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Kinetic-hydrodynamic models considering climatic influence on the domestic sewage treatment by constructed wetlands in tropical country

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ABSTRACT. Typical constructed wetlands (CW) sizing methods in tropical countries rarely considers climate parameters as evapotranspiration (EPT) and rainfall (Ra), even though high levels of EPT and Ra can change the pollutant removal kinetic and Wastewater hydrodynamic. This paper aims to evaluate the climatic influences (EPT and Ra) on fit of several kinetic-hydrodynamic models used to describe the sewage organic matter removal in a real scale vertical (VSSF-CW) and horizontal (HSSF-CW) subsurface flow constructed wetland. Sewage quality (Biochemical Oxygen Demand - BOD and Chemical Oxygen Demand - COD) and sewage flow rates data were applied of First Order, Grau-Second Order, Monod, Monod Multi and Stover-Kincannon kinetic models, combined with ideal continuous stirred-tank reactor (CSTR) and plug-flow reactor (PF) hydrodynamic models. Monod, Monod Multi and Stover-Kincannon models (in CSTR) were more able to represent organic matter removal in CWs. Models considering EPT and Ra were more adequate or with no statistical difference compared with conventional models (that don't consider EPT and Ra), except for BOD in VSSF-CW.

Keywords: evapotranspiration; pluviometrical precipitation; organic load.

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Introduction

It is well-known that in tropical countries, there are three main methods for the design of wastewater treatment by constructed wetlands (CW): (1) models that combines kinetic pollutant removal and hydrodynamic flow; (2) *per capita* treatment bed area/volume specification and (3) applied hydraulic and/or organic load specification (Kadlec & Wallace, 2009; Sezerino, Bento, Decezaro, Magri, & Philippi, 2015). The major benefit of those methods is that the CW's design is simplified. On the other hand, many important variables can be neglected in CW wastewater treatment design, such as the evapotranspiration (EPT) and rainfall (Ra).

So, from these sizing methods, the most used is (1), that witch combines removal pollutant kinetic (usually First Order) with a hydrodynamic flow (plug-flow reactor – PFR or continuous stirred-tank reactor - CSTR), and the CWs with horizontal hydraulic flow, for example, are mostly dimensioned according to the First Order kinetic model for PFR - Kickuth equation or K-C* model (Kadlec, 2000; Mucha, Wójcik, Jóźwiakowski, & Gajewska, 2018; Gajewska et al., 2020).

There are some issues with using this sizing method, and equations for pollutants removing as First Order kinetics may not represent reality (Kadlec, 2000; Saeed & Sun, 2011). For, First Order kinetic models have some limitations: they are more sensitive to variations in the concentration of pollutants being treated over time; consider that irreversible reactions occur in sewage treatment processes; consider only one single limiting substrate (with homogeneous characteristics) in treatment process (Von Sperling, 2014). Many of CWs treatment beds may exhibit hydrodynamics without PFR behavior, such as, vertical flow CWs, implying that Kickuth equation cannot be appropriate. Such misunderstandings can generate CWs that are oversized or smaller than required. Also, dispersed flow hydrodynamic models have analytical resolution complexity when associated with kinetic models of degradation of pollutants different than First Order. Thus, those models require resolution by complex numerical methods.

Also, it is important to say that others current mathematical models are used (less frequently) for CW sizing in tropical countries, from simple mathematical equations (with analytical solution) to complex systems of equations with numerical solution (Huang et al., 2014; Ren & Gang, 2015; Sabokrouhiyeh, Bottacin-Busolin, Savickis, Nepf, & Marion, 2017). Complex mathematical models tend to present greater capacity for description (better statistical adjustment of data) of the treatment mechanisms; however, they present complex resolutions, making them inaccessible for some professionals (as they need expensive computer software). On the other hand, simplified models may not adequately represent reality. So, this study aimed to evaluate the applicability of ideal hydrodynamic models (CSTR and PFR), which have analytical resolution when associated with pollutant degradation kinetics which can be easily used by engineers in CW's projects.

In order to develop standard methods for CW design in tropical countries, which would help in the larger diffusion of the use of this technology, sizing models should have at least the following characteristics: high representativeness in the description of the behaviour of pollutants; range in the number of pollution parameters portrayed by the model (organic matter, nitrogen and phosphorus); relatively ease in analytical resolution.

