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Kinetic Characteristics of Thermophilic Aerobic Membrane Reactor (TAMR) for Iraqi Municipal Wastewater

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ABSTRACT

We evaluated the performance of a wastewater treatment plant with a thermophilic aerobic membrane reactor (TAMR) system. The two kinetic models used to describe its behavior are the Stover-Kincannon modification and secondary order treatments. One could predict the kinetic parameters for removing both chemical oxygen demand (COD) and ammonium nitrogen (NH_4^+-N) from the wastewater substrate. The substrate removal rate was 1.66 per day within a correlation coefficient of 0.9978. Also, those coefficients for COD concentration are 0.9977 and 0.9965, according to the modified model. As for COD, the probable maximum utilization rate was estimated to be 60.24 g\L·day. The saturation value is about 64.81 g\L·day. However, the maximal uptake by biomass of ammonia nitrogen is 32.42 g/L·day, and the saturation constant is 30.12 g/L·day. Stover-Kincannon's modified model has been shown to be an effective method for the treatment of sewage – and it even makes fairly accurate predictions as to what will happen wth the COD and the ammonia nitrogen content in sewage. In addition, it is useful for optimizing wastwater treatment that is both simple and highly efficient at producing accurate predictions

Keywords: aerobic membrane reactor, kinetic model, wastewater, COD.

INTRODUCTION

Environment pollution has become a global critical concern today because of climate change, urbanization and population growth (Al-Bayati et al., 2023; Hussein, 2010; Kalash et al., 2022). Water is a significant waste stream with diverse contaminants in different volumes and quality levels (Al-Furaiji and Kalash, 2020). Recently, the thermophilic aerobic membrane reactor (TAMR) has been used in treating sewage using oxygen to dismantle organic matter (Collivignarelli et al., 2019; Collivignarelli et al., 2018). Biological processes are accelerated, and retention time is reduced as temperatures range from 45 to 65 °C. Water treatment systems such as TAMRs are widely used in industrial and municipal settings (Collivignarelli et al., 2015). In addition to requiring high temperatures, TAMR systems can also remove organic matter and other contaminants more effectively than other wastewater treatment systems (Miao et al., 2020). For example, wastewater from a sugar mill, effluents from slaughterhouses, and effluents from dyebaths and dyes (Collivignarelli et al., 2021; Mahmood and Waisi, 2021; Mohammed et al., 2023). This process is often used as the primary step in a multi-stage treatment line because of the wide variety of reactor designs (Yee et al., 2019), or using a single-stage process, an organic load can be removed by 97% (Yee et al., 2019). TAMR utilizing up flow is one of the earliest designs well-defined in design and operation (Yee et al., 2019). Regardless of their configuration, most A (TAMR) operate in a mesophilic environment (30–35°C). Some industrial wastewater systems produce wastewater at temperatures that make operation in a thermophilic range (50–60°C) desirable, such as in distilleries and canneries (Yilmaz et al., 2008). A thermophilic aerobic membrane reactor (TAMR), intrinsically, has a higher activity; it is said to be more susceptible to environmental changes than a mesophilic reactor (Ahn and Forster, 2000; Al-Furaiji et al., 2022). A thermophilic aerobic membrane reactor (TAMR) could perform significantly better than a mesophilic reactor in any specific wastewater application (Nga et al., 2020). This is the major technological concern when evaluating the possible of TAMR reactor for any specific wastewater application. Neither thermophilic nor mesophilic reactor have been directly compared in the literature (Wijekoon et al., 2011). As a result of their research, Dinsdale et al. (1997) found that a thermophilic up flow sludge blanket reactor (UASB) could only maintain a marginally higher OLR than a mesophilic UASB at 11.4 kg COD per $m^3 \cdot$day as compared to 10 kg COD per $m^3 \cdot$day. An analysis of biological treatment systems is required in order to describe and predict their performance, process modeling is accepted (Kalash et al., 2022). Thermophilic digestion, on the other hand, has received little attention despite various models described for mesophilic digestion reactors (Ramachandran et al., 2019).

