MECHANISM OF MEMBRANE FOULING IN HYBRID MEMBRANE PHOTOCATALYTIC REACTOR FOR PALM OIL MILL SECONDARY EFFLUENT TREATMENT

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ABSTRACT

Palm oil mill secondary effluent (POMSE) is a byproduct of the biological treatment of palm oil mill effluent. This research aims to investigate the mechanism of membrane fouling in the treatment of POMSE using a hybrid membrane photocatalytic reactor (MPR). The effectiveness of MPR in POMSE treatment is currently limited due to membrane fouling on the membrane surface. This study focuses on understanding the various mechanisms of membrane fouling, including complete blocking, intermediate blocking, standard blocking, and cake filtration. The determination of each fouling mechanism is achieved through an analysis of normalized flux data employing the Wiesner and Aptel equation. The results demonstrate a high degree of model fitness ($R^2 = 0.9576$) for MPR Run 3, confirming its effectiveness. Based on the (R^2) values and the fitted parameter (Ks^(-1)), it is evident that, under varying pH levels, catalyst types, catalyst loading, and initial POMSE concentrations, the cake formation fouling mechanism prevails in MPR Run. In conclusion, this research holds promising potential for implementation in the wastewater treatment industry while ensuring compliance with environmental regulations.

Keywords: *Membrane fouling, Palm oil mill secondary effluent, Membrane photocatalytic reactor*

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1.0 INTRODUCTION

The oil palm tree is renowned for its significant oil production, primarily utilized for cooking in developing countries. Originally native to West Africa, it is now extensively cultivated in Malaysia and Indonesia, the world's largest palm oil-producing nations [1-5]. Palm oil, being a highly profitable crop, has gained attention for its potential health benefits due to its higher saturated fat content compared to vegetable oil [6-10]. The palm oil industry is well-known for its vast production scale and the high-quality cooking oil it produces, predominantly for use in developing countries. However, it has also contributed to environmental degradation through the generation of substantial by-products during the extraction process, particularly in terms of water quality. The treated palm oil mill effluent (POME) through biological treatment results in what is termed palm oil mill secondary effluent (POMSE). POMSE, a secondary effluent treated from the raw POME, exhibits high turbidity, color intensity, and an organic load of biochemical oxygen demand (BOD) that still fails to meet the environmental department's discharge requirements, emitting an unpleasant odor due to its elevated phosphate and nitrogen content [11-15]. As a consequence, it

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necessitates treatment before discharge into the environment, such as lakes and rivers, to prevent adverse effects on aquatic life and water supplies.

Membrane fouling is a phenomenon that occurs in membrane filtration and leads to a decline in permeate flux. This presents a significant challenge in membrane filtration systems, particularly in industries that employ membrane technology, such as wastewater treatment [16-20]. Membrane fouling typically results from the deposition of particles and suspended solids on the membrane surface and even within the membrane pores. It can be classified as either reversible or irreversible fouling based on the strength of attachment to the membrane. Reversible fouling occurs only on the surface of the membrane and can be removed by reverse permeate flow at the end of each filtration cycle. Irreversible fouling, on the other hand, occurs within the membrane pores and cannot be eliminated by reverse permeate flow; chemical cleaning is the only option, but the membrane may not fully recover its original flux. In current wastewater treatment methods, various approaches, including physical, chemical, biological, and sludge treatment methods, are implemented. The chemical method, specifically the coagulation and flocculation process, is commonly employed in industrial processing. However, this conventional method involves high costs, particularly in the procurement of alum, which must be added to the untreated POMSE. Costs escalate with the volume of POMSE requiring treatment.

The membrane photocatalytic reactor (MPR) emerges as a promising method for treating palm oil mill effluent, especially the secondary effluent POMSE [21-24]. An MPR is a reactor system that integrates photocatalysis and membrane technology. It employs a membrane with a dual function: to act as a physical barrier separating the photocatalyst from the reaction mixture and to serve as a selective filter, permitting only certain molecules to pass while blocking others. The photocatalyst can either be immobilized on the membrane's surface (photocatalytic membranes) or suspended within the reaction mixture. MPR offers several advantages over traditional methods, including precise control of residence time, confinement of the photocatalyst within the membrane's environment, simultaneous photocatalyst and membrane filtration, and enhanced photocatalyst capacity [25].