For the representativeness of the processes of pollutants removal in CWs to be high, the influence of important variables such as evapotranspiration (EPT) and rainfall (Ra) cannot be neglected (Headley, Davison, Huett, & Müller, 2012; Milani et al., 2019). There are few mathematical models used to represent CWs that consider EPT and Ra in sewage treatment processes, and in general, design equations do not take into account water losses or gains during treatment processes. However, high rates of EPT and Ra, like in Brazil, can change the quality (modifying pollutant concentration) and hydrodynamics (including hydraulic retention time - HRT) of the sewage in CW.

As a result, high Ra values can promote the dilution (reduction of concentration) of pollutants in the wastewater treatment environment. On the other hand, high rates of EPT can cause an increase in the concentration of pollutants, and both situations can impact the effectiveness of hydraulic-kinetic models in representing the degradation of organic matter, for example, in CW. It is suggested that the insertion (even indirectly) of EPT and Ra parameters in the kinetic-hydrodynamic models can increase the representativeness of the pollutant removal processes and contribute to the standardization of CWs sizing in tropical countries.

So, as mentioned before, this paper aims to evaluate the climatic influences (EPT and Ra) on fit of several kinetic-hydrodynamic models used to describe the sewage organic matter removal in constructed wetlands.

Material and methods

The methodology adopted in this research involved the following sequential steps was: designing and constructing of a real scale CW sewage treatment plant; qualitative and quantitative monitoring of raw and treated sewage by this treatment plant; and, with the results data, drawing a statistical evaluation of the kinetic-hydrodynamic considered models.

Sewage treatment plant

An experimental sewage treatment plant was constructed at the Rio Verde campus of the Goiano Federal Institute, Goiás, Brazil (Latitude: 17°48'19.93"S; Longitude: 50°54'24.30"O), to treat only domestic wastewater from four residences (ten persons) of employees who work and live within that campus.

The treatment system consisted of septic tank, pumping well and two CWs (in series) treatment beds. The first bed has vertical subsurface hydraulic flow (VSSF-CW) and the second has horizontal subsurface flow (HSSF-CW). Figure 1 shows the flowchart of the treatment plant.

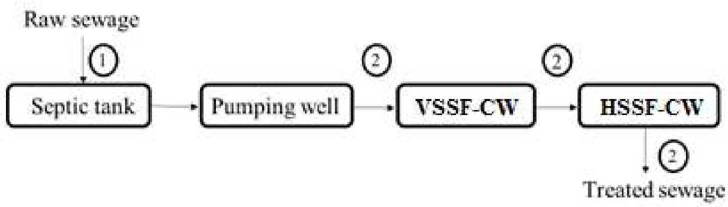

Figure 1. Flowchart of the implanted domestic sewage treatment process. 1: Sewage sampling; 2: Sewage sampling and flow monitoring.

Firstly, it was necessary to adopt a sewage pumping system (after septic tank) due to the low slope of the ground and the impossibility of free sewage flow to the CWs beds.

The characteristics of implanted treatment beds (CWs) are presented in Table 1.

Table 1. Characteristics of implanted CWs-type treatment beds.

Parameter	VSSF-CW	HSSF-CW
Length (m)	2,8	10,0
Width (m)	2,8	2,0
Depth (m)	0,8	0,4
nHRT (d)	2,5	3,0
Slope (º)	60,0	60,0
Plant species	Chrysopogon zizanioides	Chrysopogon zizanioides
Support médium	Gravel (UC = 1,7; n: 45,1%)	Gravel (UC = 1,4; n: 46,7%)
Support medium saturation	Saturated	Semi-saturated
Flow Direction	Down	Left – right
Waterproofing	HDPE (1,5 mm)	HDPE (1,5 mm)

Note: VSSF-CW = vertical subsurface flow constructed wetland; HSSF-CW = horizontal subsurface flow constructed wetland; nHRT = nominal hydraulic retention time (d); UC = uniformity coefficient; n = media porosity (%); HDPE = high density polyethylene.