The significant advantage of thermophilic aerobic reactors is their efficient in reducing organic compounds. These systems also reduce greenhouse gas emissions and contribute to energy savings because of the high-temperature conditions (Yee et al., 2019). Furthermore, thermophilic aerobic reactors are adaptable and can be integrated with other advanced wastewater treatment technologies (Abeynayaka and Visvanathan, 2011a). In the future, more sustainable and environmentally friendly wastewater management might be achieved by improving the design and operation of thermophilic aerobic reactors (Abeynayaka and Visvanathan, 2011b). Kinetic wastewater treatment modeling can help understand complex processes. The researchers might improve mathematical models to describe the interaction of the biochemical reactions with environmental factors (Daigger, 2011; Ni and Yuan, 2015). Mostly, the first and second-order kinetic models and the Stover-Kincannon model are commonly applied for wastewater treatment (Ahn and Forster, 2000; Nga et al., 2020).

The Stover-Kincannon modified model was utilized to characterize the behaviour of microbial systems in wastewater treatment. By this model, the consumption rate of the substrate was assumed to be proportionate to the substrate and microorganism concentrations (Ahn and Forster, 2000; Kalash et al., 2022). This model also includes saturation to find the microorganism limited ability for substrate consumption in a day. For instance, TAMR are sensitive to substrate concentration fluctuation, and thus Stover-Kincannon modified model may be used to expect their performance (Raj and Murthy, 1999). The other kinetic model is the first order model which is a typical model assumes a simple proportion between the substrate consumption and its concentration (Nga et al., 2020) unlike the Stover-Kincannon model. This model depicts the behavior of microbial systems in wastewater treatment when substrate concentration is not a limiting constraint (González-Martínez et al., 2000). The second-order kinetic model is more complicated that assumes the substrate consumption rate is proportion to the substrate and microorganism concentrations (Nga et al., 2020). However, in this model, the substrate concentration has a more significant impact than the microorganism concentration. This model may represent the microorganism behavior in waste water treatment under a situation of high substrate concentration and low microorganism concentration (Raj and Murthy, 1999). Using these kinetic models, thermophilic aerobic membrane reactors can be designed and operated optimally. It is possible to predict the optimal hydraulic retention time and substrate loading rate for a given substrate concentration by using the Stover-Kincannon modified model, while the maximum treatment capacity of the reactor can be estimated using first and second order models (Debik and Coskun, 2009).

MATERIALS AND METHODS

Bioreactor configuration

A 10 L plexiglas TAMR reactor with aerobic conditions was used. On the reactor body, two sampling ports were located at different heights, as shown in Figure 1. This apparatus had two main sections: one for wastewater and activated sludge and one for UF membranes. From the bottom of the column, an aeration system was provided by a blower, air diffuser, and oxygen. Continuous wastewater was pumped from the feed tank into the system using a peristaltic pump. The UF membranes handled the wastewater discharged from the reactor's upper part. An aeration cycle was conducted for 30 minutes, a settling cycle for

10 minutes, and effluent withdrawal for 2 minutes using a programmable logic controller.

This experimental study used wastewater collected on the Ministry of Science and Technology campus. The wastewater used in this study is characterized in Table 1.

It is provided with a digestion reactor (LT200, Hach, USA) and a spectrophotometer (DR 5000 UV-Vis, Hach, Germany) used to analyze the concentration of COD. Water and Wastewater Standard Methods have been used to quantify COD in raw influent WW (Carranzo, 2012).

Table 1. The wastewater characterization used in this study

Parameter	Unit	Concentration
BOD	mg/L	250–300
COD	mg/L	499–650
NH_4-N	mg/L	32.8–37.9
Turbidity	NTU	120–175
Conductivity	mS/m	0.67–0.98
pH	-	6.9–7.8

Kinetic modeling

One of the most usually used methods for identifying kinetic constants in stationary systems is the Stover-Kincannon and Stover-Kincannon modified model. This model was applied to the simulation of continuous wastewater treatment using trickling filters (Raj and Murthy, 1999), a hybrid anaerobic reactor (Büyükkamaci and Filibeli, 2002), and a submerged biofilter for municipal sewage (González-Martínez et al., 2000). This study used Stover-Kincannon's modified kinetic model to analyze chemical oxygen demand (COD) and ammonium (NH_4^+) removal in TAMR reactors operating at different organic loading rates. The Stover-Kincannon formulae in Eq. (1) and (2) deal with the substance removal rate at a steady state based on organic loading rates (Kapdan, 2005; Nga et al., 2020):

$$\frac{ds}{dt} = \frac{Q}{V}(S_i - S_e) \tag{1}$$

$$\frac{ds}{dt} = \frac{U_{max}\left(QS_i/V\right)}{K_B + \left(QS_i/V\right)} \tag{2}$$

where: ds/dt – the rate of removal substrate (g/L·day), K_B – constant of saturation (g/L·day), V – capacity of the reactor (L), U_{max} – utilization of maximum rate (g/L·day), Q – flow rate (L/day).

