Water Science & Technology

Water Science & Technology Vol 85 No 6, 1720 doi: 10.2166/wst.2022.074

Kinetic models evaluation for chemical organic matter removal prediction in a full-scale primary facultative pond treating municipal wastewater

Javad Alavi and Sepideh Ansari*

Department of Environmental Sciences and Engineering, Kheradgarayan Motahar Institute of Higher Education, Mashhad, Iran
*Corresponding author. E-mail: aysanansari1991@gmail.com

JA, 0000-0003-2126-4219; SA, 0000-0002-3139-2719

ABSTRACT

This study focuses on determining the bio-kinetic coefficients of chemical oxygen demand (COD) removal in full-scale primary facultative ponds (PFPs) system on the basis of 3-year continuous operation. The mean removal of chemical oxygen demand (COD), total suspended solid (TSS) and volatile suspended solid (VSS) were 80, 59 and 49%, respectively. The first-order model paired with continuous stirred-tank reactor (CSTR) and plug flow (PF) regimes, PF k–C*, Stover-Kincannon and Grau second-order models were applied to link COD concentrations at the inlet and outlet of the system and to compare the predictive power of models for the estimation of effluent COD concentrations. The Stover-Kincannon model showed the best adaptability ($r^2 = 0.9294$) with the maximum substrate utilization rate (U_{max}) of 79.14 g/L· d and saturation constant (K_B) of 80.65 g/L· d, whereas the Grau second-order model was the best model to predict outlet COD concentrations ($r^2 = 0.6925$). The computed constants, m and n, of the Grau second-order model were 0.6725 and 15.867 d^{-1}, respectively. While the Stover-Kincannon kinetic rates obtained in this study can be used to design the PFP systems in similar operational conditions, the appropriate prediction of pond behavior can be achieved using the Grau model.

Key words: first-order removal rate, kinetic constant rates, organic matter biodegradation, primary facultative pond, second-order removal rate, Stover-Kincannon model

HIGHLIGHTS

- A kinetic study on primary facultative ponds treating municipal wastewater for COD removal was performed.
- Stover-Kincannon model provided the best link between the inlet and outlet COD concentrations ($r^2 = 0.9294$).
- The Grau second-order model showed the best power of prediction for daily outlet COD values ($r^2 = 0.6925$).
- Aerial first-order and K-C* models also provided acceptable performance in COD prediction.

INTRODUCTION

Waste stabilization ponds (WSPs) as sanitation technologies are widely employed in small communities and developing countries because of their simplicity and low capital and operational expenditures (Butler *et al.* 2017; Passos *et al.* 2019). The system entirely contains natural processes and sub-processes in which wastewater is treated by biochemical reactions involving bacteria and algae (Faleschini *et al.* 2012). Facultative ponds (FPs) are characterized by shallow basins having an upper aerobic zone with available free-oxygen at the surface of the pond and a lower anaerobic zone with a lower depth area and no available free oxygen. The process is classified as primary facultative ponds (PFPs) and secondary facultative ponds (SFPs). The former receives raw wastewater (after preliminary treatment), whereas the latter receives pre-treated wastewater (typically the effluent from anaerobic lagoons) (Mara 2004).

FPs exhibit complex behavior in spite of being classified as simple and basic operational systems (Ho *et al.* 2017) because of the simultaneous existence of aerobic, facultative and anaerobic zones and the synergy and mutualistic relationship between photosynthetic algae/cyanobacteria and heterotrophic bacteria, which is the key feature inside the pond systems (Sah *et al.* 2011). Moreover, ponds are highly dynamic and subject to various operational and environmental parameters, which make the development of an all-encompassing model and forecasting the performance of the systems a challenge for designers (Sah *et al.* 2011; Alves *et al.* 2020).

A major concern/aim of treating wastewater in WSPs is organic matter removal. Chemical oxygen demand (COD) removal in the ponds may be attributed to several parameters such as temperature and detention time, which make the models susceptible to uncertainty, variability and complexity in integrating processes and sub-processes. Kinetic models have been introduced and used commonly to describe the removal of organic compounds in the stabilization ponds (Okoro & Nwaiwu 2017) and also, they can be used as a route to describe and predict the performance of biological treatment systems (Okoli & Okonkwo 2016). It is essential to understand the kinetics of pollutants in the system as it leads to proper design parameters and pond performance enhancement. Apart from many kinetic models available in literature, the most common models to describe WSPs is the first order kinetic model combined with plug flow and CSTR (continuous flow stirred tank reactors) regimes (Sun & Saeed 2009; Khosravi *et al.* 2013a). Also, the other kinetic models such as k–C*, Grau second-order and Stover–Kincannon models have been studied in the literature to determine their adaptability to find a relationship between the organic compounds at the inlet and outlet of WSPs. However, the main problem in replacing these models is that they are simplified and based on dependent mathematical relations. Therefore, selection of the best kinetic models for providing optimum design and predicting pollutant removal are vital to avoid malfunctions in different types of WSPs. Khosravi *et al.* (2013b) applied three models including the first-order substrate removal, Grau second-order and Stover-Kincannon models to determine the kinetic coefficients of sCOD (soluble COD) removal in WSP. The correlation coefficient was the highest for Stover-Kincannon Model ($r^2 = 0.907$), which represented the highest correlation between the values of influent and effluent in comparison with the other models. However, Gratziou & Chalatsi (2015) reported that the first order-plug flow (PF) constant rate provided the best mathematical relationship between the results and real data ($r^2 > 0.80$) for COD degradation compared to the other used models (first order-CSTR, K-C* and Stover-Kincannon models). The results of K-C* equation showed a promising result for modeling COD removal in stabilization ponds. Also, they concluded that reaction constant rates have a very strong relationship with hydraulic retention time. The prediction of removal rates of organic matter from WSPs at different retention times were studied by Okoro & Nwaiwu (2017) using first order, Monod, Grau and the Stover Kincannon models by fitting models to experimental data. Whereas the Stover Kincannon model showed a better adaptability (r^2), the Grau model provides the best prediction of the substrate removal efficiency. Da Silva *et al.* (2010) compared the reaction constant rates of ideal first-order-PF model with the first order-CSTR model in six full-scale PFPs. They concluded that a PF regime with $k = 0.013$ day^{-1} ($r^2 = 0.96$) provided a better fit than the CSTR flow pattern with $k = 0.019$ day^{-1} ($r^2 = 0.93$). While it is very important to the design and sizing of the WSPs based on the knowledge of pollutant removal reaction rate constants (Gratziou & Chalatsi 2015), the comparative assessment of full-scale PFPs in the context of the reaction constants of organic matters biodegradation is very scarce as the literatures have mainly focused on the computation of the kinetic rates in the WSPs and the SFPs. A main knowledge gap in PFPs is to select the best model for mapping organic matter removal and predicting the behavior of the ponds. The gap will be addressed in this study by determining the different kinetic constant rates for organic matter removal and comparing the predictability powers of models.

The main objective of this study is to evaluate the adaptability of different kinetic models to link organic matter concentrations at the inlet and outlet and to compare the accuracy of COD removal prediction by kinetic models in a full-scale PFP as a secondary treatment of municipal wastewater on the basis of 3-year continuous operation. This investigation will help find the best kinetic models to design full-scale PFPs to achieve optimum sizing and predict the chemical organic matter concentrations of the effluent, which have not been discussed in the literature.