Despite the benefits of membrane filtration, membrane fouling remains a significant challenge. Fouling typically results from the accumulation of substances on the membrane's surface or within its pores, leading to a decline in membrane performance [26]. The fouling process can impact the separation efficiency for the targeted species in the feed, increase membrane separation resistance, and reduce overall efficiency. However, limited research has been conducted on the membrane fouling mechanism, especially in the context of POMSE treatment using a hybrid MPR. Therefore, this study investigates the mechanism of membrane fouling in a hybrid MPR for POMSE treatment.

2.0 MATERIALS AND METHODS

The summary of research activities is given in Figure 1.

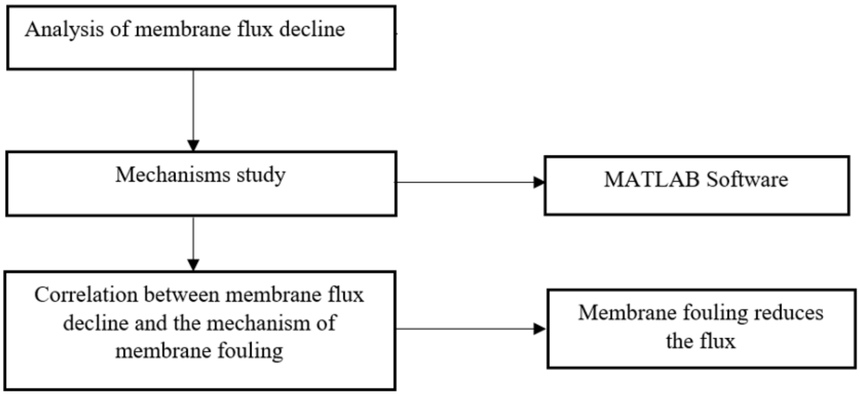

Figure 1: Summary of methodology

2.1 Analysis of Flux Decline

The flux decline analysis was analysed through a series of equation involved comprises of the volume of the permeate (V) per unit area (A) per unit time (t), in order to obtain the pure water flux (J_o) according to the equation:

$$J_o = \frac{V}{At} \qquad \text{Eq. 1}$$

Meanwhile, for instantaneous permeate flux (J) for a particular run of MPR, was evaluated in the interval of time t_1 and t_2 by:

$$J = \frac{(V_2 - V_1)}{A(t_2 - t_1)} \qquad \text{Eq. 2}$$

In addition, under various parameter involved in a particular system, the flux was identified as a normalized flux and calculated using the equation:

$$\text{Normalized flux} = \frac{J}{J_o} \qquad \text{Eq. 3}$$

Analysis of flux decline was established through a few parameters used which are pH, catalyst, catalyst loading and also initial concentration of POMSE sample.

2.2 Mechanism of membrane fouling

The elucidation of membrane fouling mechanisms in the hybrid membrane photocatalytic reactor for the treatment of POMSE involved the application of four standardized blocking models. Among these models, the Wiesner and Aptel equation played a pivotal role in identifying the specific fouling mechanism. These fouling mechanisms encompassed complete blocking, standard blocking, intermediate blocking, and cake filtration, as outlined in reference [27]. The utilization of these models was instrumental in discerning the various types of fouling mechanisms that manifested within the specific membrane system.

The linearized form of the Wiesner and Aptel model, as depicted in Table 1, presented four distinct equations, each associated with a specific constant value (n). These constants varied depending on the nature of the fouling mechanism under consideration. Through rigorous analysis and experimentation, the linearized equations were meticulously fitted to the obtained flux data. This fitting process was conducted using MATLAB R2016b software, facilitating a comprehensive understanding of the fouling mechanisms at play and enabling the development of effective mitigation strategies.