The inversion of the substrate removal rate must also be reflected in Eq. (3), resulting from the inlinearization of Eq. (1) and (2), as written below:

$$\frac{ds}{dt} = \frac{V}{Q(S_i - S_e)} = \frac{K_B}{U_{max}} * \frac{V}{QS_i} + \frac{1}{U_{max}} \tag{3}$$

where: V/Q_{Si} and $V/Q(Si\text{-}Se)$ have an inverse linear relationship, with K_B/U_{max} being the slope and $1/U_{max}$ being the intercept.

Eq. (4) can be used to calculate the effluent substrate concentration after obtaining the kinetic constants K_B and U_{max} for influent substrate concentration and organic loading rate.

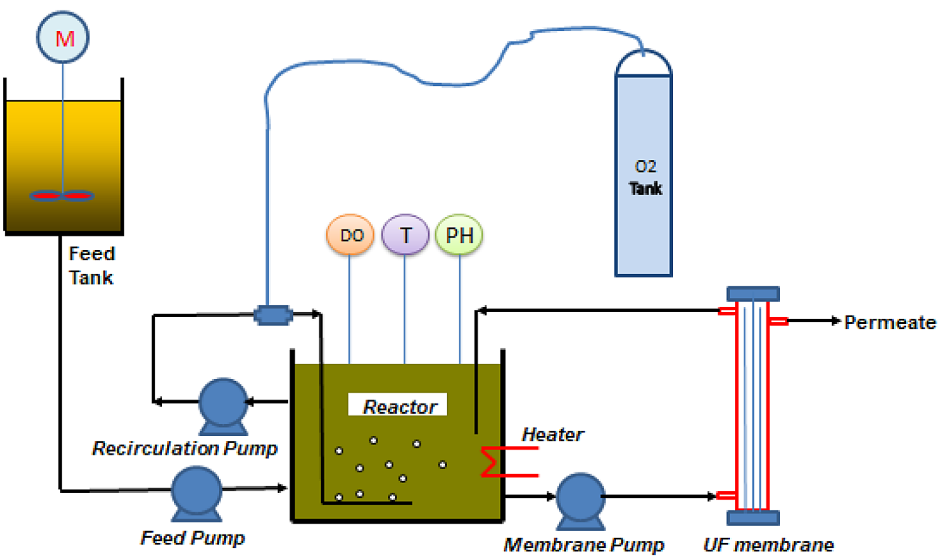

Figure 1. Experiment diagram for the current study (Kalash et al., 2023)

$$S_e = S_i - \frac{U_{max} S_i}{K_B + \left({QS_i}/{V} \right)} \tag{4}$$

For wastewater treatment to be effective, it is crucial to understand the kinetics of the reactions (Debik and Coskun, 2009).

The application of the first-order model

Understanding how wastewater treatment reactions work and their kinetics is also important. A rate of reaction is a term used to describe a chemical or species reaction (Debik and Coskun, 2009).

Reaction rates for first-order reactions are directly proportional to reagent concentrations. The variations in substrate concentration rate can be demonstrated as follows:

$$\frac{-ds}{dt} = \frac{QS_i}{V} - \frac{QS_e}{v} - K_1 S_e \tag{5}$$

Under pseudo-steady-state, the ($-ds/dt$) is insignificant, so Eq. (5) can be rewritten as follows:

$$\frac{S_i}{S_e} - 1 = K_1\ HRT \tag{6}$$

where: S_e – effluent concentrations (mg/L), S_i – influent concentrations (mg/L), $K_{1(S)}$ – substrate removal rate constant.