MATERIALS AND METHODS

Site location and process description

Esfarayen wastewater treatment plant (EWWTP), with an area of 33 ha located in the North-East of Iran. The region has two types of climates: temperate mountain climate and moderate, and warm and dry with mean annual precipitation and evaporation rates of 248 mm and 1,767 mm/year, respectively. The average monthly air temperature ranges from 2.8 °C to 27 °C. The first module has been in operation since 2000 with capacity of 4,000 m^3/day and the existing nominal capacity of the plant is 8,000 m^3/day with an area of about 20 ha. The plant receives domestic wastewater without agro-industrial liquid wastes. The pre-treatment units comprise mechanical and manual coarse screens and velocity-controlled grit chambers. The existing secondary treatment units consist of four PFPs operated in parallel, a maturation pond and chlorine contact basin (Figure 1). Design basis values of PFPs are also summarized in Table 1. The average organic loading rate is 200 kg

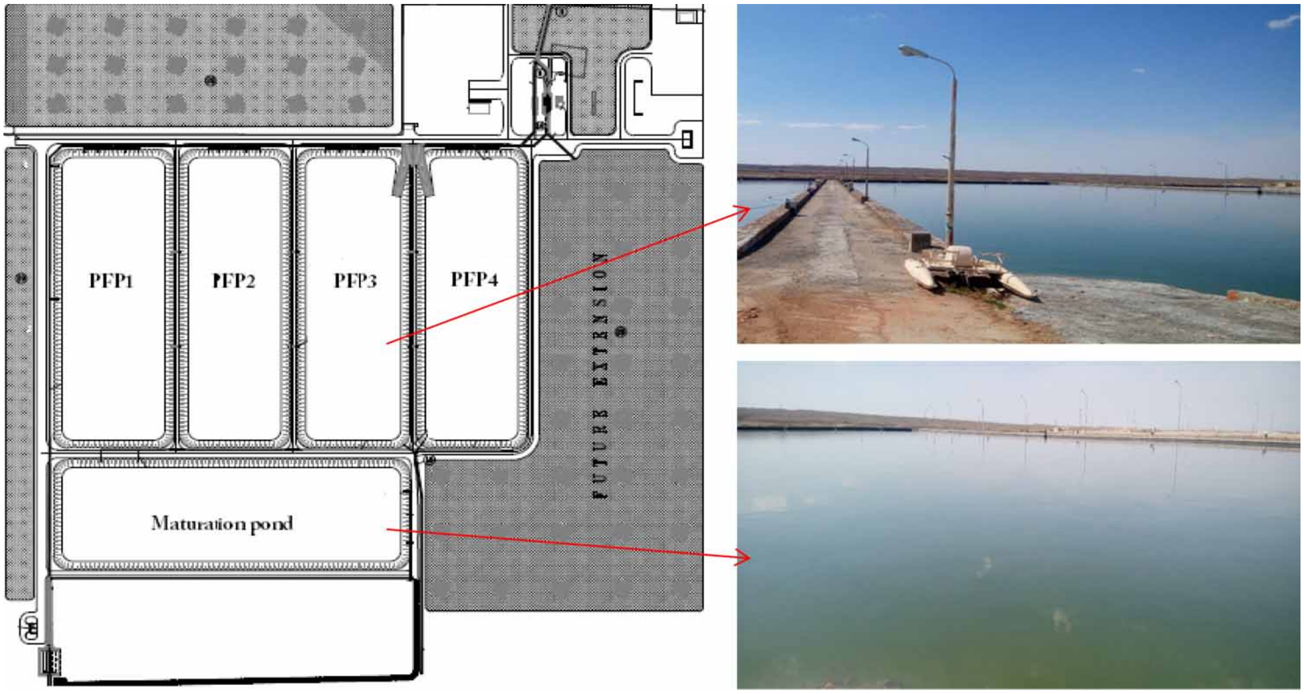

Figure 1 | Layout of EWWTP and photographs of the PFPs and maturation pond.

Table 1 | Details of PFPs in Esfarayen WWTP

Parameter and unit	Value
Average flow during study, m^3/d	7,066
Total number of ponds	4
Length of each pond at the top level of water, m	261
Width of each pond at the top level of water, m	89
Length at the bottom of each pond, m	250
Width at the bottom of each pond, m	78
Depth, m	2.7
Hydraulic retention time, day	33

BOD_5/ha·d which is in line with proposed values (100–400 kg BOD_5/ha·d) for designing PFPs to remove BOD on the basis of a relatively low surface loading (Shilton 2006).

Sample collection and analytical methods

Samples from the inlet and outlet of PFPs were weekly collected over a three-year period from January 2016 to December 2018 consisting of 141 data sets. Each data set of long-term sampling included flow rate, COD, biochemical oxygen demand (BOD_5), total suspended solids (TSS), volatile suspended solids (VSS), temperature, electrical conductivity (EC), and alkalinity at the inlet and COD, TSS, VSS, temperature, dissolved oxygen (DO) and alkalinity at the outlet. Samples were taken by 1.5 L plastic bottles rinsed by the effluent before sampling. Then, the bottles were labeled, sealed, stored away from the sunlight, transported on an ice chest to the laboratory located in EWWTP, and stored at 4 °C to be analyzed before 6 hours. The parameters were examined by the reference analytical procedures and protocols on the basis of the Standard Methods for the Examination of Water and Wastewater (APHA 2005). Organic matter was determined as COD (Jenway 6405 UV/VIS spectrophotometer, code: 5220-C) and BOD_5 (5-day BOD test, dilutions and DO electrode, code: 5210-B). TSS and volatile suspended solid (VSS) parameters were examined on the basis of oven-drying (Pat arya Sanat, Iran) at

103–105 °C and 550 °C, respectively (codes: 2540-D and 2540-E). EC was determined by electrometric method (HACH Lange HQ40D Multiparameter, code: 2510-B). Titration was also carried out to measure alkalinity (code: 2320).

Kinetic models selection and equations

A kinetic model simplifies the relationship of variables affecting COD removal in WSPs, which is applicable for the design of the units. Moreover, performance prediction and unit optimization are obtained by using chemical organic matter removal constant rates and their models. Substrate removal rate can be determined using first-order, Grau second-order and Stover–Kincannon models as the most fundamental and popular models (Abyar *et al.* 2017). As analytical models for the design of PFPs are on the basis of first-order kinetics and surface loading rate, the aerial first-order models were selected to be assessed. In addition to the first-order models, Grau second-order and Stover-Kincannon models are the fundamental ones to exhibit substrate removal rate in WSPs. The k–C* model was proposed by Kadlec & Knight (1996) to incorporate aerial loading rate, concentration at the inlet and outlet of the wetlands and a temperature-based kinetic rate in the wetlands. Since similar characteristics with wetlands can be seen in the pond systems such as no sludge removal throughout the operations, the performance of the k–C* model introduced for the modeling of wetlands can be used to predict the outlet of the ponds (Gratziou & Chalatsi 2015). To describe the chemical organic matter removal rate in PFP in this case study, five models including first-order models combined with PF and CSTR patterns, PF k–C*, Stover-Kincannon and Grau second-order models were used, compared and explained as follows:

Model 1: first-order kinetic model combined with PF pattern, k_1

The first equation, Kickuth equation, was developed by combining the first-order kinetic with PF regime (Equation (1)).

$$k_1 = \frac{Q(\ln C_{in} - lnC_{out})}{A} \tag{1}$$

where Q is the daily flow rate (m^3/d); C_{in} and C_{out} are organic matter concentrations (mg/L) at inlet and outlet; A is the surface area of ponds (m^2) and k_1 is the kinetic rate (m/d).