Table 1: Blocking filtration laws

Blocking filtration law	Constant	Linearized equation
Complete blocking model	2	$-\ln\left(\frac{J_o}{J}\right) - 1 = Kt$
Standard blocking model	1.5	$\sqrt{\frac{J_o}{J}} - 1 = Kt$
Intermediate blocking model	1	$\left(\frac{J_o}{J}\right) - 1 = Kt$
Cake filtration model	0	$\left(\frac{J_o}{J}\right)^2 - 1 = Kt$

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The analysis of membrane fouling mechanisms involves the use of four distinct blocking models, each representing unique scenarios with varying characteristics. These models may seem contradictory due to their individual attributes:

Complete Blocking: In this scenario, particles completely obstruct the pores on the membrane's surface, resulting in the cessation of water flow through the membrane. This type of blocking is akin to a complete blockade, where water cannot pass through due to pore obstruction.

Standard Blocking: Standard blocking occurs when particles deposit on the membrane wall's surface, gradually reducing the volume of membrane pores. While water flow is not entirely halted as in complete blocking, it becomes progressively restricted as more particles accumulate. This fouling type leads to a gradual decline in membrane performance.

Intermediate Blocking: Intermediate blocking occurs when particles deposit on other particles, forming double or triple layers. These multiple layers can eventually obstruct some of the membrane pores, causing a partial reduction in water flow. It represents a scenario where fouling is more complex than standard blocking but not as severe as complete blocking.

Cake Filtration: Cake filtration takes place when particles accumulate on the membrane surface to such an extent that, over time, the membrane becomes significantly less effective or even unusable. This buildup of particles resembles the formation of a cake-like layer on the membrane, which hampers water flow and severely impacts system performance.

Figure 2 likely illustrates these blocking models in a schematic diagram, showcasing how each model manifests and contributes to membrane fouling in different ways. These models, while distinct, collectively provide a comprehensive understanding of the fouling mechanisms that can occur in a hybrid membrane photocatalytic reactor for palm oil mill secondary effluent treatment. The choice of which model best represents the real-world fouling situation depends on the specific characteristics of the effluent and the membrane system under investigation.

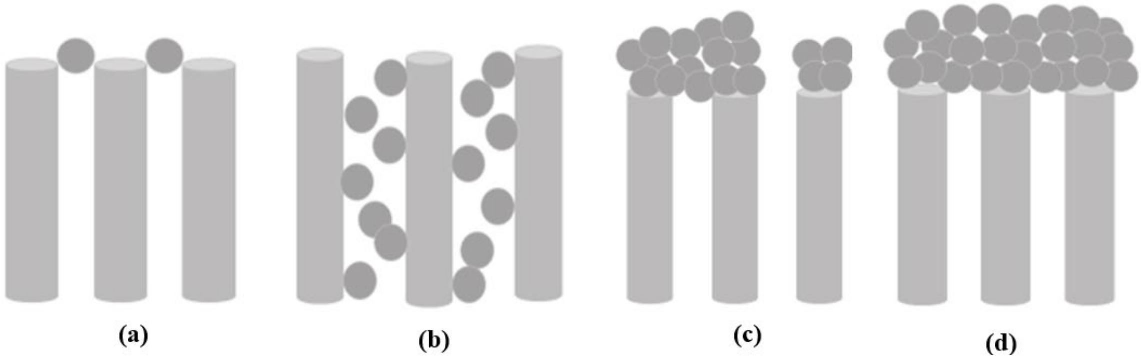

Figure 2: Schematic diagram of blocking models (a) complete blocking (b) standard blocking (c) intermediate blocking (d) cake filtration

3.0 RESULTS AND DISCUSSION

3.1 Analysis of Flux Decline

The investigation into flux decline in the hybrid membrane photocatalytic reactor for POMSE treatment encompassed an examination of several critical parameters, including pH, catalyst type, catalyst loading, and the initial POMSE concentration. The results of this analysis unveiled a

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discernible pattern of normalized flux reduction over time. This gradual decrease in flux was graphically represented, with the highest flux observed at the commencement of the treatment process and the lowest flux recorded at its conclusion. Table 2 and Figure 3 clearly depict that within the initial 5 minutes of the treatment process, the normalized flux remained relatively high, at a value of 0.4. However, as the treatment process progressed, this value progressively decreased. In the final 5 minutes of the process, the normalized flux reached its minimum level, measuring at 0.14. Throughout the majority of the treatment process, there was no significant reduction in normalized flux, signifying the system's stability.