The application of the second-order model

The reaction rate in a second-order reaction is proportional to the reagent concentration squared. To define wastewater system kinetic constants, the second-order model is most commonly used (Grau et al., 1975). It contained parameters measured routinely and was developed for wastewater treatment systems (Debik and Coskun, 2009). Based on the equation below, this model can be described as follows (Büyükkamaci and Filibeli, 2002; Grau et al., 1975):

$$\frac{-ds}{dt}\ K_{2(s)} x \left(\frac{S_e}{S_i} \right)^2 \tag{7}$$

When Eq. (7) is linearized and integrated, the following results will be obtained:

$$\frac{S_i \theta}{(S_i - S_e)} = \theta + \frac{S_i}{K_{2(s)} x_o} \tag{8}$$

Using Eq. (8) as A constant for the right part, the equation will be derived as follows:

$$\frac{S_i \theta}{(S_i - S_e)} = A + B\theta \tag{9}$$

The given constant: $A = S_i/(K_{2(S)} \cdot X_o)$, B – larger than unity.

The substrate removal efficiency (E) is calculated as (Si/Se)/Si. Therefore, Eq. (9) can be written as follows:

$$\frac{\theta}{E} = A + B\theta \tag{10}$$

where: $K_{2(S)}$ – constant of substrate removal rate, S_i – influent concentrations (mg/L), X – the biomass concentration (mg VSS/L), S_e – effluent concentrations.

RESULTS AND DISCUSSION

COD removal efficiency

Figure 2 shows the removal efficiency for the TAMR reactor. The thermophilic average output and input concentrations of COD were 100 and 561 mg/l. Removal efficiency for COD was estimated between 70.55 and 94.99% (Kalash et al., 2023). A high level of process and quality stability was also observed during the experiments.

TAMR reactors have been studied and operated for wastewater treatment in our test, the average removal efficiency was 90.1%, and this agrees with that reported by (Collivignarelli et al., 2018; Collivignarelli et al., 2019) but significantly higher than that reported by (Debik and Coskun, 2009), and one order of magnitude higher than that reported by (Dinsdale et al., 1997) even COD removal. In earlier studies, with actual results reported by several authors. (Faridnasr et al., 2016) used batch reactors to treat wastewater from the sugar industry and achieved 85% and 79% removal efficiencies, respectively. In a pilot plant scale study by Taylor et al. (Pramanik et al., 2012), 83% of COD was removed from domestic wastewater using an aerated biological filter.

Kinetic model

An estimate constant of COD from modified Stover-Kincannon

Figure 3 shows the plot for the TAMR reactor based on the Stover-Kincannon model's equation. We plotted a linear correlation between V/Q_{Si} and $V/[Q(S_i - S_e)]$. Based on these values for U_{max} and K_B, the reactor should produce 60.24 g/L·day and 64.81 g/L·day. Compared to the mesophilic reactor, thermophilic reactors' maximum utilization rate constant is higher. The R^2 (correlation constants) for the reactor gives 0.9977, so it can

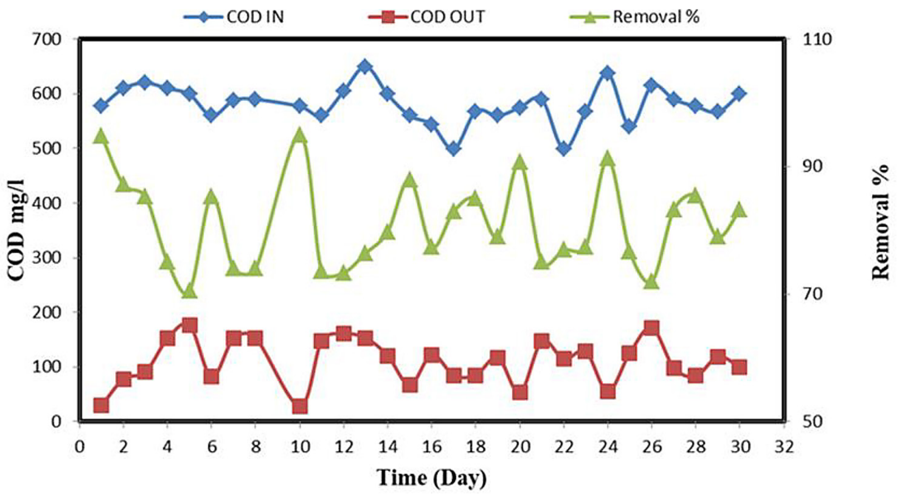

Figure 2. COD input and output and performance removal of the thermophilic reactor (Kalash et al., 2023)

be concluded that the Stover-Kincannon modified model can be used to define the performances of the TAMR reactor.

