

Evaluation Of A Membrane Bioreactor For The Treatment Of Oil Refinery Runoff From Al-Dora Facility In Baghdad, Iraq, And Its Multi-Kinetic Modeling

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An oily effluent from the Al-Dora petroleum refinery in Baghdad, Iraq, was investigated to evaluate the performance of a membrane bioreactor (MBR) under various operating conditions. The system was operated at hydraulic retention times (HRTs) ranging from 12 to 24 hours, with mixed liquor suspended solids (MLSS) concentrations of 6.8 and 8.7 g/L. Evolutionary polynomial regression (EPR) was employed to integrate several kinetic models, including first-order, modified Stover–Kincannon, and Grau second-order models, to predict and interpret bioreactor performance. Experimental results showed that at an MLSS concentration of 8.7 g/L and an HRT of 24 hours, the chemical oxygen demand (COD) removal efficiency reached approximately 96.4%. Overall, the findings demonstrated that higher MLSS concentrations and longer HRTs positively influenced the organic removal efficiency of the MBR system. The EPR model exhibited high predictive accuracy, confirming its effectiveness in describing the nonlinear behavior of MBRs treating refinery effluent. Optimization analysis based on EPR modeling identified optimal operating conditions at an HRT of approximately 21 hours and an MLSS concentration of about 8.3 g/L. Furthermore, kinetic evaluation revealed that the modified Stover–Kincannon and Grau second-order models provided a more realistic representation of COD removal behavior within the investigated operating range, outperforming the first-order kinetic model.

Keywords: Membrane bioreactor (MBR), Oily wastewater treatment, Petroleum refinery effluent, Chemical oxygen demand (COD) removal, Mixed liquor suspended solids (MLSS).

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1. Introduction

Wastewater from petroleum refineries often contains a complex mixture of aliphatic and aromatic hydrocarbons, inorganic compounds, heavy metals, and dissolved and suspended solid particles [1, 2]. Significant volumes of wastewater are produced by these refineries. Waste water produced by petroleum refineries is between 0.4 and 1.6 times the quantity of crude oil that is processed in the refineries [3, 4]. The average daily amount of water utilized

per barrel of crude oil that is refined in the refineries is from 65 to 90 gallons per barrel of oil that is refined. These levels of wastewater production, in conjunction with the ever-increasing environmental discharge regulations and the growing problem of water scarcity, particularly in arid and semi-arid regions, lend support to the importance of recycling and reusing wastewater in the process of refining petroleum and prompt the implementation of efficient waste treatment technologies [3]. Primary and secondary treatment are the two types of treatment that are typically

provided by the majority of petroleum refinery waste water (PRW) treatment plants. Additionally, secondary treatment often makes use of activated sludge systems in order to break down the dissolved organic material and the emulsified hydrocarbons that are still present [5, 6]. Primary treatment typically involves the physical and physicochemical separation of oils in the form of free and emulsified oils. In recent years, membrane bioreactors (MBRs) have emerged as a novel kind of advanced PRW treatment. This is due to the fact that MBRs produce effluents of superior quality and may be utilized without experiencing any failure [7, 8]. In spite of the fact that the Dorr-Oliver Company first developed the MBR technology in the late 1960s for the purpose of treating sewage on board ships, the technology has undergone significant development over the course of the last few decades and is now utilized for the treatment of a wide variety of municipal and industrial wastewater [4, 7, 9].

The efficacy of MBRs in the treatment of effluents from urban and industrial settings has been demonstrated by a number of studies [4, 10, 11]. A cross-flow MBR system that utilized tubular ceramic membranes was evaluated by Rahman and Al-Malack [7], who were the first to proclaim the utilization of MBR for the treatment of PRW. A comparative investigation of submerged MBRs with polymeric flat-sheet and hollow-fiber membranes was carried out by Torres et al. [12] for a later time. The use of batch reactor membrane sequencing with a HRT ranging from 8 to 24 hours was also studied by Shariati et al. [6] when it came to the treatment of synthetic PRW. MBR systems have been examined in recent times as a potential means of enhancing the treatment of wastewater from refractory refineries [4]. This combination of direct UV photolysis and UV/H₂O₂ enhanced oxidation systems has been considered. The performance and environmental conditions of MBR systems are dependent on a variety of parameters [7]. Both the organic loading rate (OLR) and the associated notion of hydraulic retention time (HRT) are extremely significant in the process of developing and operating biological treatment systems [13]. The OLR and HRT are the most important of these rates. The volume of the reactor, the cost of the capital, and the efficiency of the treatment are all directly influenced by HRT. Long HRTs have a tendency to boost the efficiency of the removal of organic pollutants [14, 15]. This is despite the fact that low HRTs, which indicate large OLRs, result in smaller reactor models. The problem of membrane fouling is one of the most fundamental reasons that the MBR technology has not become extensively adopted [16]. This is despite the fact that the advantages of membrane fouling are readily apparent. The