Hydraulic loading rate (HLR) is also explained as follows:

$$q = \frac{Q}{A} \tag{2}$$

where Q and A are the same parameters mentioned above and q is the hydraulic loading rate (m/d). Equation (1) can be represented as Equation (3).

$$k_1 = q(\ln C_{in} - lnC_{out}) \tag{3}$$

Model 2: first order kinetic model with CSTR flow pattern, k_2

The combined first-order kinetic and CSTR flow pattern as shown in Equation (4) is simplified in terms of kinetic rate constant (k_2, m/d):

$$k_2 = \frac{q(C_{in} - C_{out})}{C_{out}} \tag{4}$$

where C_{in}, C_{out}, and q are the same parameters mentioned before.

Model 3: PF k–C* model, k_3

Kadlec & Knight (1996) proposed the k–C* model shown in Equation (5) is a combination of PF equation with aqueous mass balance in the wetlands.

$$k_3 = qln\left(\frac{C_{in} - C^*}{C_{out} - C^*}\right) \tag{5}$$

where C_{in}, C_{out} and q are the same parameters, k_3 is the removal rate constant (m/d) and C^* is background concentration (mg/L).

They assumed an exponential removal rate to reflect a non-zero background wetland concentration (C^*) and proposed Equation (6) for the computation of apparent background concentration.

$$C^*_{COD} = 3.5 + 0.053C_{in} \tag{6}$$

where C_{in} is pollutant concentration (mg/L) at the inlet (COD in this research) and C^*_{COD} is the background COD concentration (mg/L).

In general, Equations (3)–(5) can be rearranged into the Equation (7) to estimate the kinetic rates (k_n). For each equation, constant rate value is achieved through linear regression by plotting $f(C_{in},C_{out})$ versus $1/q$ (Sun & Saeed 2009).

$$k_n = \frac{\mathrm{f}(\mathrm{C_{in}}, \mathrm{C_{out}})}{1/\mathrm{q}} \tag{7}$$

Model 4: Stover-Kincannon model

This kinetic model proposed by Stover & Kincannon (1982) has been widely applied in different biological processes. In the model shown in Equation (8), the substrate removal rate is expressed as a function of the organic loading rate by monomolecular kinetics for biofilm reactors (Borghei *et al.* 2008). Therefore, the Stover-Kincannon model mainly focuses on the biomass attached as a main factor for the removal instead of the biomass suspended in biological systems (Rangel-Peraza *et al.* 2017).

$$\left(\frac{dC}{dt}\right)^{-1} = \frac{V}{Q(C_{in} - C_{out})} = \frac{K_B}{U_{max}}\left(\frac{V}{QC_{in}}\right) + \frac{1}{U_{max}} \tag{8}$$

where dC/dt represents the pollutant removal rate (g/L·d), U_{max} is the maximum rate of substrate removal (g/L·d) and K_B is saturation constant (g/L·d).

The kinetic parameters K_B and U_{max} can be obtained by plotting Equation (8). By a plot of the inverse of the loading removal rate versus the inverse of the total loading rate, the parameters can be computed. Accordingly, a linear plot is obtained to determine ($1/U_{max}$) as the intercept of the plot and (K_B/U_{max}), which is the slope of the line.

Model 5: Grau second-order model

A bio-kinetic model shown in Equation (9) proposed by Grau *et al.* (1975) can be expressed as a general form of the second-order kinetic model.

$$-\frac{dC}{dt} = kX\left(\frac{C_{out}}{C_{in}}\right)^2 \tag{9}$$

where $-dC/dt$ is the substrate removal rate (g/L·d); k is the second-order biodegradation constant rate (d^{-1}); X is biomass concentration (g VSS/L) and C_{in} and C_{out} indicate the influent and effluent substrate concentrations (g/L), respectively.

Equation (9) is simplified and linearized as Equation (10).

$$\frac{VC_{in}}{Q(C_{in} - C_{out})} = m\left(\frac{V}{Q}\right) + n \tag{10}$$

where m (dimensionless) and n (per day) are the slope and intercept of plot, respectively. C_{in}, C_{out}, Q and V represent pollutant concentrations at inlet and outlet (mg/L), flow rate (m^3/day) and volume of the ponds (m^3).

The kinetic constant rates (m and n) are determined from the slope and intercept of the linear plot on the basis of Equation (10), respectively.

Model evaluation metrics

Eight indices including the coefficient of determination (r^2), the mean squared error (MSE), the normalized mean square error (NMSE), the root mean square error (RMSE), the relative root mean square error (RRMSE), the index of agreement (IA), model efficiency (ME) and mean absolute error (MAE) are applied in this investigation to compare the prediction power of the bio-kinetic models. The coefficient of determination (r^2) explains the extent of linear correlation between two sets of data (Equation (11)), which ranges from 0 to 1. A higher r^2 value indicates a closer linear relation between predicted and actual data. The NMSE (Equation (12)) determines the overall deviations between estimated and measured data. A smaller NMSE value presents closer prediction. The RMSE indicates how concentrated the data is around the line of best fit. The indicator (Equation (13)) always is non-negative and a value near 0 would indicate a perfect fit. The RRMSE index (Equation (14)), which ranges from 0 to ∞ determines the differences between the estimated and actual data. A value near 0 represents closer fit. The IA index (Equation (15)) shows the degree of model prediction error and ranges between 0 and 1. A value of 1 indicates a perfect prediction and 0 shows no agreement. The Nash–Sutcliffe index of ME (Equation (16)) ranging from $-\infty$ to 1 represents the variation in actual values accounted for by the model. The closer the model efficiency is to 1, the more accurate the model is. MAE (Equation (17)) is the mean absolute distance between predicted data and actual ones ranging from 0 to ∞ and lower values are more acceptable. The MSE index (Equation (18)) measures the average squared difference between the predicted data and observed ones. The index is always non-negative, and values near zero show closer prediction.