It is worth to mention that the application of sewage in the treatment system was discontinuous and variable, proportional to variation in wastewater generation by the residents. As the pumping well filled (with useful volume of 500 L), the sewage pre-treated by the septic tank was pumped (through a 0.75 HP submerged hydraulic pump) to VSSF-CW and from this to HSSF-CW. On average, the flow rate applied to VSSF-CW was 644.8 L d^{-1}. In HSSF-CW, the average influent flow was 568.0 L d^{-1}, indicating water loss (probably by EPT) in treatment beds.

Monitoring treatment system

To measure sewage flow in the CWs, volumetric hydrometers were implanted (Altair brand ¾”, C type – minimum flow of 15 L h^{-1}) to quantify, daily, the inflow and outflow of sewage in each CW bed (Figure 1), and ata from 471 days over 16 months of monitoring were obtained.

Biweekly samples of inflow and outflow sewage were collected at each CWs, as well as raw sewage (before entering the septic tank, according Figure 1) for quantitative evaluation of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and dissolved oxygen (DO) for data application to kinetic-hydrodynamic models. In all, 33 data were collected for COD and DO, and 22 data for BOD, corresponding to a monitoring period of 16 and 11 months for COD and BOD, respectively.

The analytical methods used (performed on duplicate samples) to quantify COD, BOD, DO in the sewage were 5220 D (closed reflux, colorimetric method), 5210 B (5-day BOD test), 4500-O C (azide modification) respectively, according to the “Standard Methods for the Examination of Water and Wastewater” (American Public Health Association [APHA], 1999).

Evaluated models

Later, linear fit (by statistical regression) for each of five kinetic models of organic matter degradation, combined with two idealized hydrodynamic models, in two situations (with and without the influence of Ra and EPT) was evaluated. In all, the levels of statistical linear fit of 28 kinetic-hydrodynamic models were evaluated, as shown in Table 2.

A preliminary hydrodynamic traced test indicates VSSF-CW hydrodynamic with slight deviation to CSTR behaviour (d = 1.58 and N = 1.54), while HSSF-CW indicated high dispersion (d = 0.63 and N = 4.53) and high PFR deviation, suggesting that the most appropriate hydrodynamic model to represent HSSF-CW is dispersed flow. Because of that, in this research, CSTR hydrodynamic model behaviour was evaluated in both CWs beds and PFR only for HSSF-CW. Monod Multi kinetics was only evaluated with CSTR hydrodynamics, because considering PFR would imply complex models that only allow numerical solution.

Thus, combining ideal steady state hydrodynamic flow equations (CSTR or PFR) with the pollutant removal kinetics (First Order, Grau Second Order, Monod, Monod Multi and Stover-Kincannon), the kinetic-hydrodynamic models without Ra and EPT influence were obtained (Table 3), since only inflow and outflow organic matter concentrations (substrate) were considered in the equations.

Table 2. Combination of the kinetic-hydrodynamic models used. Considering two different scenarios (with and no climate influence) there are 28 models.

Models	Constructed wetland	Hydrodynamics	Kinetics
1	VSSF-CW	CSTR	First Order
2		CSTR	Grau Second Order
3		CSTR	Monod
4		CSTR	Monod Multi
5		CSTR	Stover-Kincannon
6	HSSF-CW	PFR	First Order
7		PFR	Grau Second Order
8		PFR	Monod
9		PFR	Stover-Kincannon
10		CSTR	First Order
11		CSTR	Grau Second Order
12		CSTR	Monod
13		CSTR	Monod Multi
14		CSTR	Stover-Kincannon

Note: CSTR = continuous stirred-tank reactor; PFR = plug-flow reactor.

Table 3. Kinetic-hydrodynamic models evaluated according to the association of hydrodynamic flow and pollutant removal kinetics without climate influence.