presence of resistant and inhibitory compounds in industrial wastewater, such as PRW, contributes to the further enhancement of fouling behavior. This, in turn, increases the relevance of the HRT in determining the performance of the bioreactor as well as the likelihood of fouling [6, 17]. It is regarded to be crucial in identifying the kind of sludge, resilience to filtration, and rate of fouling [18]. The mixed liquid suspended solids (MLSS) concentration is another key operational parameter that is required to be evaluated. Even while increased levels of MLSS contribute to longer sludge retention periods (SRTs) and a drop in the ratio of food to microorganisms (F/M), increases in MLSS levels do increase the likelihood of fouling. To achieve a balance between the effectiveness of the therapy and the expenses associated with the surgeries, it is necessary to determine the ideal concentration of MLSS. In addition, the selection of membrane materials is an essential component in the functioning of the MBR. Some of the factors that can have a substantial impact on fouling behavior are changes in membrane morphology, pore size distributions, surface hydrophobicity, and chemical resistance [7, 19]. They exhibit high permeability, mechanical strength, chemical and thermal stability, and relatively good fouling resistance, which makes them very appropriate in the oily waste water treatment processes [20, 21]. Polyvinylidene fluoride (PVDF) membranes are one of the materials that are used in the waste water treatment processes the most frequently. There are a number of reasons for this.

When it comes to comprehending, predicting, and optimizing the functioning of the bioreactor, mathematical modeling is an essential tool as [22]. In order to improve the monitoring and management of the process, as well as the scaling up of the process, these models are helpful in arranging experimental data inside a particular framework using a specific framework. In addition, outcome modeling may be employed to ascertain the predominant aspects that regulate substrate removal, anticipate the overall performance in full-scale operation, and maximize the parameters under which the operation is carried out [23, 24]. Both Grau et al. [25] and Grady and Williams [26] made the observation that the concentration of the influent should not be considered to be independent of the concentration of the effluent when studying mixed microbial cultures. To describe substrate removal kinetics in terms of influent substrate concentration and reactor loading, first-order, Grau second-order, and modified Stover-Kincannon models are frequently utilized [22, 23, 27]. This is because these models are commonly employed. An aerobic submerged membrane bioreactor that was equipped with an immersed PVDF membrane was developed for the purpose

of treating actual petroleum refinery effluent at the Al-Dora Refinery in Baghdad, Iraq. The major objective of this article was to investigate the effectiveness of this bioreactor in treating the wastewater. Both the elimination of chemical oxygen demand (COD) and the realistic fluctuations in the characteristics of the influent wastewater were taken into consideration during the evaluation of the bioreactor, which was carried out at a variety of hydraulic retention durations and MLSS concentrations. Furthermore, in order to anticipate and explain the bioreactor performances, evolutionary polymer regression (EPR) and three different kinetic models were utilized. These models were first-order, Grau second-order, and modified Stover-Kincannon. In addition to providing kinetic parameters that may be utilized in the process of improving and scaling up the procedure, this study provides a major knowledge of the validity of MBR technology in the treatment of refinery wastewater under the operational circumstances of Iraq.

2. Materials and methods

2.1. Experimental Design

Figure 1 provides a schematic representation of the experimental design that was utilized during the duration of this aforementioned investigation. The system consisted of a laboratory-scale aerobic membrane bioreactor (MBR) with an effective working volume of 6.2 liters. It was equipped with a commercial polyvinylidene fluoride (PVDF) flat-sheet membrane module (PVDF-MFB). A summary of the membrane specs may be found in Table 1. The membrane module that was buried into the aeration tank was provided by Sepro Membranes, which is located in the United States.