$$\mathrm{r}^2 = \frac{\sum_{i=1}^{n}(Y_{pred,i} - \bar{Y}_{pred})(Y_{obs,i} - \bar{Y}_{obs})}{\sqrt{\sum_{i=1}^{n}(Y_{pred,i} - \bar{Y}_{pred})^2 \sum_{i=1}^{n}(Y_{obs,i} - \bar{Y}_{obs})^2}} \tag{11}$$

$$\mathrm{NMSE} = \frac{\sum_{i=1}^{n}(Y_{obs,i} - Y_{pred,i})^2}{\sum_{i=1}^{n}(Y_{pred,i})^2} \tag{12}$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(Y_{obs,i} - Y_{pred,i})^2} \tag{13}$$

$$\mathrm{RRMSE} = \frac{\sqrt{\frac{1}{n}\sum_{i=1}^{n}(Y_{obs,i} - Y_{pred,i})^2}}{\bar{Y}_{obs}} \tag{14}$$

$$\mathrm{IA} = 1 - \frac{\sum_{i=1}^{n}(Y_{obs,i} - Y_{pred,i})^2}{\sum_{i=1}^{n}(|Y_{obs,i} - \bar{Y}_{obs}| + |Y_{pred,i} - \bar{Y}_{obs}|)^2} \tag{15}$$

$$\mathrm{ME} = 1 - \frac{\sum_{i=1}^{n}(Y_{obs,i} - Y_{pred,i})^2}{\sum_{i=1}^{n}(Y_{obs,i} - \bar{Y}_{obs})^2} \tag{16}$$

$$\mathrm{MAE} = \frac{1}{n}\sum_{i=1}^{n}|Y_{obs,i} - Y_{pred,i}| \tag{17}$$

$$\mathrm{MSE} = \frac{1}{n}\sum_{i=1}^{n}(Y_{obs,i} - Y_{pred,i})^2 \tag{18}$$

where n is the number of the observed data; $Y_{obs,i}$, $Y_{pred,i}$ and $\bar{Y}_{obs}$ are the observed, predicted and mean observed values, respectively.

To evaluate the robustness of the models, the discrepancy ratio (DR) index was also used to assess the properties of errors (Equation (19)). This index also provides more information about the performance of models in terms of error distribution according to the maximum acceptable error range. The developed discrepancy ratio (DDR) index was also proposed by Noori *et al.* (2010) for the modification of the DR index to assess the properties of errors shown as Equation (20).

$$DR = \text{Log}\left(\frac{Y_{pred,i}}{Y_{obs,i}}\right) \quad (19)$$

$$DDR = \left(\frac{Y_{pred,i}}{Y_{obs,i}}\right) - 1 \quad (20)$$

where $Y_{obs,i}$ and $Y_{pred,i}$ are the observed and predicted values, respectively.

Statistical analysis

The statistical analyses were conducted using Microsoft Excel spreadsheet (Microsoft, 2010, USA). The software was also applied to calculate the outlet values obtained by bio-kinetic models. The error distribution was analyzed by using the 'vegan' package of the R software (version 3.0.3). To evaluate the differences between influent and effluent parameters, the statistical significance was determined by paired two-sample t-test with a significance level of p-value $\leq$0.05.

Raw sewage characteristics

Table 2 shows the raw wastewater characteristics in EWWTP. The mean concentration of COD was 590 ± 141 mg/L ranging between 382 and 795 mg/L and influent BOD_5 concentration ranged between 176 and 380 mg/L with the average value of 263 mg/L. The mean BOD_5: COD ratio is 0.45 indicates the bio-treatability of sewage. Regarding suspended solids, the range of TSS concentrations was between 143 and 416 mg/L and VSS values ranged from 40 to 105 mg/L. The influent is classified as medium municipal wastewater in terms of organic matters while the sewage is characterized as low-strength wastewater in terms of the VSS parameter according to the recommended typical values of untreated domestic wastewater (Metcalf & Eddy 2003). The range of TSS values at the inlet is wide from low- to high-strength domestic sewage. The electrical conductivity (EC) of the wastewater was in the range of 1,546–2,480 μS/cm and the moderate EC values represent the presence of moderate amounts of dissolved inorganic substances in ionized form. The alkalinity level in the form of $CaCO_{-3}$ ranged between 520 and 840 mg/L showing alkaline character in the influent.

RESULTS AND DISCUSSION

Overall performance and effluent characteristics

The treatment efficiencies of the PFP systems and effluent characteristics are summarized in Table 3 during three years of continuous operation. The results show that the mean effluent COD declined significantly up to 119 ± 52 mg/L (with a removal efficiency of 80%). The finding is consistent with the results presented by Alves *et al.* (2020), who reported the reduction of 69 to 82% of COD in the facultative ponds. Da Silva *et al.* (2010) also evaluated the performance of six full-scale PFPs, and they found that the average removal of unfiltered and filtered COD was equal to 50 and 83%, respectively.

Table 2 | Raw wastewater characteristics in Esfarayen WWTP

	Inlet			
Parameters	**Ave**	**Max**	**Min**	**Number of samples**
COD, mg/L	590 ± 141	795	382	141
BOD_5, mg/L	263 ± 55	380	176	
TSS, mg/L	234 ± 51	416	143	
VSS, mg/L	62 ± 11	105	40	
EC, μS/cm	2,051 ± 186	2,480	1,546	
Temperature, °C	20.7 ± 4.0	28	12	
DO, mg/L	~0	–	–	
Alkalinity, mg/L $CaCO_3$	673 ± 70	840	520	31

Table 3 | Performance of PFPs and effluent concentrations

	Outlet parameters			Removal efficiency (%)		
Parameters	**Ave**	**Max**	**Min**	**Ave**	**Max**	**Min**
COD, mg/L	119 ± 52	205	39	80 ± 7	91.5	66
TSS, mg/L	92 ± 27	262	34	59 ± 14	85	29
VSS, mg/L	31 ± 5	46	20	49 ± 12	73	10
Temperature, °C	18 ±7	28	4	–		
DO, mg/L	1.2 ± 0.8	3.5	0.2	–		
Alkalinity, mg/L $CaCO_3$	688 ± 85	920	500	–		

The average removal efficiency of TSS was 59% with the effluent concentration of 92 ± 27 mg/L. The mean VSS concentration was almost halved from 62 ± 11 to 31 ± 5 mg/L with removal efficiency of 49%. The *p*-values in a paired two-sample t-test for COD, TSS and VSS concentration at inlet and outlet was near zero, presenting that the statistical difference between the concentrations at the inlet and outlet was extremely significant.

In terms of alkalinity, inlet concentration increased partially from 673 ± 70 to 688 ± 85 mg/L $CaCO_3$ with the *p*-value of 0.12, indicating a statistically insignificant difference. The mean values of temperatures at the inlet ranged between 12 to 28 °C, while the effluent presented mean temperature in the range of 4 to 28 °C. There was an increase in dissolved oxygen (DO) concentration from almost 0 to 1.2 mg/L. The enhancement in photosynthetic activity and reduction in organic matter concentration are the main reasons for the increase in DO concentrations (Martínez *et al.* 2014; Wallace *et al.* 2016).

COD removal kinetics

The reaction constant rates of COD removal in the PFPs were determined using kinetic models including first order-PF, first order-CSTR, PF k–C*, Stover-Kincannon and Grau second-order models. After the statistical and mathematical processing of the collected data, the values of COD removal reaction rates were obtained from Equations (3)–(5), (8) and (10) and presented in Table 4. The correlation coefficient (r^2) was used to select the most suitable and adoptable models (Yap *et al.* 2020).

