for the catalyst with a calcination temperature of 600°C, the highest flux was obtained with a composition of 1:1. Overall, the highest flux was recorded for the 2:1 catalyst at a calcination temperature of 500°C, amounting to 7.9286

LMH, which means 7.9286 kg of permeate or treated product can be produced per square meter of membrane surface area per hour.

At each calcination temperature, the highest flux is achieved using the ZrCo 2:1 catalyst, with the optimal temperature being 500°C. This suggests that the ZrCo 2:1 catalyst at 500°C has reached an optimal balance between porosity and surface area, thereby enhancing the mass transfer of reactants. The highest flux value was not achieved at the calcination temperature of 600°C, likely due to the sintering effect, which can reduce the surface area (Raso et al., 2023). Additionally, calcination at 500°C may strengthen the structural bonds of the catalyst, allowing it to maintain its active form during operation (Afonasenko et al., 2022).

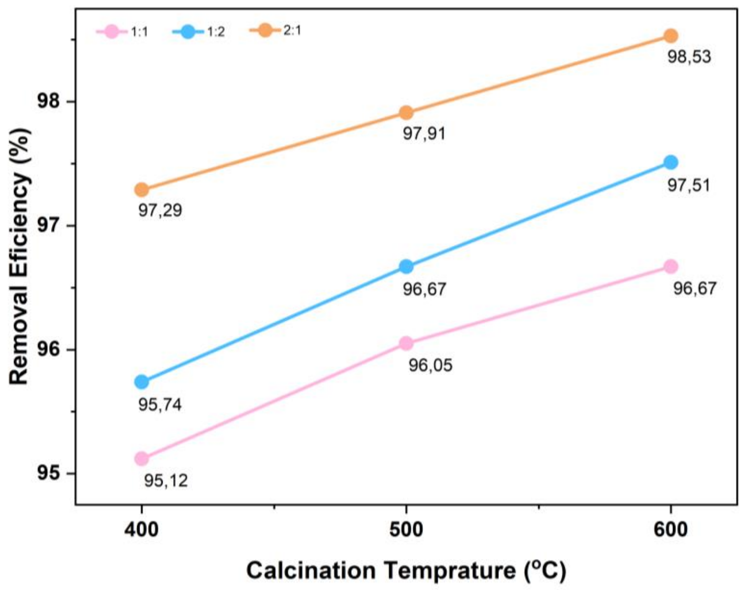

Figure 2. Removal efficiency catalyst composition and calcination temperature

The removal efficiency graph shows an observed increase in percentage removal from 400°C to 600°C. The highest percentage of removal at a calcination temperature of 400°C was found in the 2:1 catalyst, reaching 97.29%. A similar trend occurred for the catalyst at 500°C, where the composition with the highest removal efficiency was also 2:1, achieving 97.91%. The catalyst at 600°C exhibited the highest overall removal efficiency, with the 2:1 composition achieving a percentage removal of 98.53%. The lowest removal value overall was recorded for the 1:1 catalyst, particularly at the calcination temperature of 400°C.

In contrast to the optimal flux value at a calcination temperature of 500°C, the highest ibuprofen removal efficiency is observed when using the ZrCo 2:1 catalyst calcined at 600°C. Several possibilities may account for this observation: when the catalyst is calcined at 600°C, it may undergo phase changes that enhance its reactivity toward ibuprofen as a feed solution in the membrane distillation process. Furthermore, as previously mentioned, the flux value of the catalyst at 600°C is lower than that at 500°C, likely due to the sintering effect that can reduce surface area (Raso et al., 2023). However, the higher temperature of 600°C can also lead to the formation of more stable and effective active sites over time, thereby improving its performance in the degradation of ibuprofen (Aguila et al., 2016).

Thus, the catalyst chosen for the concentration optimization process is the 2:1 composition with a calcination temperature of 600°C. This catalyst was selected due to its superior effectiveness in the degradation of ibuprofen waste, as indicated by its removal efficiency. Although its flux of 7.2038 LMH is not the highest, it still falls within the ideal flux range for membrane distillation. The 2:1 catalyst at a calcination temperature of 600°C likely operates optimally because it contains more zirconium than cobalt. The increased zirconium content contributes to structural stability and results in a larger surface area for the catalyst, allowing for more effective sites for ibuprofen degradation (Othman et al., 2024).