The MBR was run under aerobic conditions, and the dissolved oxygen (DO) concentration was maintained at 2.6 ± 0.3 mg/L by keeping the air flowing continuously through the MBR. All the experimental runs were done at a system temperature of 22 ± 2 C. Table 2 gives a summary of the main operational parameters of the MBR, such as hydraulic retention time (HRT), mixed liquor suspended solids (MLSS), and permeate flux.

Real wastewater from a petroleum refinery was used as the influent for the MBR. This wastewater was collected from the effluent of the API oil-water separator unit at the Al-Dora Refinery wastewater treatment plant in Baghdad, Iraq. On a daily basis, samples were collected under an influent system, and the physicochemical characteristics of these samples are presented in Table 3. The membrane was scourged with air in order to limit the amount of fouling that occurred, and aeration was delivered continually in order to assist the transfer of adequate oxygen.

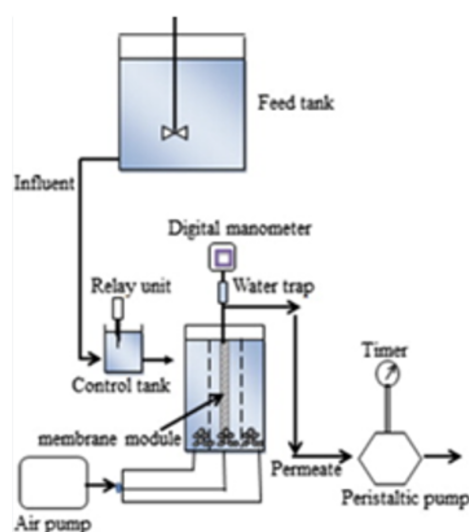


Fig. 1. The MBR system represented schematically

The other step during the experimental period was that the membrane was kept clean through a two-step cleaning protocol. Physical cleaning was initially done by the use of permeate backwashing about 14-15 h, which was then followed by the use of chemical cleaning that was done using 5% (w/v) sodium hypochlorite (NaOCl) solution on the membrane in about 7 h time.

2.2. Analytical methods

All of the experiments included measurements of chemical oxygen demand (COD), and mixed liquor suspended solids (MLSS) as per the Standard Methods of the Examination of Water and Wastewater [28]. Temperature, pH and dissolved oxygen (DO) were measured on-site using the Metrohm 827 pH meter and WTW inoLab Oxi 730 dissolved oxygen meter, respectively. Measurements were done in three replications and average values were reported to maintain the reliability of the analysis.

2.3. Model development

According to the modeling theory in place, it is possible to utilize white-box, grey-box, and black-box models to analyze the behavior of a system, make predictions and conduct interpretation of mechanisms that govern system behavior [29]. White-box models are constructed solely based on first principles; however, the applicability of white-box models is commonly constrained by the large data volume and complexity of systems. Black-box models are purely experimental, statistically-fit, and provide simplicity, but cannot be interpreted mechanistically. Grey-box models integrates physical knowledge with data-driven techniques

Table 1. Membrane structures properties.

Properties	Values
Materials	Polyvinylidene fluoride (PVDF)
Configurations	Flatsheet
Pores sizes (μm)	0.38
Effective surface area (cm^2)	640
Lengths (cm)	16
Membranes fluxes ($\text{L}/\text{m}^2 \cdot \text{h}$)	4.5–8.5

Table 2. Different hydraulic retention times (HRT) each have their own unique operational properties.

Parameters	1–14 days	14–28 days	28–40 days	40–52 days	52–62 days	62–72 days
MLSS (g/L)	8.7	8.7	8.6	8.6	6.8	6.8
HRT (h)	24	18	15	12	24	18
Flux ($\text{L}/\text{m}^2 \cdot \text{h}$)	4.2	6.2	7.1	8.3	4.3	6.1

Table 3. Characteristics of the oily wastewater.