Notably, an interesting observation was made between the 45th and 55th minutes of the treatment process. During this interval, there was a slight but significant decline in flux when compared to readings at other time points. Specifically, at the 45th minute, the normalized flux registered at 0.28, which decreased to 0.24 at the 50th minute and further dropped to 0.22 at the 55th minute. This observed dip in normalized flux between the 45th and 55th minutes suggests that specific dynamic factors or processes may come into play within the reactor during this timeframe, affecting the membrane's performance. Further investigation and analysis of the particular conditions, such as alterations in pH, catalyst behavior, or membrane fouling, during this time interval could yield valuable insights for optimizing the performance of the hybrid membrane photocatalytic reactor for POMSE treatment.

Table 2: MPR Run 3 with pH 2 POMSE concentration 75% catalyst loading 0.12g/L

No	Time (hr)	Volume (L)	Solution flux (J)	Normalised flux (J/Jo)
1	0.08	0.0040	23.3009	0.4000
2	0.17	0.0036	20.9708	0.3600
3	0.25	0.0034	19.8058	0.3400
4	0.33	0.0034	19.8058	0.3400
5	0.42	0.0032	18.6407	0.3200
6	0.50	0.0028	16.3106	0.2800
7	0.58	0.0028	16.3106	0.2800
8	0.67	0.0028	16.3106	0.2800
9	0.75	0.0028	16.3106	0.2800
10	0.83	0.0024	13.9805	0.2400
11	0.92	0.0022	12.8155	0.2200
12	1.00	0.0022	12.8155	0.2200
13	1.08	0.0022	12.8155	0.2200
14	1.17	0.0022	12.8155	0.2200
15	1.25	0.0022	12.8155	0.2200
16	1.33	0.0020	11.6504	0.2000
17	1.42	0.0020	11.6504	0.2000
18	1.50	0.0020	11.6504	0.2000
19	1.58	0.0020	11.6504	0.2000
20	1.67	0.0020	11.6504	0.2000
21	1.75	0.0018	10.4854	0.1800
22	1.83	0.0018	10.4854	0.1800
23	1.92	0.0018	10.4854	0.1800
24	2.00	0.0016	9.3203	0.1600
25	2.08	0.0016	9.3203	0.1600
26	2.17	0.0016	9.3203	0.1600
27	2.25	0.0016	9.3203	0.1600
28	2.33	0.0014	8.1553	0.1400
29	2.42	0.0014	8.1553	0.1400
30	2.50	0.0014	8.1553	0.1400
31	2.58	0.0014	8.1553	0.1400
32	2.67	0.0014	8.1553	0.1400
33	2.75	0.0014	8.1553	0.1400
34	2.83	0.0014	8.1553	0.1400
35	2.92	0.0014	8.1553	0.1400

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36	3.00	0.0014	8.1553	0.1400

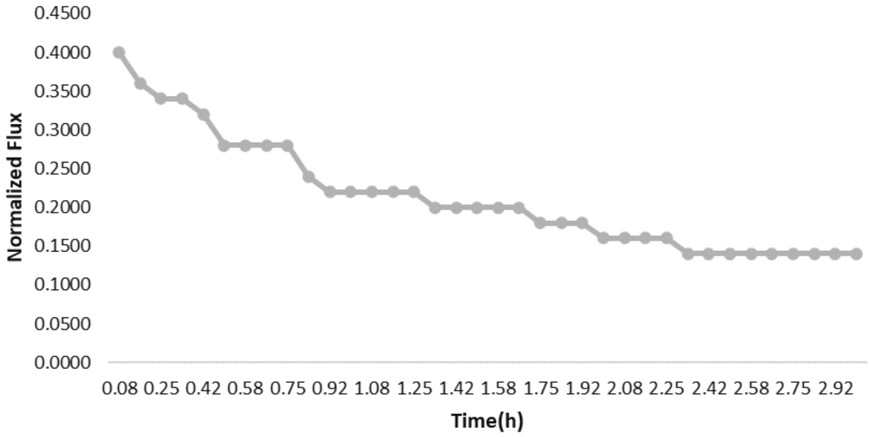

Figure 3: Normalized flux against time for MPR Run 3

3.2 Mechanism study via MATLAB software

The study on the mechanism of membrane fouling in the MPR for the treatment of POMSE involved the utilization of four standardized blocking models, with a central role attributed to the Wiesner and Aptel equation. These models encompassed complete blocking, standard blocking, intermediate blocking, and cake filtration, each providing unique insights into the fouling process.