Additionally, cobalt promotes the formation of hydroxyl radicals in catalytic reactions, supported by the presence of zirconium, which helps stabilize reactive species (Wu et al., 2024).

3.2. Optimum Conditions for the Concentration of ZrCo Catalyst for Ibuprofen Degradation in Membrane Distillation

After optimizing the catalyst composition and calcination temperature, the next step is determining the optimum catalyst concentration to apply to the porous membrane surface. Several variations were used to select the optimum catalyst concentration conditions: 0 wt%, 0.1 wt%, 0.25 wt%, and 0.5 wt%. The method employed to identify the optimum catalyst concentration conditions is the same as that used for determining the optimum composition and calcination temperature, with the adjustment that the amount of catalyst applied to the membrane surface corresponds to the specified concentration variations. The concentration of wastewater containing ibuprofen was 7.26 mg/L, synthesized using the same process. The measurement results can be seen in (Figure 3) and (Figure 4) below.

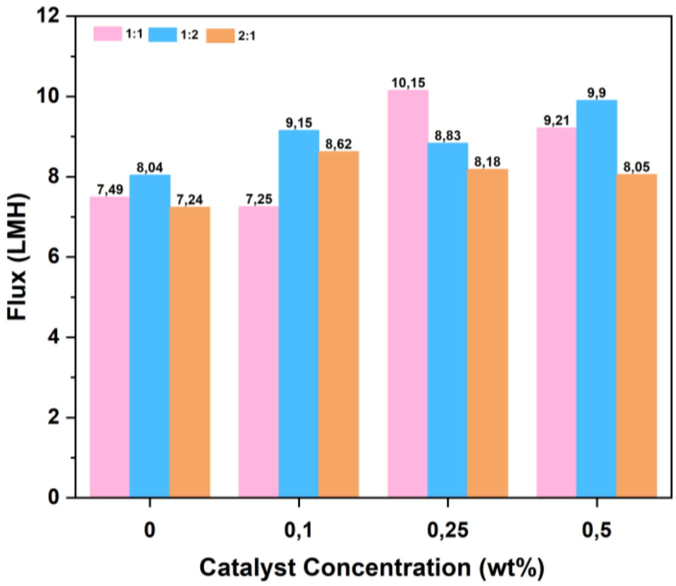

Figure 3. Flux catalyst concentration

The catalyst optimization was determined based on the membrane distillation process's removal efficiency and flux values. The catalysts used for this concentration optimization included all compositions: 1:1, 1:2, and 2:1, with a calcination temperature of 600°C. As shown in **Figure 3**, the membrane without a catalyst exhibited the lowest flux value. At a concentration of 0.1 wt%, the highest flux was achieved with the 1:2 catalyst, measuring 9.15 LMH. For the concentration of 0.25 wt%, the highest value was obtained with the 1:1 catalyst, reaching 10.15 LMH, the highest overall flux value. At a catalyst concentration of 0.5 wt%, the highest flux was recorded with the 1:2 catalyst at 9.9 LMH.

The flux at a concentration of 0.25 wt% is higher than that at 0.5 wt%. This is due to a more uniform distribution of catalyst particles on the membrane surface, which enhances the mass transfer rate (Janowska *et al.*, 2020). Additionally, blockage of the membrane pores can occur when high catalyst concentrations are used, hindering the mass transfer process. Furthermore, thermal efficiency plays a role, as applying catalysts at lower concentrations results in better heat transfer, leading to increased flux (Jiříček *et al.*, 2016).