The Stover-Kincannon modified model has been applied effectively to a thermophilic and mesophilic reactor for wastewater working with a hanging sponge bioreactor (Nga et al., 2020), wastewater using virtual starch (Yu et al., 1998), and liquid waste from paper pulp (Ahn and Forster, 2002, 2000), anaerobic hybrid reactor using fixed bed reactor (Büyükkamaci and Filibeli, 2002) and treatment of synthetic wastewater polluted with dyestuff using packed bed column reactors (Kapdan, 2005).

The formulas below Eq. (11) demonstrate the COD rate expression obtained from the TAMR reactor.

$$\frac{Q(S_i - S_e)}{V} = \frac{60.24\left({QS_i}/{V}\right)}{64.81 + \left({QS_i}/{V}\right)} \tag{11}$$

As a result of reforming, based on Eq (12), Eq (11) estimates the COD concentration in the effluent.

$$S_e = S_i - \frac{60.24 S_i}{64.81 + \left({QS_i}/{V}\right)} \tag{12}$$

Nga et al. (2020) found that the maximum utilization rate K_B for the hanging sponge bioreactor had a coefficient of determination R^2 = 0.9943, and they had a coefficient of determination R^2 =75.034 g/L·day. The correlation coefficient (R^2) obtained by Abyar et al. (2017) on a UASB was 0.9917, and the utilization rate K_B kinetic saturation value U_{max} was 24.75 and 25.997 g/L·day, respectively. In Kapdan (2005), dye and COD were studied in synthetic wastewater; experimental results indicated a good fit for the Stover-Kincannon model, with K_B and U_{max} at 17.8 and 19 g/L·day, respectively. Using MBBR for wastewater treatment, Hassani et al. (2014) studied the

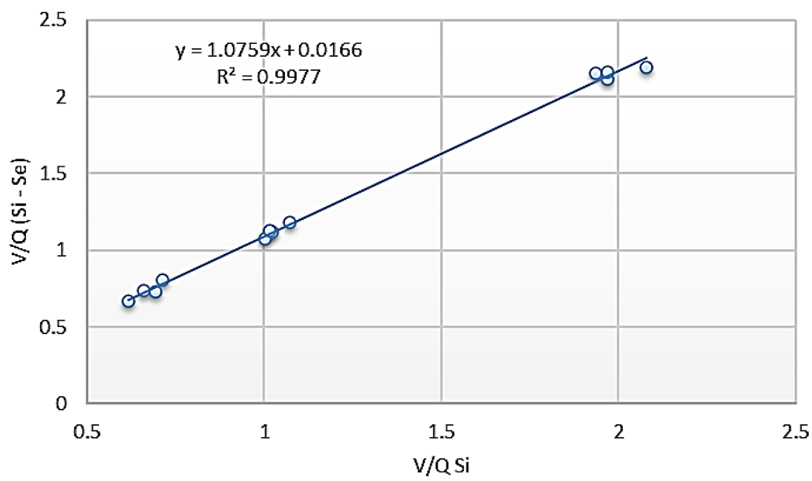

Figure 3. Stover-Kincannon modified model for COD removal in the TAMR reactor

kinetics of COD removal. The results indicated that the model of Stover-Kincannon and the experimental data agreed (R^2 = 0.9919), with U_{max} and K_B calculated at 13.14 g/L day and 13.62 g/L day, respectively.

An analysis of measured and predicted final effluent data is presented in Figure 4. In addition, Two parameters exhibit a high degree of correlation demonstrating that the model may be used to characterize TAMR reactors states. The measured and predicted values agree in Figure 4 final effluent with R^2 = 0.9036 obtained from the TAMR reactor.