Hydrodynamic	Kinetic	Kinetic-hydrodynamic model
CSTR	First Order	$\frac{Kv\,.\,Ce}{1} = \frac{(Ca - Ce)}{\theta}$
CSTR	Grau Second Order	$\frac{Kv\,.\,X}{1}\left(\frac{Ce}{Ca}\right)^2 = \frac{(Ca - Ce)}{\theta}$
CSTR	Monod	$\frac{Ce\,.\,Km}{(Ks + Ce)} = \frac{(Ca - Ce)}{\theta}$
CSTR	Monod Multi	$\frac{Km}{1}\frac{Ce1}{(Ks1 + Ce1)}\frac{Ce2}{(Ks2 + Ce2)} = \frac{(Ca - Ce)}{\theta}$
CSTR	Stover-Kincannon	$\frac{Km\,.\,Sa}{(Ks + Sa)} = \frac{(Ca - Ce)}{\theta}$
PFR	First Order	$\ln\frac{Ca}{Ce} = -ka.\theta$
PFR	Grau Second Order	$\frac{Ca}{Ce} = -ka.X.\theta$
PFR	Monod	$Ca - Ce + Ks.\ln\frac{Ca}{Ce} = -Km.\theta$
PFR	Stover-Kincannon	$Ca - Ce + \frac{Ks}{Qin}.\ln\frac{Ca}{Ce} = -Km.\theta$

Note: Ce = effluent substrate concentration (mg L^{-1}); Ca = affluent substrate concentration (mg L^{-1}); Ce1 = effluent concentration of limiting substrate 1 (mg L^{-1}); Ce2 = effluent concentration of limiting substrate 2 (mg L^{-1}); Qin = inflow sewage in CW (L d^{-1}); θ = hydraulic retention time (d^{-1}); X = reactor biomass concentration (mg SS L^{-1}); Kv = volumetric degradation constant (m d^{-1}); Ka = surface degradation constant (d^{-1}); Km = maximum reaction rate (mg L^{-1} d^{-1}); Ks = saturation constant (mg L^{-1}); Ks1 = limiting substrate saturation constant 1 (mg L^{-1}); Ks2 = limiting substrate saturation constant 2 (mg L^{-1}); Sa = applied surface pollutant load (mg m^{-2} d^{-1}).

The main substrates (pollutants) evaluated in each model, present as C concentrations, were BOD and COD. In the case of the Monod Multi model, the second limiting substrate was dissolved oxygen (DO).

In no climate influence situation, sewage inflow (Qin) and hydraulic retention time (θ) values applied to the models considered only the average daily inflow rate (from the two days before sampling) to each CW.

Ks, Ks1, Ks2 and X values were initially obtained from literature data (Table 4) and later adjusted (by model calibration) to the research field conditions, and Kv, Ka and Km are angular coefficients of the straight lines obtained by the linear regression of their respective models, corresponding to the values of the pollutants degradation kinetics.

Table 4. Literature sewage treatment constants used before calibration in kinetic-hydrodynamic models.

Parameter	Kinetic	Literature value			Reference
		BOD (mg L^{-1})	COD (mg L^{-1})	DO (mg L^{-1})	
X	Grau Second Order	6.500,0	6.500,0	-	Padilla-Gasca and Lopez (2010)
Ks	Monod	60,0	20,0	-	Sun and Saeed (2009); Saeed and Sun (2011)
Ks1	Monod Multi	60,0	20,0	-	Sun and Saeed (2009); Saeed and Sun (2011)
Ks2	Monod Multi	-	-	0,2	Saeed and Sun (2011)

To consider the effects of Ra and EPT on CWs, the concept of pollutant load L (La - affluent and Le - effluent) instead of concentration (C) was used. In addition, the hydraulic retention time (θ) of each CW bed was changed to (θm), which considered the mean of the inflow and outflow of CW (Qm – Equation 1). Table 5 summarizes equations of modified mathematical models for consideration of Ra and EPT, then, with these modified equations it is possible to include the influence (even indirectly) of Ra and EPT in sewage treatment processes in CWs.

$$Qm = \frac{Qin + Qout}{2} \quad (1)$$

In representation: Q_{in}: average (2 days before sampling) CW inflow sewage (L d^{-1}); Q_{out}: average (2 days before sampling) CW outflow sewage (L d^{-1}).

Table 5. Modified kinetic-hydrodynamic models for consideration of Ra and EPT according to the association of hydrodynamic flow and pollutant removal kinetics.