Parameters	Values
pH	6.2–7.9
BOD ₅ (mg/L)	65–215
COD (mg/L)	200–585
NO ₃ [−] (mg/L)	3.5–18.5
PO ₄ ^{3−} (mg/L)	1.6–5.2
NH ₃ (mg/L)	3.2–14.8

that offers a trade off-based approach between accuracy and interpretability [29, 30]. Based on the existing experimental data in the current research, a grey-box evolutionary poly regression (EPR) model and three white-box kinetic models were used to analyze and forecast the performance of the MBR using petroleum refinery wastewater in the Al-Dora Facility, namely the first-order, Grau second-order and the modified Stover Kincannon models.

2.3.1. Characterization of Evolutionary Polynomial Regression (EPR)

Evolutionary polynomial regression (EPR) is an interdisciplinary modeling method which combines evolutionary computing with numerical regression to produce pseudo-polynomial mathematical expressions that have the ability to model complex nonlinear systems [31]. The validity of EPR in the real-life modeling of both environmental and engineering processes has been significantly reported in the literature [32]. Examples of successful applications of EPR include the performance of submerged biofilm reactors [30], the determination of fouling and turbidity rejection in ultrafiltration membranes [33], the modeling of urban ambient carbon monoxide concentrations [34], the evaluation of the dynamics of stormwater quality [32], and the forecasting of the variation in the water level in lakes [35]. This EPR methodology is based on a multi-objective genetic

algorithm (MOGA) that is integrated with regression analysis and works in two phases [36]. The initial step would involve a mathematical structure being evolved via having a coded representation of candidate expressions in the MOGA framework. The second step involves optimization of the coefficients of the chosen pseudo-polynomial terms by numerical regression.

A generic EPR model is described as below Eq. (??) [31]:

$$y = \sum_{j=1}^n a_j \cdot \varphi_j(X) \quad (1)$$

where y is the model output, a_j is a constant coefficient, $\mathbb{N}_j$ is a function evolved in the evolutionary process, n is the maximum of the terms of the polynomials and X is the input variable matrix. Out of the five preset functions within the EPR framework, the one that had the least prediction error was chosen in order to conduct the current study. The predictive power of the constructed EPR model was measured by the coefficient of determination (CoD) that was estimated with the help of the equation (2) [36]. All EPR simulations were done with the EPR-Version 2.0SA software and the methodological descriptions are detailed in [31].

$$\text{CoD} = 1 - \frac{\sum_N (y_{\text{EPR}} - y_{\text{exp}})^2}{\sum_N (y_{\text{exp}} - \text{avg}(y_{\text{exp}}))^2} \quad (2)$$

2.3.2. First-order kinetic model

Taking the first-order substrate removal as the kinetics in the bioreactor, the substrate degradation rate may be written in 3 as:

$$-\frac{ds}{dt} = K_1 S \quad (3)$$

where S is the substrate concentration (mg L^{-1}), t is time (d), and K_1 is the first-order substrate removal constant (d^{-1}).

In the pseudo-steady-state conditions the temporal change of substrate concentration is insignificant, and the equation may be reorganised into the form of the following equation (4) [31]:

$$\frac{S_0 - S_e}{\text{HRT}} = K_1 S_e \quad (4)$$

The input substrate concentration (S_0) and output substrate concentration (S_e) are expressed in g/L , d , hydraulic retention time (HRT), L/d , and L , respectively, while the working volume of the bioreactor (V) is denoted by Q . It was by plotting S_e versus $(S_0 - S_e)/\text{HRT}$ that K_1 was defined.

2.3.3. Grau second-order kinetic model

The second order kinetic model of Grau can be formulated as the following equation 5 [25]:

$$-\frac{ds}{dt} = K_2 \left(\frac{S}{S_0} \right)^2 \quad (5)$$

After integration and linearization, the model can be expressed as 6:

$$\frac{\text{HRT}}{E} = a + b \cdot \text{HRT} \quad (6)$$

and $E = (S_0 - S_e)/S_0$ is the efficiency of substrate removal. a and b were calculated based on intercept and slope of the linear graph of HRT/E vs HRT.

2.3.4. Modified Stover–Kincannon model

The modified Stover–Kincannon model characterizes the cleaning of the substrate under steady state conditions and is best applied to high strength industrial waste effluents. The model can be written in the form of [37] in considerably the following way (7):

$$U = \frac{U_{\max} \cdot B}{K_B + B} \quad (7)$$

where U is the rate of substrate utilization ($\text{g/L} \cdot \text{d}$), $B = QS_0/V$ is the volumetric loading rate, $U_{\max}$ is the maximum substrate utilization rate ($\text{g/L} \cdot \text{d}$), and K_B is the saturation constant ($\text{g/L} \cdot \text{d}$). $U_{\max}$ and K_B were calculated using the linearized form by plotting $V/[Q(S_0 - S_e)]$ vs. $V/(QS_0)$.