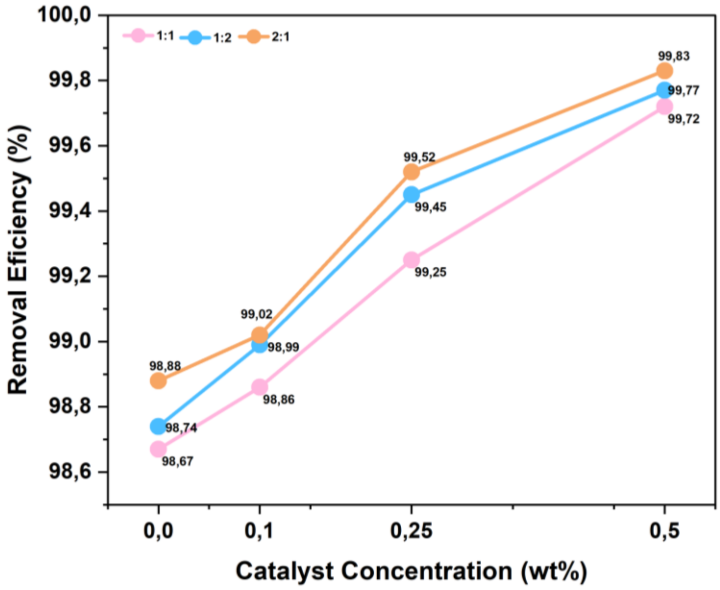

Figure 4. Removal efficiency of catalyst concentration

In the removal efficiency data, it can be observed that all catalyst compositions operated effectively, showing an increase in removal values as the catalyst concentration increased. The 1:1 Zr and Co ratio catalyst showed an increase but had lower removal efficiency compared to the other catalyst compositions. The highest removal efficiency was obtained with the 2:1 catalyst, with an overall maximum value at a concentration of 0.5 wt%, reaching 99.83%, meaning the ibuprofen concentration in the wastewater decreased from 6.395 mg/L to 0.01 mg/L. At the same concentration, the lowest removal efficiency was 99.72% with the 1:1 catalyst composition. The lowest removal occurred at a concentration of 0 wt%, or without using a catalyst, which was 98.67%.

The results show that the highest flux value and removal efficiency occur at different catalyst concentrations. The catalyst with a concentration of 0.5% exhibits higher removal efficiency. This is because higher catalyst concentrations provide more active surface area for the reaction, allowing for the degradation of a larger amount of the pollutant, in this case, ibuprofen (Shao et al., 2022). Additionally, increased reaction kinetics are also observed at higher catalyst concentrations. However, as the concentration increases further, the flux decreases due to polarization effects (Suárez, Del Río and Aravena, 2022).

Based on the research data, it was found that the use of a catalyst at a concentration of 0.5 wt% applied to the porous membrane surface worked effectively. This may be due to a balanced surface coverage, resulting in no aggregation effects (Qi et al., 2021). Additionally, at a concentration of 0.5 wt%, the formation of hydroxyl radicals may have been optimal for the degradation of ibuprofen. However, other factors that may influence the results include the type of membrane where the catalyst adheres and the pH of the wastewater. Therefore, a catalyst at a concentration of 0.5 wt% is considered more effective. Even though the flux value at this concentration is lower than a 2.5 wt% catalyst concentration, the flux value remains within a reasonable range.

3.3. Statistical Test on the Effect of ZrCo Catalyst Composition and Calcination Temperature on Flux and Ibuprofen Removal Efficiency

A normality test was conducted beforehand to determine whether the data follows a normal distribution with Minitab 19. The normality test results indicated that the catalyst's flux and removal efficiency data at each calcination temperature variation follow a normal distribution. The measurement results can be seen in (Table 3).

Table 3. Normality test for flux and removal efficiency data

	P-value		
	400℃	**500℃**	**600℃**
Flux	0.530	0.515	0.624
Removal Efficiency	0.399	0.487	0.614

The normality test was based on hypotheses for data interpretation
H_0: The data follows a normal distribution
H_1: The data does not follow a normal distribution
Rejection regions:
- If P-value < 0.05, H_0 is rejected
- If P-value > 0.05, H_0 fails to be rejected

The normality test results showed that the flux and removal efficiency data at each calcination temperature variation of the catalyst follow a normal distribution. The P-value>0.05 indicates that the null hypothesis (H_0) could not be rejected for the overall data. Therefore, it can be concluded that the data is normal (Widhiarso, 2019).