The results showed that the all models, except the first order-CSTR with kinetic coefficient of 0.4509 m/d and $r^2 = 0.3788$, have relatively good performance ($r^2 > 0.5$). However, the Stover-Kincannon model provides better fitting ($r^2 = 0.9294$), which is consistent with the previous studies such as Yap *et al.* (2020), Okoro & Nwaiwu (2017) and Khosravi *et al.* (2013b). The linear regression of the kinetic reaction constants in the Stover-Kincannon model as the best fit for COD removal was shown in Figure 2. The calculated kinetic constants (U_{max} and K_B) were 80.65 g/L·d and 79.14 g/L·d according to the plot, respectively. One of the main reasons the Stover-Kincannon model showed higher adaptability in organic matter removal in pond systems is that it only measures the input against removal in a single volume (Hosseini & Borghei 2002). Therefore, the relationship shows a good adaptation especially for the systems with real scale and complicated reaction mechanisms that occur simultaneously such as suspended growth, sedimentation and adsorption. The Grau second-order model also showed a good adaptation and fitted well with data sets ($r^2 = 0.6621$) with the kinetic coefficients of $m = 0.6725$ and

Table 4 | Reaction constant rates of COD removal

Model	Coefficient values	r^2
Model 1	$k_1 = 0.152$, m/d	0.5759
Model 2	$k_2 = 0.4509$, m/d	0.3788
Model 3	$k_3 = 0.1891$, m/d	0.5173
Model 4	$K_B = 79.14$, g/L·d $U_{max} = 80.65$, g/L·d	0.9294
Model 5	m = 0.6725 $n = 15.867$, d^{-1}	0.6621

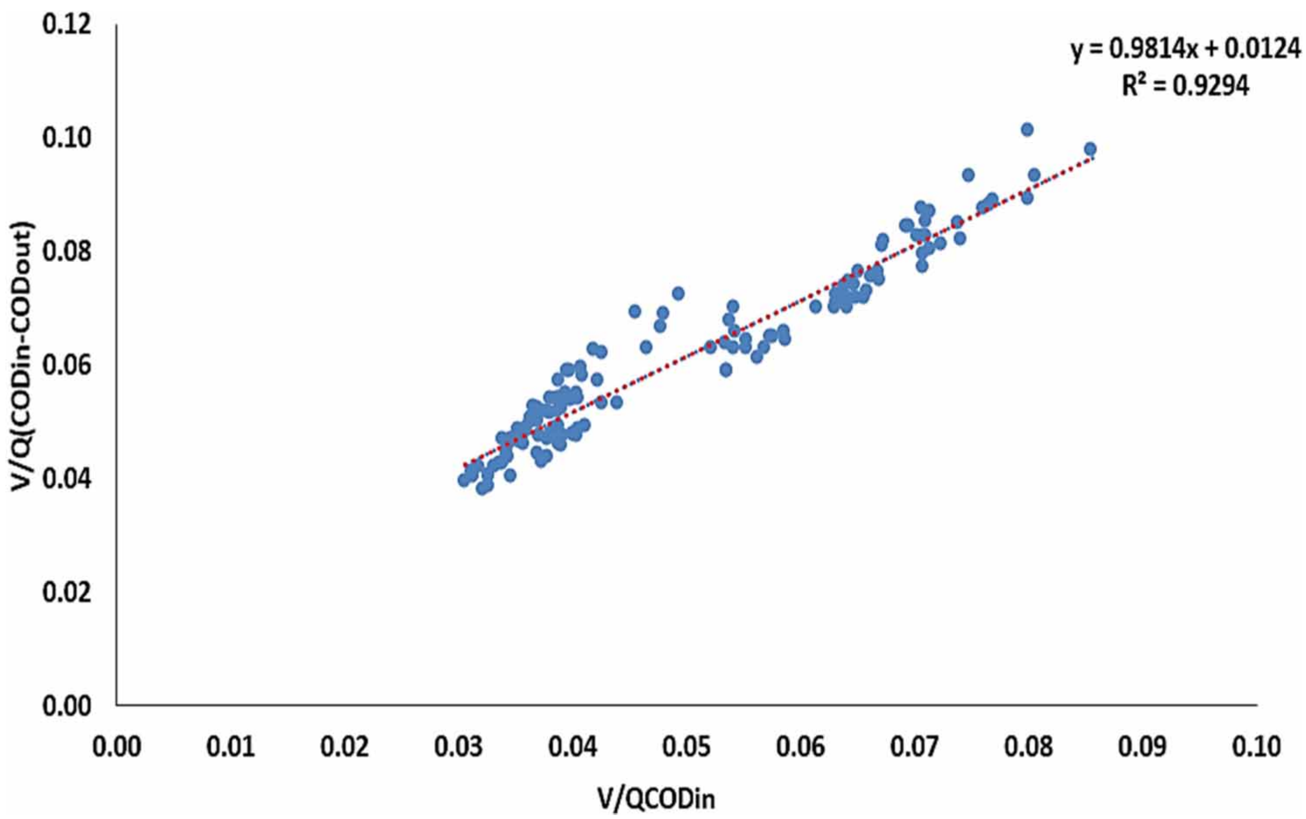

Figure 2 | Linear plot of the Stover-Kincannon model as the best fit to compute U_{max} and K_B.

$n = 15.867\ \mathrm{d}^{-1}$. The values of kinetic coefficients for the combined model of first order-PF and the Kadlec and Knight model were 0.152 m/d and 0.1891 m/d with $r^2 = 0.5759$ and $r^2 = 0.5173$, respectively.

Data prediction and model validation

Table 5 shows the predicted effluent COD concentrations obtained by substituting the value of kinetic coefficients into equations in order to test the validity of the models. Moderate correlation values (0.6925, 0.6876, 0.6598, 0.6087 and 0.5216) obtained for Grau second-order, k–C*, first order-CSTR, first order-PF and Stover-Kincannon model, respectively. Figure 3 shows these correlation coefficients obtained by kinetic models for COD removal at the outlet of PFPs. Grau second-order model was found to be the best to predict the PFPs' performance in terms of COD removal. However, the

Table 5 | Mathematical formula of kinetic models in PFPs and the coefficient of determination between actual and predicted COD values

Model	Equation	r^2
Model 1	$C_{out} = C_{in}e^{\left(-\frac{0.152}{q}\right)}$	0.6087
Model 2	$C_{out} = \dfrac{C_i}{\left(1 + \dfrac{0.4509}{q}\right)}$	0.6598
Model 3	$C_{out} = C^* + (C_{in} - C^*)e^{\left(-\frac{0.1891}{q}\right)}$	0.6876
Model 4	$C_{out} = \dfrac{C_{in} - (80.65C_{in}V)}{(79.14V + QC_{in})}$	0.5216
Model 5	$C_{out} = C_{in} - \dfrac{C_{in}}{0.6725 + \dfrac{Q15.867}{V}}$	0.6925