3. Results and discussion

3.1. The COD removal percentage

Testing the MBR's stability under different operating settings allowed us to examine the system's stability and the

MBR's COD removal capabilities. The inherent fluctuation of refinery runoff and API-unit effluent streams caused substantial day-to-day variations in the influent COD in the experimental process, as observed in the actual petroleum refinery wastewater from the Al-Dora Facility (Baghdad, Iraq). Hydraulic retention time (HRT) and suspended particles in the combined liquid both have an impact on the decrease of COD, as shown in Figure 2. Figure 2 shows the lowest COD removal efficiency from each of the six phases of the experimental program, which included two MLSS levels and four HRT values.

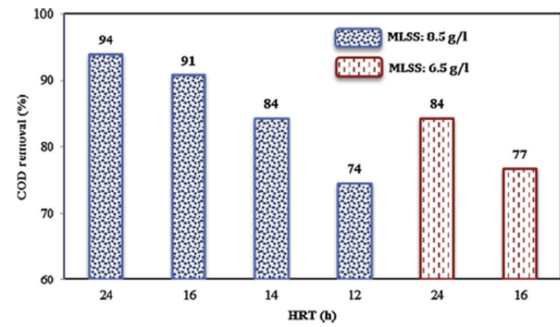


Fig. 2. The effect of HRT on the COD removal

The assessment of the shortest feasible time HRT that can be adhered to consistently is one of the most significant components of operational considerations. This is due to the fact that the retention time in use is rather long in order to maintain appropriate levels of biodegradation in industrial wastewaters. In a practical sense, the selection of HRT should be based on local discharge criteria and reuse objectives. These criteria typically indicate COD limitations that are determined by the body to which the waste is released and the kind of reuse (with more stringent restrictions at discharge to surface waters and less stringent limits at irrigation reuse) [38].

Over the course of the first four stages that were utilized for operation, the concentration of the MLSS was maintained at about 8.7 g/L continuously. The COD concentrations in the influent water ranged from 280 to 600 mg/L during Stage 1 ($\text{HRT} = 24$ hours), whereas the COD concentrations in the effluent water ranged from 9 to 34 mg/L . This indicates that the removal efficiency of COD ranged from 94.5 to 96.8 percent. During Stage 2 ($\text{HRT} = 16$ hours), the COD concentration in the influent decreases to around 200 – 395 mg/L , while the COD removal decreases to 90.5 – 91.8 mg/L with effluent COD ranging from 20 – 35 mg/L . However, when the HRT was reduced to 14 hours (Stage 3), the removal efficiency decreased even further, and the COD concentration in the effluent increased to 3876 mg/L .

This pattern demonstrates that the bioreactor was unable to sustain low levels of effluent COD at low HRT when the influent COD levels were greater, that is, when the COD levels were higher than about 460 mg/L, particularly when the influent systems were rapidly variable [39].

At Stage 4 (HRT = 12 hours), the COD removal performance was at its worst. At this stage, the removal efficiency dropped to around 75%, and the effluent COD was between 92 and 87 mg/L, which is higher than the discharge requirements for surface water. During Stages 5 and 6, the concentration of the MLSS was reduced to about 6.8 g/L before being stabilized. Influence COD and effluent COD levels were between 205 and 345 mg/L and 32-54 mg/L respectively, with corresponding removal efficiencies of 83-85. This was the fifth stage of the treatment process, which lasted for twelve hours. When the HRT was reduced to 16 hours (Stage 6), there was a further decline in the removal of COD, which was determined to be between 76 and 78 percent. Additionally, the effluent COD increased to 95120 mg/L, which is much higher than the maximum discharge limits. According to Figure 2, the effectiveness of COD removal decreased dramatically with a drop in both HRT and MLSS. This demonstrated the favorable effects of the contact time length and biomass concentration in biodegradation [40]. In addition, the efficiency of COD removal decreased significantly with higher concentrations of biomass.