An analysis of variance (ANOVA) using a two-way approach was conducted with Minitab 19 to investigate the effects of calcination temperature and catalyst type on flux and the efficiency of ibuprofen removal in membrane distillation processes. The statistical analysis was based on hypotheses and rejection regions for data interpretation.

Hypotheses:

a. Flux
   1. H_0: Calcination temperature does not affect flux
      H_1: Calcination temperature affects flux
   2. H_0: Catalyst type does not affect flux
      H_1: Catalyst type affects the flux

b. Removal Efficiency
   1. H_0: Calcination temperature does not affect the removal efficiency of ibuprofen
      H_1: Calcination temperature affects the removal efficiency of ibuprofen
   2. H_0: Catalyst type does not affect the efficiency removal of ibuprofen
      H_1: Catalyst type affects the efficiency removal of ibuprofen

Rejection regions:
- If P-value < 0.05, H_0 is rejected
- If P-value > 0.05, H_0 fails to be rejected

Table 4. Model summary Two-Way ANOVA for calcination temperature and catalyst type on flux

S	R-sq	R-sq(adj)	R-sq(pred)
0.432687	62.97%	25.95%	0.00%

Table 5. Analysis of variance two-way anova for calcination temperature and catalyst type on flux

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Zr:Co	2	0.4178	0.2089	1.12	0.412
Suhu Kalsinasi	2	0.8558	0.4279	2.29	0.218
Error	4	0.7489	0.1872		
Total	8	20.225			

Table 6. Model summary Two-Way ANOVA for calcination temperature and catalyst type on removal efficiency

S	R-sq	R-sq(adj)	R-sq(pred)
0.140870	99.16%	98.33%	95.77%

Table 7. Analysis of Variance Two-Way ANOVA for Calcination Temperature and Catalyst Type on Removal Efficiency

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Zr:Co	2	594.829	297.414	149.87	0.000
Suhu Kalsinasi	2	347.449	173.724	87.54	0.000
Error	4	0.07938	0.01984		
Total	8	950.216			

Based on the data obtained, the P-value for the effect of catalyst calcination temperature on flux was 0.218, greater than 0.05. This indicates that the calcination temperature of the catalyst does not affect the flux produced during the membrane distillation process because H_0 fails to be rejected based on the hypothesis. Similarly, the P-value for catalyst type or composition was 0.412, also greater than 0.05, based on the hypothesis H_0 fails to be rejected, leading to the conclusion that catalyst type or composition does not influence the flux produced in the membrane distillation process.

In contrast, the data for calcination temperature on removal efficiency yielded a P-value of 0.000, which is less than 0.05. Thus, H_0 is rejected. This means that the catalyst's calcination temperature significantly affects the efficiency of ibuprofen removal during the membrane distillation process. A similar result was observed for catalyst type or composition, with a P-value of 0.000 less than 0.05. Thus, H_0 is rejected, indicating that catalyst type or composition significantly influences the efficiency of ibuprofen removal (Kim, 2014).

3.4 Statistical Test on the Effect of ZrCo Catalyst Concentration on Flux and Ibuprofen Removal Efficiency

A normality test was conducted beforehand to determine whether the data follows a normal distribution with Minitab 19. The normality test results indicated that the catalyst's flux and removal efficiency data at each calcination temperature variation follow a normal distribution. The measurement results can be seen in (Table 4).

Table 4. Normality test for flux and removal efficiency data

	P-value			
	0 wt%	0.1 wt%	0.25 wt%	0.5 wt%
Flux	0.449	0.386	0.481	0.534
Removal Efficiency	0.487	0.230	0.350	0.616

The normality test was based on hypotheses for data interpretation

H_0: The data follows a normal distribution

H_1: The data does not follow a normal distribution

Rejection regions:

- If P-value < 0.05, H_0 is rejected
- If P-value > 0.05, H_0 fails to be rejected

The normality test results showed that the flux and removal efficiency data at each calcination temperature variation of the catalyst follow a normal distribution. The P-value>0.05 indicates that the null hypothesis (H_0) could not be rejected for the overall data. Therefore, it can be concluded that the data is normal (Widhiarso, 2019).