An estimate constant of NH_4^+ from modified Stover-Kincannon

In Figure 5, we can see how the model applies to ammonium removal. $V/[Q\,(Si - Se)]$, plotted against $V/(QSi)$, gives $1/U_{max}$ as the intercept point, and U_{max}/K_B represents the slope. Figure 5 shows an intercept and slope yield constant kinetic values for U_{max} and K_B of 30.12 g/L·day and 32.42 g/L·day, respectively. A modified model developed by Stover-Kincannon is approved for use with an R^2 of 0.9965. There is a significant relationship between the saturation constant (K_B) and the maximum utilization rate (U_{max}) in this study than they were to the Yang et al. (2015) study. Abbas et al. (2015) studied the oxidation of synthetic wastewater containing NH_4^+ with anaerobic bacteria. Based on this model, they obtained U_{max} = 30.12 and K_B = 33.42 g/L·day. Using this rate appearance, we can determine how much NH_4^+-N would be removed from Eq. (13).

$$\frac{Q(N_i - N_e)}{V} = \frac{30.12\left({}^{QN_i}/_{V}\right)}{33.42 + \left({}^{QN_i}/_{V}\right)} \tag{13}$$

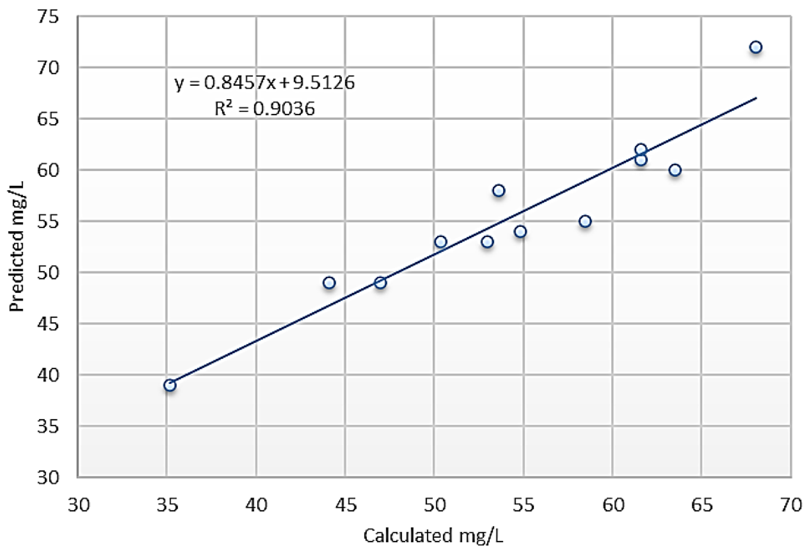

Figure 4. The comparison between predicted and measured effluent of COD concentrations

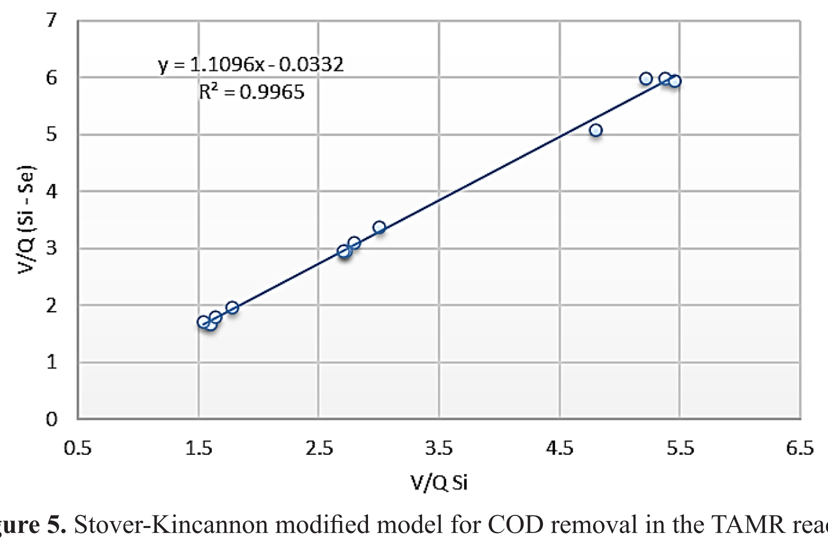

Figure 5. Stover-Kincannon modified model for COD removal in the TAMR reactor

The effluent NH_4^+ concentration can be expected by Eq. (14).

$$N_e = N_i - \frac{30.12\,N_i}{33.42 + \left(\frac{QN_i}{V}\right)} \tag{14}$$

An analysis of predicted and measured final effluent data can be found in Figure 6. The high correlation between the two parameters demonstrates that the model may be used to characterize TAMR reactor states. According to the TAMR reactor, $R^2 = 0.9613$ is a good correlation between measured and predicted final effluent in Figure.6.