Figures 4(a)-(d) present the MATLAB results, which include the determination coefficient (R^2) and the reciprocal of the specific cake resistance (Ks^(-1)), alongside graphical representations of MPR performance trends. A careful analysis of these results revealed a distinct pattern: only the cake formation mechanism exhibited a strong fit with the obtained data, as evidenced by the highest R^2 value. In contrast, the other fouling mechanisms demonstrated a significantly lower degree of model fitness, with R^2 values falling below 0.9.

Based on these findings, it is reasonable to conclude that the mechanisms of complete blocking, intermediate blocking, and standard blocking do not exert substantial influence within this specific MPR system designed for POMSE treatment. Instead, it is the cake formation mechanism that predominantly governs as the primary fouling mechanism impacting the system's performance. This insight holds significance for optimizing MPR operation and maintenance, directing focus toward addressing cake formation and developing strategies to mitigate its impact on membrane fouling. Consequently, this optimization enhances the overall efficiency of the POMSE treatment process.

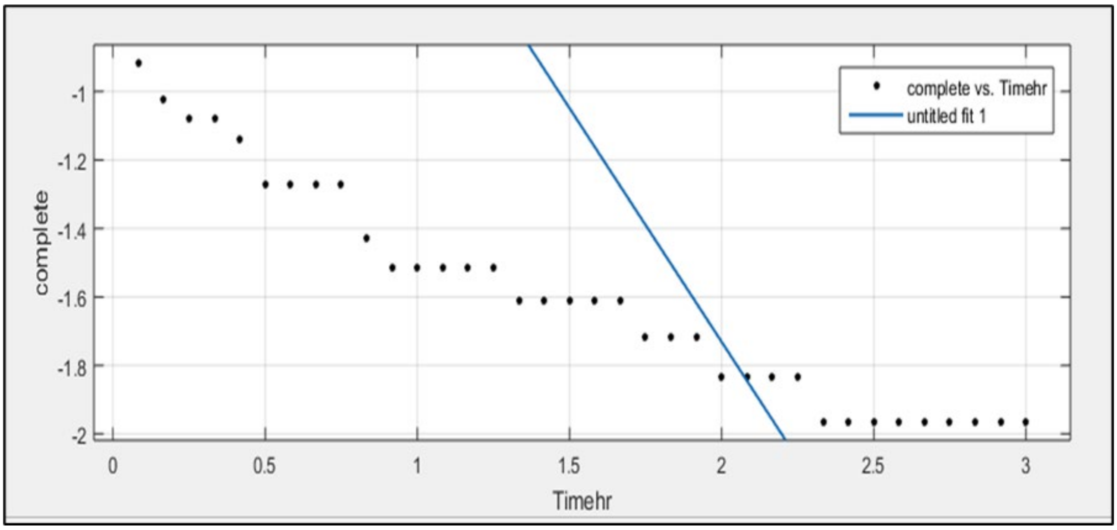

Figure 4 (a): MATLAB result for complete blocking

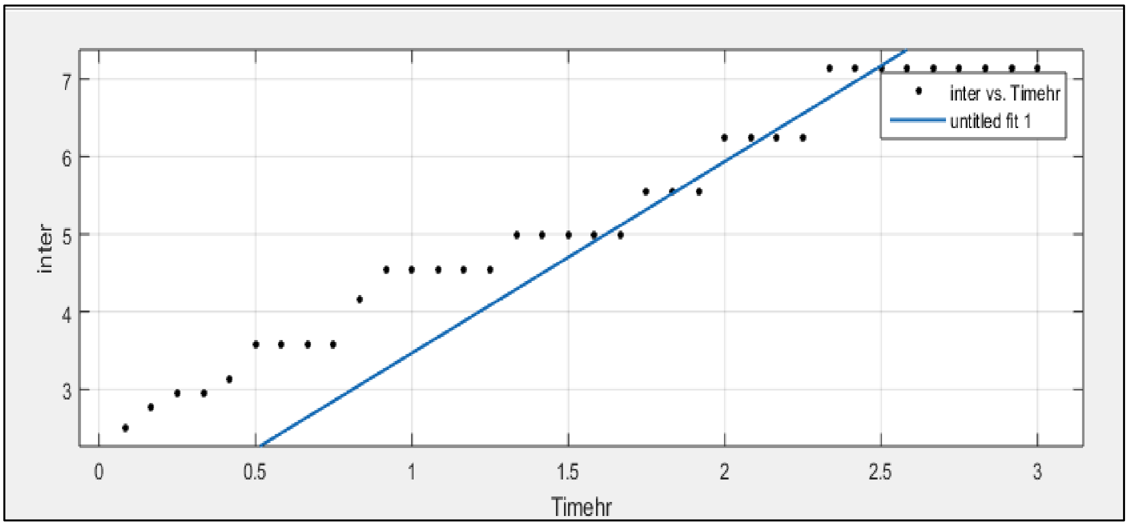

Figure 4 (b): MATLAB result for intermediate blocking

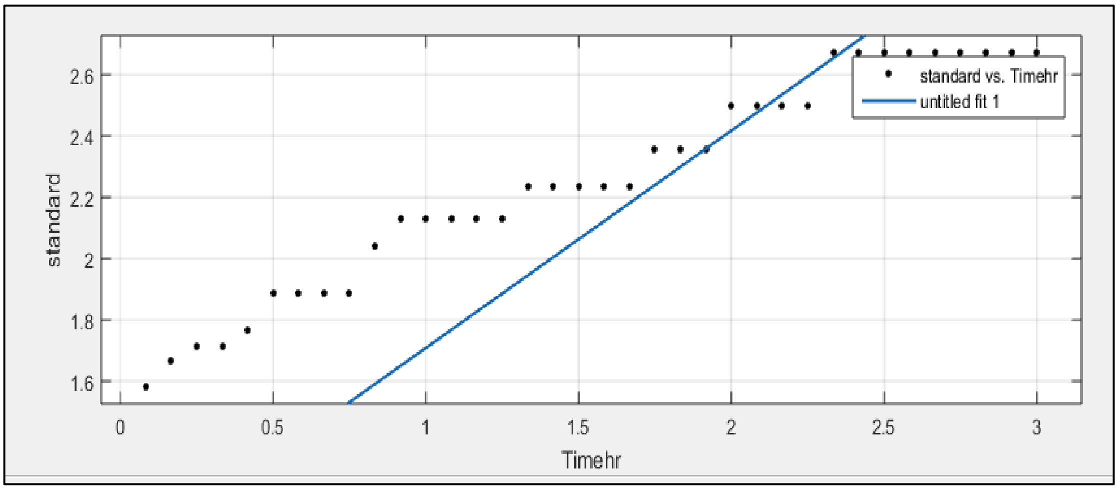

Figure 4 (c): MATLAB result for standard blocking

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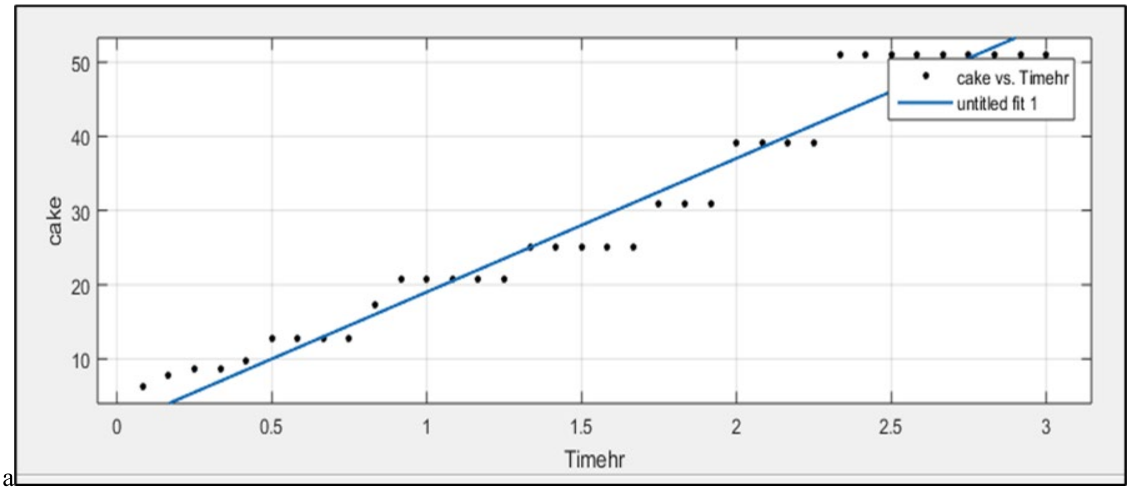

a

Figure 4 (d): MATLAB result for cake formation

3.3 Correlation between membrane flux decline and mechanism of membrane fouling