When it comes to the removal of COD from submerged MBRs that are used to treat industrial effluents, the similar impact has been seen. This is because the short HRTs create a bigger organic loading stress and a poorer biodegradation completeness [41]. In a similar vein, previous studies have shown that an increased MLSS may be advantageous for the removal of COD; however, it may also result in rapid fouling of the membrane, underscoring the need of establishing an optimal operating range [42]. In the context of Al-Dora refinery wastewater, the findings suggest that a viable trade-off between performance and reactor area can be achieved by operating at approximately MLSS $\approx$ 8.7 g/L with HRT $\approx$ 14 hours. This is a practical approach that aims to achieve low effluent COD at a realistic cost and time. However, it is worth noting that peak influent COD events may require a longer HRT or equalization.

3.2. MBR performance foretelling by EPR.

The configuration of parameters utilized in the EPR analysis is detailed in Table 4. You may find the empirical model (Eq.) using the EPR tool. 9). Using influent COD, HRT, and MLSS as a foundation, to estimate effluent COD. In general, there is a wide range of complexity and predictive

power that may be generated by EPR outputs (for instance, in terms of CoD and mean square error, MSE). A more sophisticated mathematical expression can improve the fit, but it can also lead to over-fitting and miss the main physical/biological activity if applied too simplistically. The capacity of EPR to generate several candidate models is thus useful for selecting an efficient structure by comparing patterns and errors across them.

The chosen EPR model in the current research had been acceptable predictive strength (criteria value of about CoD $\approx$ 0.92 and MSE $\approx$ 112), which justified the applicability of EPR in modelling MBR performance under variable influent conditions [43].

$$\text{COD}_{\text{out}} = 0.612 \text{COD}_{\text{in}} - 0.0119 (\text{COD}_{\text{in}} \cdot \text{MLSS} \cdot \text{HRT}) - 18.9^{0.5} \quad (8)$$

Comparison was made between predicted outputs (8 and Figure 3) demonstrates the results of the experiment. The fact that the observed correlation is close to the ideal (the correlation coefficient is nearly $R^2 = 0.94$ –0.95) suggests that the chosen EPR structure can be trusted to measure COD_{out} changes, and it can be utilized in the process of operational sensitivity evaluation. be utilized in the process of operational sensitivity evaluation.

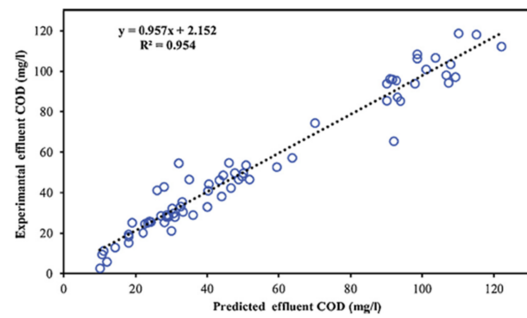


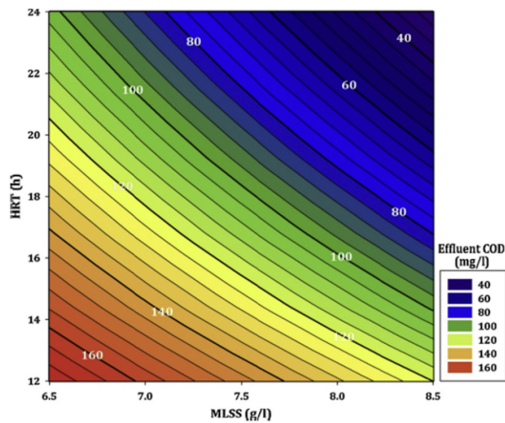
Fig. 3. Evaluation of the anticipated COD levels in the effluent using EPR compared to the experimental readings

Influent COD, HRT, and MLSS were examined using a one-factor-at-a-time sensitivity method. With HRT and MLSS maintained constant (i.e., at lower values of 12 h and 6.8 g/L), the effect of influent strength on COD_{out} in the stressed condition became clear as the influent COD ranged from 200 to 600 mg/L (in multiple steps). For example, the influent COD increased by about 46 to 175 mg/L. By lowering COD_{out} to intermediate levels of 46 and 22 mg/L and increasing MLSS from 6.8 to 8.7 g/L and HRT from 12

Table 4. The settings of Evolutionary Polynomial Regression (EPR).