An analysis of variance (ANOVA) using a two-way approach was conducted with Minitab 19 to investigate the effects of catalyst concentration and catalyst type on flux and the efficiency of ibuprofen removal in membrane distillation processes. The statistical analysis was based on hypotheses and rejection regions for data interpretation.

Hypotheses:

a. Flux
   1. H_0: Catalyst Concentration does not affect flux
      H_1: Catalyst Concentration affects flux
   2. H_0: Catalyst type does not affect flux
      H_1: Catalyst type affects the flux

b. Removal Efficiency
   1. H_0: Catalyst Concentration does not affect the removal efficiency of ibuprofen
      H_1: Catalyst Concentration affects the removal efficiency of ibuprofen
   2. H_0: Catalyst type does not affect the efficiency removal of ibuprofen
      H_1: Catalyst type affects the efficiency removal of ibuprofen

Rejection regions:

P-value < 0,05, H_0 is rejected

P-value > 0,05, H_0 fails to be rejected

Table 8. Model Summary Two-Way ANOVA for Catalyst Concentration and Catalyst Type on Flux

S	R-sq	R-sq(adj)	R-sq(pred)
0.835246	59.82%	26.34%	0.00%

Table 9. Analysis of variance Two-Way ANOVA for catalyst concentration and catalyst type on flux

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Zr:Co	2	1.835	0.9176	1.32	0.336
Suhu Kalsinasi	3	4.397	14.657	2.10	0.202
Error	6	4.186	0.6976		
Total	11	10.418			

Table 10. Model summary Two-Way ANOVA for catalyst concentration and catalyst type on removal efficiency

S	R-sq	R-sq(adj)	R-sq(pred)
0.0436208	99.41%	98.92%	97.64%

Table 11. Analysis of variance Two-Way ANOVA for catalyst concentration and catalyst type on removal efficiency

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Zr:Co	2	0.07125	0.035625	18.72	0.003
Suhu Kalsinasi	3	185.643	0.618811	325.21	0.000
Error	6	0.01142	0.001903		
Total	11	193.910			

Based on the data obtained, the P-value for the effect of catalyst concentration on flux was 0.202, greater than 0.05. Therefore, H_0 fails to be rejected. This indicates that catalyst concentration does not affect the flux produced during the membrane distillation process. Similarly, the P-value for catalyst type or composition was 0.336, exceeding 0.05. Therefore, H_0 fails to be rejected, concluding that catalyst type or composition does not influence the flux produced in the membrane distillation process.

In contrast, the data for catalyst concentration on removal efficiency yielded a P-value of 0.000, less than 0.05, based on the hypothesis H_0 is rejected. This means that catalyst concentration significantly affects the efficiency of ibuprofen removal during the membrane distillation process. A similar result was observed for catalyst type or composition, with a P-value of 0.003. Therefore, H_0 is rejected, indicating that catalyst type or composition influences the efficiency of ibuprofen removal (Pandis, 2015).

4. Conclusion

The optimization of the ZrCo catalyst in membrane distillation was conducted to remove ibuprofen. Based on the optimum conditions, ZrCo, as indicated by the flux and removal efficiency values, successfully catalyzed the degradation of ibuprofen. Among all calcination temperatures, the most effective catalyst, based on removal efficiency, was the catalyst with a 2:1 composition. However, overall, the 2:1 catalyst calcined at 600°C emerged as the optimal catalyst, achieving a removal efficiency of 98.53% with a flux value of 7.2038 LMH. In the catalyst concentration optimization, all catalyst ratios were tested at a calcination temperature of 600°C, revealing optimal efficiency at a concentration of 0.5 wt% with a 2:1 catalyst ratio with a flux value of 8.05 LMH. Overall, the optimal catalyst was determined to be at a concentration of 0.5 wt% with a 2:1 ratio and a calcination temperature of 600°C. For future research, adjustments to various factors affecting catalyst performance or membrane distillation performance can be made to achieve maximum processing efficiency and facilitate implementation at an industrial scale.

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