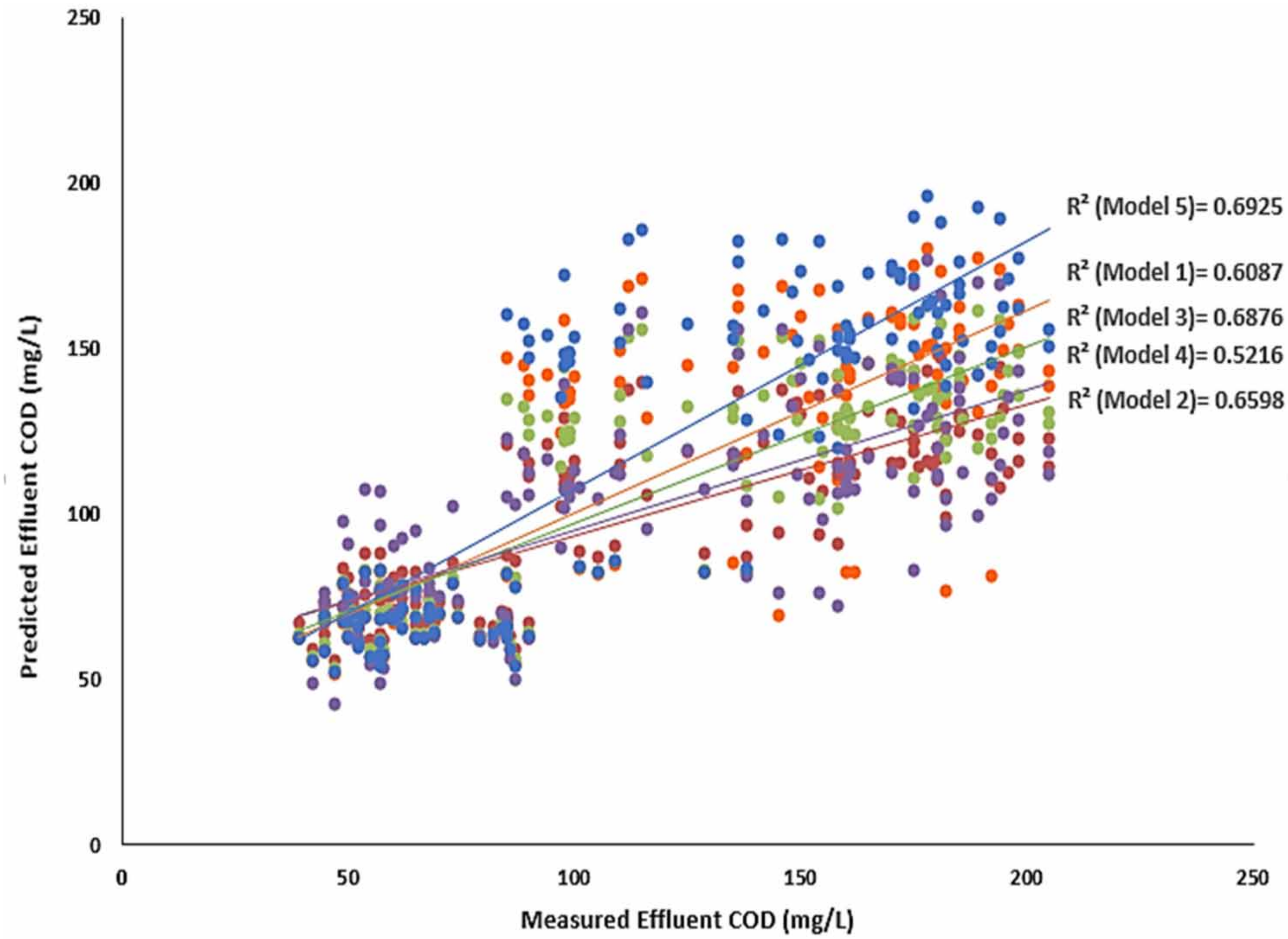

Figure 3 | Correlation coefficients of measured and predicted COD values at the outlet of PFPs.

performance of the model 1, model 2 and model 3 were still acceptable since no significant difference was observed between their accuracy.

The correlation coefficient of COD removal and comparison of measured and predicted COD values at the outlet of PFPs by the best model (Grau second-order model) is presented in Figure 4. Figure 4(a) shows that it is reasonable to use this model as a best fit line to predict COD removal. Also, Figure 4(b) shows insignificant difference between measured and predicted effluent COD values obtained by the second-order Grau model in most samples.

The performance accuracy of the models using different statistical indices is also compared in Table 6. The statistical metrics of kinetic models like ME and IA showed that the Grau second-order model predicted outlet COD removal more accurately compared to the other models (ME = 0.68 and IA = 0.91). In contrast, model 4 (Stover-Kincannon) offered the lowest precision with an ME value of 0.43 and IA equal to 0.76. Table 7 also shows the statistical indices of DR values calculated for the comparison of error distribution of values predicted by kinetic models. The results show that all models except the Grau second-order model generally predicted values lower than actual ones because the mean DR values are negative. Also, a narrower range of DR values was obtained in the K-C* and Grau models in contrast to the wide range of indexes, which can be seen in the Stover-Kincannon and the first-order models.

Moreover, the Gaussian function of DDR values was computed and represented in a standard normal distribution format. The standard normal distributions (QDDR) were computed for each model and then plotted in Figure 5. Generally, more tendencies in the error distribution graph to the centerline and the larger value of the maximum QDDR are equal to more accuracy (Noori *et al.* 2010). Model 3 (aerial K-C* model) and 5 (Grau model) provided the best accuracy in comparison with the other models in terms of DDR values referring to Figure 5. On the other hand, model 4 (Stover-Kincannon model) and model 2 (the first-order model coupled with CSTR flow pattern) represented lower accuracy for the prediction

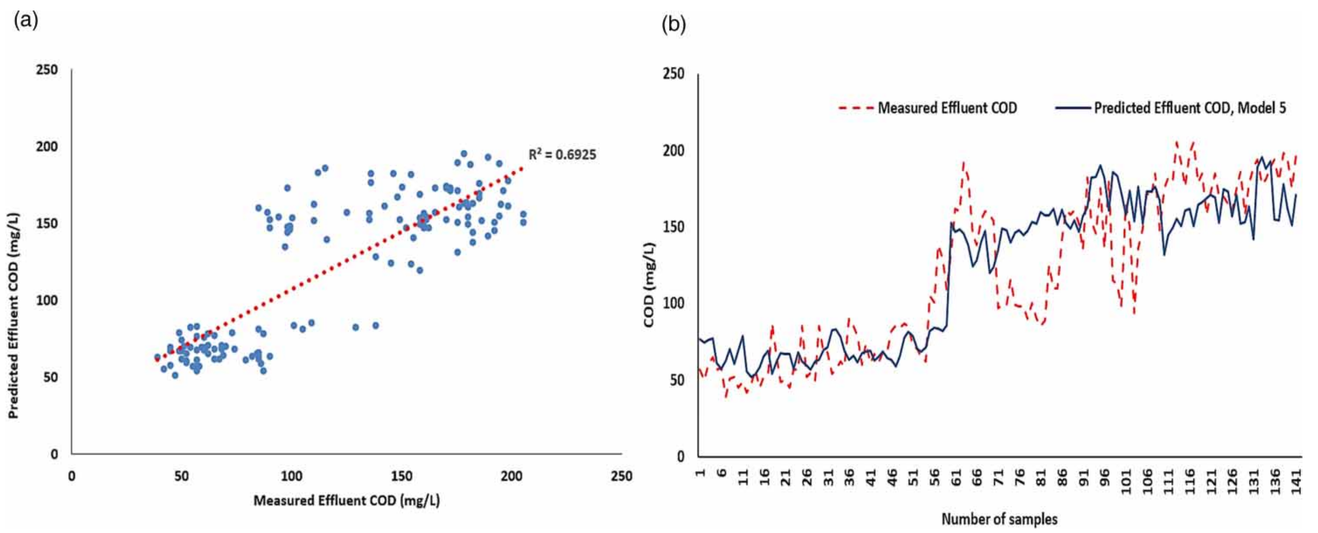

Figure 4 | (a) Correlation coefficient and (b) comparison of measured and predicted COD values in second-order Grau model.