EPR type	Regressions type	Functions	Range of exponent	MOGA strategy	Number of Generations
Case 3 (2)	Static	No function	[0–0.55:2]	min (a_i , SSE)	16

to 24 hours, respectively, the beneficial effects of biomass concentration and contact time were demonstrated. The operational goals for the highest influent COD case (= 600 mg/L) were determined by considering multiple scenarios (Figure 4). While a 24-hour HRT and 8.7 g/L MLSS are predicted to be the smallest COD_{out}, this setup may not be the most time or cost-effective [44]. The EPR response surface suggests that COD_{out} with common discharge objectives may be realistically pursued at around 21 hours after start time (HRT) and 8.3 g/L of maximum leachate solids (MLSS), especially during high-COD occurrences.

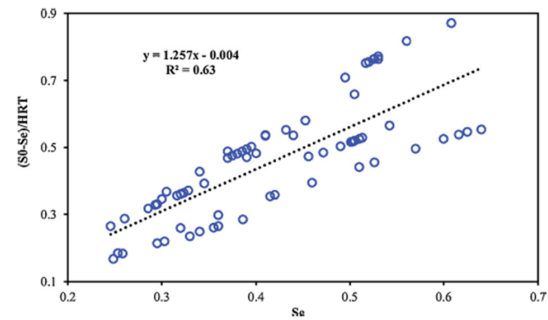
**Fig. 4.** The COD content in the effluent is shown against the parameters of HRT and MLSS in a contour plot

3.3. Substrate removal kinetics

3.3.1. First-order model of substrate removal

Figure 5 demonstrates the dependence between effluent substrate concentration (S_e) and $[(S_0 - S_e)/HRT]$ on the basis of the equation (3). The slope estimate of the rate constant K_1 of the first-order substrate removal was about 1.22 d^{-1} . The relatively small correlation ($R^2 = 0.6164$) shows that first-order kinetics are not sufficient to describe the COD removal over the entire operating range despite the fact that the magnitude of K_1 lies within a range of values reported in the biological treatment systems. Such a restricted fit is in line with the complicated partially recalcitrant character of refinery wastewater wherein elimination performance is affected by saturation impacts, inhibitory

chemical and fluctuating biodegradability [45].

**Fig. 5.** A graph representing the first-order model for removing substrates

3.3.2. Grau second-order model

The second order model of Grau was utilized to explain better the COD removal behavior in the MBR. The linearized form (Eq. (5), Figure 6) which demonstrates a good correlation with the experimental data ($R^2 = 0.91\text{--}0.93$) which means that this model can also describe the observed removal trends with high precision. The intercept and slope were used to obtain the kinetic coefficients a and b and predict the effluent COD using the (Eq. (9)) below [46]:

$$\frac{S_0 - S_e}{S_0} = \frac{\text{HRT}}{0.148 + 0.952 \text{ HRT}} \quad (9)$$

The variation in Grau coefficients found in the literature is not surprising because various wastewater makeup, loading rates and reactor set up vary [47]. In refinery wastewater, the values of coefficients are highly dependent on the influent strength and concentration of the biomass, indicating that the ability to remove the substrates also depends on the biodegradability and operating window [48].

3.3.3. Modified Stover–Kincannon model

The adjusted Stover–Kincannon model identifies the rate of substrate utilization in relation to organic loading rate in a steady-state situation. The fitted relationship as depicted in Figure 7 indicated that it was in excellent agreement with the data ($R^2 = 0.97\text{--}0.98$), which is why it is possible to state that this model was suitable to explain the process of COD removal in the MBR used in the treatment of Al-Dora refinery wastewater. The kinetic constants were