APPLYING A FIRST AND SECOND-ORDER KINETIC MODEL

First-order kinetic model

According to Figure 7, the experimental data of the bioreactor were taken into account using first-order substrate removal kinetics. The constant (K_1) was obtained by plotting $(S_i - S_e)/HRT$ versus S_i = 1.0458/day for COD removal with the R^2 of 0.16. In accordance with the experimental data (R^2 = 0.16), this model was not acceptable. In Eq. (15), K_1 was substituted as follows:

$$\frac{S_i}{S_e} - 1 = 1.0458\,HRT \tag{15}$$

Second-order kinetic model

Table 2 defines the second-order kinetic model, and Figure 8 shows the values (A) and (B) of the TAMR reactor. With an R^2 of 0.9978, (A) and (B) were determined to be important at 1.079 and 0.0054, respectively. A summary of these values is shown in Table 2 as a result of estimating the second-order rate constants ($K_{2(S)}$) based on the values (A). The data provided in the Table 2 are the results of a test run for COD removal using

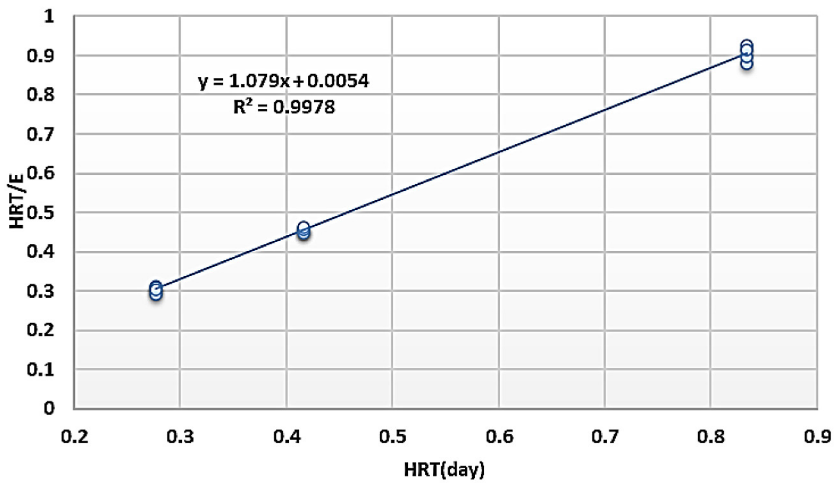

Figure. 6. The comparison between predicted and measured effluent of NH_4^+ concentrations