Table 6 | Comparison of statistical metrics in kinetic models for COD removal prediction

Model	MSE	NMSE	RMSE	RRMSE	IA	ME	MAE
Model 1	1,524	0.142	39.0	0.33	0.75	0.43	31.5
Model 2	1,109	0.079	33.3	0.28	0.87	0.59	26.0
Model 3	1,070	0.085	32.7	0.27	0.85	0.60	26.7
Model 4	1,618	0.140	40.2	0.33	0.76	0.40	31.4
Model 5	842	0.050	29.0	0.25	0.91	0.68	22.6

Table 7 | Comparison of DR values in kinetic models

Model	Ave	Max	Min	Range (DR_{max}-DR_{min})
Model 1	– 0.012	0.239	– 0.374	0.613
Model 2	– 0.040	0.233	– 0.266	0.499
Model 3	– 0.021	0.214	– 0.221	0.435
Model 4	– 0.037	0.299	– 0.341	0.640
Model 5	0.021	0.274	– 0.217	0.492

of outlet COD. In general, it could be inferred that the Grau second-order model can be used to predict effluent COD values with the highest precision while Stover-Kincannon model can be used to represent the real biological degradation that takes place during the treatment of wastewater by microorganisms in a PFP system treating municipal wastewater.

Table 8 provides the comparison of the reaction constant rates reported in the literature with the calculated kinetic constants in this study. It can be seen that the large variability in the kinetic rate constants of WSPs has been well documented in the literature. As can be seen in Table 8, the kinetic rates of organic matter degradation determined by different authors vary in a wide range because of a large number of characteristics presenting the complex web of interactions as well as external factors like weather conditions and detention time affecting the performance of the process.

Gratziou & Chalatsi (2015) compared three full scale WAP systems consisting of one facultative pond and one or two maturation ponds to treat municipal wastewater in North Greece. The computed COD removal rates of the first order PF model

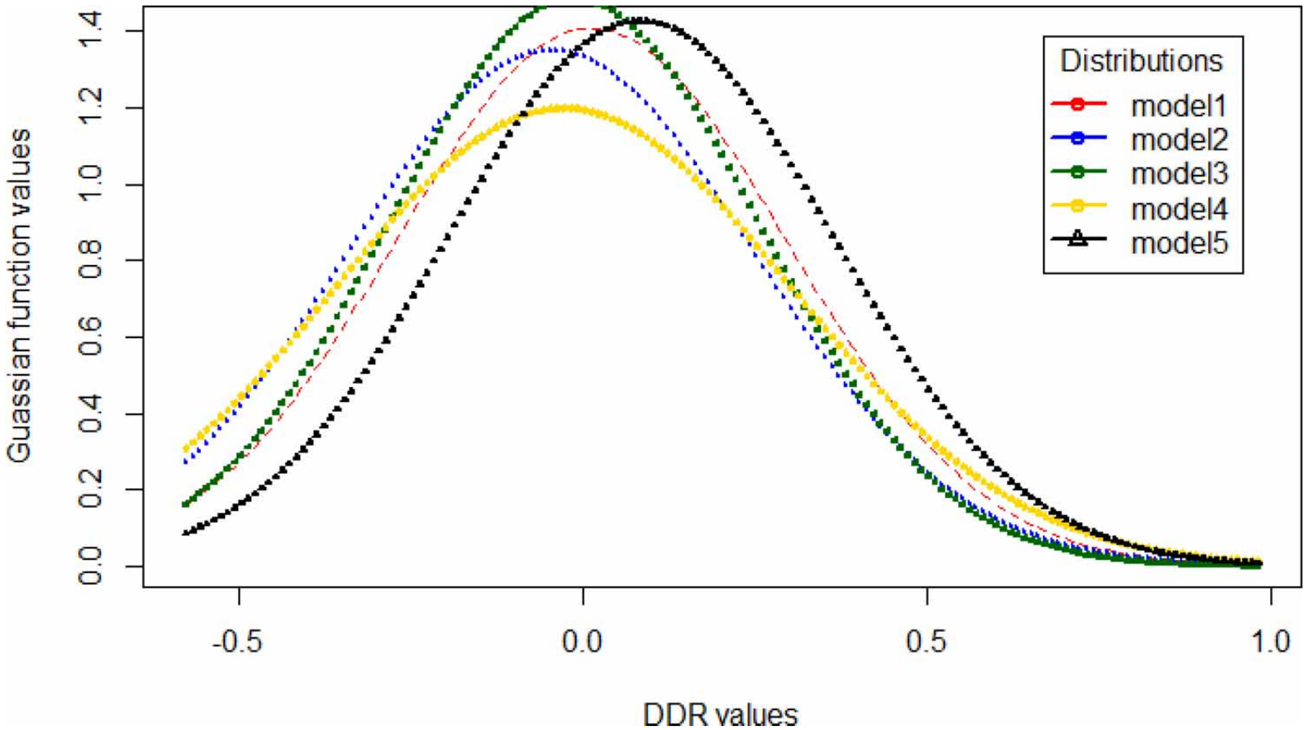

Figure 5 | Standardized normal distribution chart of DDR values in kinetic models.

were equal to 0.0808, 0.0993 and 0.2492 m/d, which are relatively close to the values reported in this research (0.152 m/d). Da Silva *et al.* (2010) also proposed the reaction constant rates of 0.013 d^{-1} for COD and 0.034 d^{-1} for fCOD removal computed through the analysis of data collected from six full-scale PFP systems in Northeast Brazil treating domestic wastewater. The computed COD removal rate of the first order-CSTR model is 0.4509 m/d, which is higher than the values reported by Gratziou & Chalatsi (2015).

As mentioned before, the Stover-Kincannon model was the most suitable in describing the performance of the system whereas the Grau model predicts the efficiency of substrate removal more accurately. The result concurs with the values mentioned by Okoro & Nwaiwu (2017) and Khosravi *et al.* (2013b). Applying this model by Okoro & Nwaiwu (2017) and Khosravi *et al.* (2013b), the kinetic rate constants were found to be ($K_B = 0.118$ g/L·d and $U_{max} = 0.200$ g/L·d) and ($K_B =$ 128.5 g/L·d and $U_{max} = 23.81$ g/L·d), respectively. These kinetic coefficients were lower than the rates computed in this research ($K_B = 79.14$ g/L·d and $U_{max} = 80.65$ g/L·d), except K_B reported by Khosravi *et al.* (2013b), which may be attributed to the appropriate average temperature of effluent (18 °C) in the case study and high hydraulic retention time (HRT) (33 day). The close values of these constants calculated in this study shows that the process efficiency will decline as organic loading rate increases (Ahn & Forster 2000).