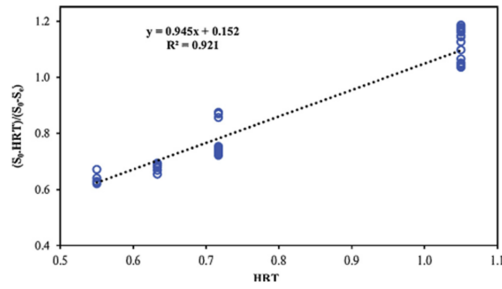


Fig. 6. The plot of the Grau second-order substrate removal model

obtained by means of the linear plot of $V/[Q(S_0 - S_e)]$ vs. $V/(QS_0)$, $U_{\max} = 6.25$ and $K_B = 6.70$ g/(L · d). Based on the same, effluent COD prediction could be done through the following equation (10) [49]:

$$S_e = S_0 - \frac{U_{\max} \left(\frac{QS_0}{V} \right)}{K_B + \left(\frac{QS_0}{V} \right)} S_0 \quad (10)$$

The similarity in the magnitude of $U_{\max}$ and K_B suggests that the organic loading can quickly diminish the removal efficiency, which is also in line with treating the wastewater that has complex or refractory fractions [Li2020f]. Generally, it is typical to find lower $U_{\max}$ and K_B values with lower biodegradability substrates and higher constants with readily biodegradable municipal wastewater [49].

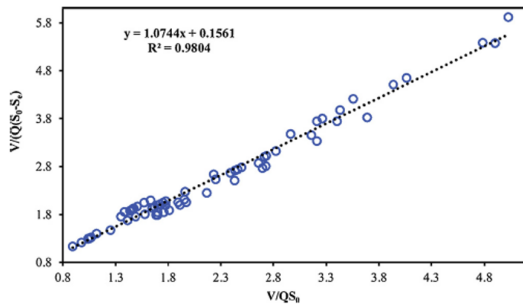


Fig. 7. Plot of the Stover-Kincannon model

4. Conclusions

The paper compared the results of the laboratory-scale submerged PVDF-MBR filtration of real petroleum refinery wastewater of the Al-Dora Facility (Baghdad, Iraq) in various hydraulic retention times and MLSS concentrations. The influent COD was significantly different

(around 200–500 mg/L) and the effluent COD was around 9–128 mg/L depending on the conditions of operation. COD removal was the greatest at HRT = 24 h and MLSS = 8.7 g/L, and lowest at HRT = 12 h, at which effluent COD steadily rose above usual stringent levels of discharge. The evolutionary polynomial regression (EPR) model achieved great predictive power (average R^2 was about 0.94–0.95) and allowed to perform sensitivity analysis of the important operating variables. The EPR analysis has shown that the COD variation has a strong control over the COD_{out} at the stressed condition, and the HRT and MLSS increase significantly in enhancing the quality of effluents. To achieve a balance between production and operation cost-effectiveness, operating window close to HRT = 21 h and MLSS = 8.3 g/L was found to be a feasible compromise between high-COD conditions and the operational economy based on the high-COD situations typical of Al-Dora refinery fluctuations. Of the kinetic models tested, the first-order model had low accuracy, and the Grau second-order model and modified Stover–Kincannon models had much higher accuracy to the dynamics of COD removal. The models can thus be used in predicting the performance, scale-up, as well as the optimization of the operational performance of the MBR systems used to treat refinery wastewater under the condition of Iraq.

Nomenclature

Symbol	Definition	Unit
S_0	Influent COD concentration	mg L ⁻¹
S_e	Effluent COD concentration	mg L ⁻¹
COD	Chemical Oxygen Demand	mg L ⁻¹
HRT (θ)	Hydraulic retention time	h (or d in kinetic equations)
MLSS	Mixed liquor suspended solids	g L ⁻¹
Q	Influent flow rate	L d ⁻¹
V	Effective reactor volume	L
U	Substrate utilization rate	g L ⁻¹ d ⁻¹
B	Organic loading rate	g L ⁻¹ d ⁻¹
$U_{\max}$	Maximum substrate utilization rate	g L ⁻¹ d ⁻¹
K_B	Saturation constant (Modified Stover–Kincannon model)	g L ⁻¹ d ⁻¹
K_1	First-order substrate removal constant	d ⁻¹
a, b	Grau second-order kinetic constants	dimensionless
E	COD removal efficiency	%
DO	Dissolved oxygen	mg L ⁻¹
PVDF	Polyvinylidene fluoride membrane	—
EPR	Evolutionary Polynomial Regression	—
CoD	Coefficient of Determination	—
MSE	Mean Square Error	mg ² L ⁻²

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