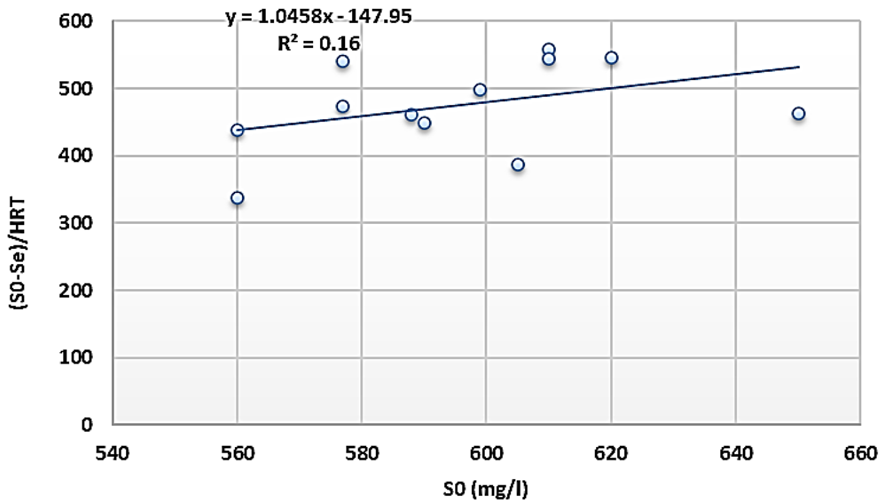

Figure 7. A first-order kinetic model is used to model the TAMR

Table 2. The obtained information from the Second-order kinetic model

Test Run	COD in mg/L	COD out mg/L	Removal (E) %	Flow rate ml/min	Biomass conc. mg/L	HRT day	HRT/E	$K_{2(s)}$ per day
1	577	29.7	94	25	312.7	0.833	0.878	1.608
2	610	42.7	93	25	323.6	0.833	0.896	1.642
3	620	62	90	25	321.0	0.833	0.925	1.683
4	610	54.9	91	25	318.5	0.833	0.915	1.668
5	599	41.9	93	50	317.6	0.416	0.448	1.643
6	560	50.4	91	50	291.9	0.416	0.457	1.672
7	588	52.9	91	50	306.8	0.416	0.457	1.670
8	590	59	90	50	305.1	0.416	0.462	1.685
9	577	28.9	94	75	308.7	0.277	0.292	1.628
10	560	61.6	89	75	286.6	0.277	0.312	1.702
11	605	60.5	90	75	313.1	0.277	0.308	1.684
12	650	52	92	75	342.7	0.277	0.301	1.652

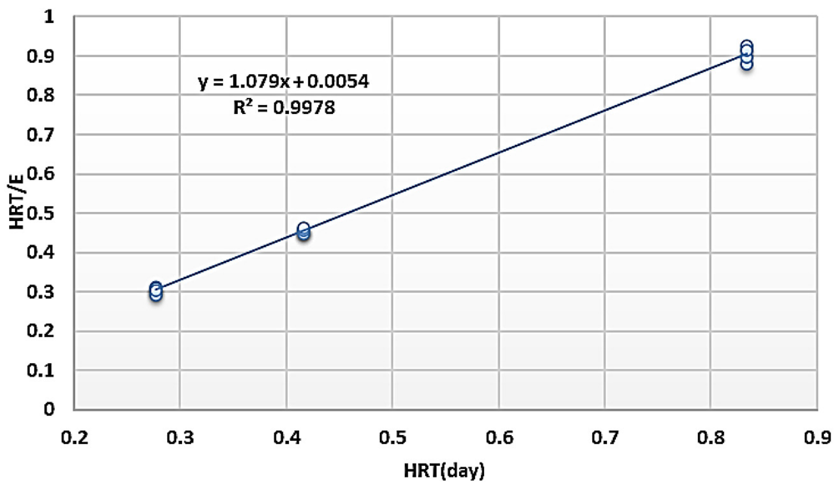

Figure 8. Second-order kinetics modeling of TAMR reactor

biomass concentration at various HRT values. The test involved a total of four runs, and for each run, the COD concentration in mg/L, the removal percentage, the flow rate in ml/min, and the biomass concentration in mg/L were recorded. The run results indicated that the values of COD removal percentages and HRT are correlated positively. In addition, the obtained results show that it has little effect on COD removal efficiency when biomass content is increased.

This formula is used to calculate the effluent substrate concentration in the reactor:

$$: S_i * (1 - \frac{HRT}{1.079 + 0.0054H} \quad (16)$$

CONCLUSIONS

This study is concerned with the performance of a lab-scale thermophilic aerobic membrane reactor. The results show that particular kinetic models, such as the modified Stover/Kincannon and the second-order, are applicable in the determination of system treatment efficiency. These models accurately forecasted the amounts of the substance in wastewater and can be used to optimize the treatment process of wastewater. The correlation coefficient found 0.9978 shows that there is a good relationship between the variables and the modified Stover/Kincannon and second-order models are competent in foreseeing COD $NH4^+$-N elimination as well. For the TAMR system, $K_{2(S)}$, substrate removal rate constant was 1.66 per day, indicating a high efficiency in removing COD and $NH4^+$-N. By applying the Stover-Kincannon modified model, the estimated concentration coefficients of COD and NH_4^+-N were 0.9977 and 0.9965, respectively. Further, the predicted K_B and U_{max} were 60.24 for COD while it was 30.12 g/L·day. Due to the simplicity in use and accuracy of these models for predicting kinetic parameters on COD and NH_4^+-N removals, such models are valuable tools for optimizing waste water treatment systems and helping them become more efficient.

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