The Grau second-order model coefficients (m and n) for COD removal were 0.6725 and 15.867 d^{-1}, respectively, which are lower than the values reported by Khosravi *et al.* (2013b) ($m = 5.091$ and $n = 39.28$ d^{-1}). The values of m and n also were found to be 4.910 and 1.583 d^{-1} by Okoro & Nwaiwu (2017) FPs with an HRT of 10 days, but the corresponding rates were 0.429 and 1.623 d^{-1} in an anaerobic pond and 0.706 and 1.155 d^{-1} in a maturation pond with the same HRT. The initial substrate concentration has positive effects on m value coefficient. The reported Grau second-order model coefficients in different studies are in a relatively wide range due to different substrate concentrations resulting from the stage of the treatment process. In the SFPs, biologically pre-treated effluent containing lower concentrations is treated whereas the raw wastewater characterized by higher organic matter concentrations is treated in PFPs.

Since the PFPs receive raw wastewater (as opposed to SFPs receiving pre-treated wastewater), the loading of organic matter obviously is greater than SFPs. As a result, in most cases but not all, the reaction constant rates/the substrate removal rate obtained in PFPs are higher than the values reported in the literature, which mainly indicate the kinetic rates in SFPs. The kinetic coefficients calculated in this study can be used as a quick reference to predict the performance efficiency of FPs in terms of COD removal for municipal or other wastewater types.

Table 8 | Comparison of kinetic constant rates for COD removal in waste stabilization and facultative ponds

Kinetic model	Kinetic type	Source of wastewater	Process	Kinetic Rate	Reference
First order-CSTR model	Volume-based rate constant	Piggery wastewater	Anaerobic pond HRT = 10 days	5.510, d^{-1}	Okoro & Nwaiwu (2017)
			FP HRT = 10 days	0.540, d^{-1}	
			Maturation pond HRT = 10 days	1.114, d^{-1}	
Stover-Kincannon model			Anaerobic pond HRT = 10 days	–	
			FP HRT = 10 days	$K_B = 0.118$, g/L·d $Umax = 0.200$, g/L·d	
			Maturation pond HRT = 10 days	$K_B = 0.425$, g/L·d $U_{max} = 0.500$, g/L·d	
Grau second-order model			Anaerobic pond HRT = 10 days	$m = 0.429$ $n = 1.623$, d^{-1}	
			FP HRT = 10 days	$m = 4.910$ $n = 1.583$, d^{-1}	
			Maturation pond HRT = 10 days	$m = 0.706$ $n = 1.155$, d^{-1}	
First order-PF model	Area-based rate constant	Municipal wastewater	WSP (No.1)	0.0808, m/d	Gratziou & Chalatsi (2015)
			WSP (No.2)	0.0993, m/d	
			WSP (No.3)	0.2492, m/d	
First order-CSTR model	Area-based rate constant		WSP (No.1)	0.0161, m/d	
			WSP (No.2)	0.0349, m/d	
			WSP (No.3)	0.0384, m/d	
	Volume-based rate constant		WSP (No.1)	0.0774, d^{-1}	
			WSP (No.2)	0.1817, d^{-1}	
			WSP (No.3)	0.0448, d^{-1}	
PF k–C* model	Area-based rate constant		WSP (No.1)	0.0121, m/d	
			WSP (No.2)	0.0229, m/d	
			WSP (No.3)	0.0346, m/d	
Stover-Kincannon model	Volume-based rate constant		WSP (No.1)	$K_B = 27.9845$, g/L·d $U_{max} = 0.0197$, g/L·d	
			WSP (No.2)	$K_B = 22.4078$, g/L·d $U_{max} = 0.034$, g/L·d	
			WSP (No.3)	$K_B = 25.65037$, g/L·d $U_{max} = 0.011$, g/L·d	
First order-CSTR model	Volume-based rate constant	Municipal wastewater	WSP (Anaerobic pond+ FP+ Maturation pond)	0.060, d^{-1}	Khosravi *et al.* (2013b)
Stover-Kincannon model				$K_B = 128.5$, g/L·d $U_{max} = 23.81$, g/L·d	

(*Continued.*)

Table 8 | Continued

Kinetic model	Kinetic type	Source of wastewater	Process	Kinetic Rate	Reference
Grau second-order model				$m = 5.091$ $n = 39.28$, d^{-1}	
First order-PF model	Volume-based rate constant	Municipal wastewater	PFPs	COD = 0.013, d^{-1} fCOD = 0.034, d^{-1}	Da Silva *et al.* (2010)
First order-CSTR model				COD = 0.019, d^{-1} fCOD = 0.091, d^{-1}	
First order-PF model, K_1	Area-based rate constant	Municipal wastewater	PFPs	0.152, m/d	This study
First order-CSTR model, K_2				0.4509, m/d	
PF k–C* model, K_3				0.1891, m/d	
Stover-Kincannon model	Volume-based rate constant			$K_B = 79.14$, g/L·d $U_{max} = 80.65$, g/L·d	
Grau second-order model				$m = 0.6725$ $n = 15.867$, d^{-1}	

CONCLUSION

This research aims at evaluating the overall performance and determining the bio-kinetic coefficients of COD removal in PFPs employed as a secondary treatment of municipal wastewater. The removal efficiency of COD was found to be significant (80%) as the concentration declined from 590 to 119 mg/L. The differences between the concentration of TSS and VSS at the inlet and outlet were also extremely significant with the removal efficiency of 59 and 49%, respectively. Unlike many studies in which the SFPs were used to evaluate the kinetics of organic matter removal, the full-scale PFPs were used in this study to compare the predictive power of five kinetic models that have been applied widely to estimate the substrate removal rate.

While the Stover-Kincannon model offered better accuracy ($r^2 = 0.9294$) in comparison with the other models to define the system most appropriately, the Grau second-order model can be used to predict effluent COD values properly ($r^2 = 0.6925$). The maximum utilization rate (U_{max}) and saturation constant (K_B) were higher in this study compared to some studies that utilized SFPs, which may explain the higher values of the inlet chemical organic matters concentration. The kinetic rate constants (m and n) for Grau second-order model obtained in this research were 0.6725 and 15.867 d^{-1}, respectively which are relatively lower than the values ($m = 5.091$ and $n = 39.28$ d^{-1}) reported by Khosravi *et al.* (2013b) and much lower than ones found by Okoro & Nwaiwu (2017) for an SFP with the HRT of 10 days (4.910 and 1.583 d^{-1}). The difference between bio-kinetic rates reported in different literatures and ones found in this study is due to the stage of the process, which receives raw wastewater characterized by higher concentrations of organic matter.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge deputy directors and operators in North Khorasan Province Water and Wastewater Company for their support during the study.

COMPETING INTERESTS

The authors declare no conflict of interest.

FUNDING

The research received no funds.

CONFLICT OF INTEREST

The authors declare no conflict of interest to any party.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 28 August 2021; accepted in revised form 17 February 2022. Available online 28 February 2022