Table 3 offers a comprehensive summary of the degree of model fitness (R^2) and the fitted parameter (Ks^(-1)) for all four fouling mechanisms investigated in the study. The cake formation mechanism exhibited the highest R^2 value, indicating that, within the specified parameters, the dominant fouling mechanism in the hybrid MPR designed for the treatment of POMSE was indeed cake formation. This outcome can be attributed to the continual adherence of residual particles to the membrane's surface, leading to their gradual accumulation and thickening over time. Several factors within the experimental setup contribute to this phenomenon:

The concentration of POMSE in the sample proved to be sufficient for promoting the accumulation of particles on the membrane surface. Elevated levels of particulate matter in the effluent play a significant role in the development of a cake layer on the membrane. The study suggests that the catalyst loading in the MPR system may not have been adequate for the effective degradation of the pollutants present in the POMSE sample. As a result, non-degraded pollutants remained suspended in the wastewater, further contributing to particle accumulation on the membrane. The high R^2 value for the cake formation mechanism indicates its predominance in the MPR system. The accumulation of particles on the membrane surface, influenced by the POMSE concentration and the catalyst's effectiveness, underscores the importance of optimizing various operational parameters to mitigate fouling and enhance the efficiency of the POMSE treatment process in the hybrid membrane photocatalytic reactor.

Table 3: Degree of model fitness (R^2) and fitted parameter ($K(s^{-1})$) for all 4 types of fouling mechanism

Blocking filtration law	R^2	K (s^{-1})
Complete blocking	-9.439	-1.366
Intermediate blocking	0.713	2.469
Standard blocking	0.05624	0.7086
Cake formation	0.9576	18.02

4.0 CONCLUSION

The conclusions drawn from the findings and analysis of this study are as follows:

1. Normalized Flux Decline: Throughout the investigation, a consistent trend was observed, indicating a progressive reduction in normalized flux over time. This decline was primarily attributed to the accumulation and deposition of POMSE particles on the surface of the

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membrane within the hybrid MPR. As time advanced, the gradual buildup of these particles on the membrane hindered the flow of treated water through the system.

2. Identified Fouling Mechanism: The study successfully identified the primary mechanism responsible for membrane fouling under the optimal conditions of POMSE treatment. It was determined that the predominant mechanism was cake filtration. This predominance was primarily due to the high concentration of POMSE present in the sample. The elevated concentration of POMSE particles made the degradation of these particles by the catalyst inefficient, resulting in their accumulation on the membrane surface. This accumulation of particles aligns with the characteristics of cake filtration, where a layer of particles forms and hampers membrane performance.

In summary, the research established that the gradual decline in normalized flux during the POMSE treatment process was a consequence of the accumulation and deposition of POMSE particles on the membrane surface. This fouling mechanism, identified as cake filtration, was primarily attributed to the high concentration of POMSE, which impeded efficient particle degradation. These findings provide valuable insights into the factors influencing the performance of the hybrid membrane photocatalytic reactor for POMSE treatment and underscore the significance of optimizing system parameters to enhance the effectiveness of treatment processes.

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