Hydrodynamic	Kinetic	Kinetic-hydrodynamic model
CSTR	First Order	$\frac{Kv \,.\, Le}{1} = \frac{(La - Le)}{\theta m}$
CSTR	Grau Second Order	$\frac{Kv \,.\, X}{1}\left(\frac{Le}{La}\right)^2 = \frac{(La - Le)}{\theta m}$
CSTR	Monod	$\frac{Le \,.\, Km}{(Ls + Le)} = \frac{(La - Le)}{\theta m}$
CSTR	Monod Multi	$\frac{Km}{1}\frac{Le1}{(Ls1 + Le1)}\frac{Le2}{(Ls2 + Le2)} = \frac{(La - Le)}{\theta m}$
CSTR	Stover-Kincannon	$\frac{Km \,.\, La}{(Ls + La)} = \frac{(La - Le)}{\theta m}$
PFR	First Order	$\ln\frac{La}{Le} = -ka.\theta m$
PFR	Grau Second Order	$\frac{La}{Le} = -ka.\theta m$
PFR	Monod	$La - Le + Ls.\ln\frac{La}{Le} = -Km.\theta m$
PFR	Stover-Kincannon	$La - Le + \frac{Ls}{Qm}.\ln\frac{La}{Le} = -Km.\theta m$

Note: Le = substrate effluent load (mg d^{-1}); La = substrate affluent load (mg d^{-1}); Le1 = effluent load of limiting substrate 1 (mg d^{-1}); Le2 = effluent load of limiting substrate 2 (mg d^{-1}); Qm = average of inflow and outflow sewage in CW (L d^{-1}); θm = average hydraulic retention time (d^{-1}); X = reactor biomass concentration (mg SS L^{-1}); Kv = volumetric degradation constant (m d^{-1}); Ka = surface degradation constant (d^{-1}); Km = maximum reaction rate (mg L^{-1} d^{-1}); Ls = saturation load constant (mg L^{-1}); Ls1 = limiting substrate saturation load constant 1 (mg d^{-1}); Ls2 = limiting substrate saturation load constant 2 (mgd^{-1}).

The individual behaviour of BOD and COD were also evaluated in each model (besides DO as the second limiting substrate for Monod Multi model).

Thus, the Ls, Ls1 and Ls2 were initially obtained by multiplying the respective values in Table 4 by the average flow data (Qm) in each CW and later calibrated to the real conditions. As the Kv, Ka and Km are also the angular coefficients of the lines and values of the pollutants degradation kinetics.

Statistical evaluation

To estimate kinetic (Kv, Ka and Km) of pollutant transformation in VSSF-CW and HSSF-CW, the fit linear adjustment of the kinetic-hydrodynamic equations of Tables 3 and 5 was performed according to the form y(t) = B + A.t.

As shown, A = Kv, Ka or Km, pollutant degradation kinetics; y(t) = isolated fraction numerator; t = denominator of the isolated fraction. Subsequently, the linear regression of the set of points of the graph was performed, obtaining R^2 (Pearson coefficient) value. Figure 2 exemplifies the result of COD behaviour evaluation according to the Monod-CSTR model (without climate influence) in the VSSF-CW.

The coefficient of determination (R^2 - Equation 2) was used to estimate the adequacy of each model in the description of the studied processes.

$$R^2 = \frac{[\sum_{i=1}^{N}(Xi - \overline{X})\,(Yi - \overline{Y})]^2}{\sum_{i=1}^{N}(Xi - \overline{X})^2\ \sum_{i=1}^{N}(Yi - \overline{Y})^2} \quad (2)$$

In representation: Xi, Yi = individual data obtained, $\overline{X}$, $\overline{Y}$ = data averages, N = number of samples.

Another statistical parameter used to evaluate the performance of the models in the data description was the "Relative Mean Square Error Root" (RMSER), given by Equation (3).

$$RMSER^2 = \frac{\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(Yi - \hat{Y}i\right)^2}}{\overline{Y}} \quad (3)$$

In representation: Yi = observed value, Yî = model estimated value.

As seen, the RMSER value also ranges from 0 to 1 and measures the difference between the data estimated by the model and the values observed in the field, and RMSER close to 0 corresponds to perfect models.

Following, a statistical significance between the kinetics of the studied scenarios (with and without climate influence) was evaluated by t-student (bilateral and homoscedastic sample) and F-Fisher (bilateral) tests, with significance level p = 0,05. Prior to this step, the data from each model were subjected to analysis by the Kolmogorov-Smirnov and Shapiro Wilk tests, which indicated normality of the data, and a GraphPad Prism 7® software was used to assess normality and statistical significance.

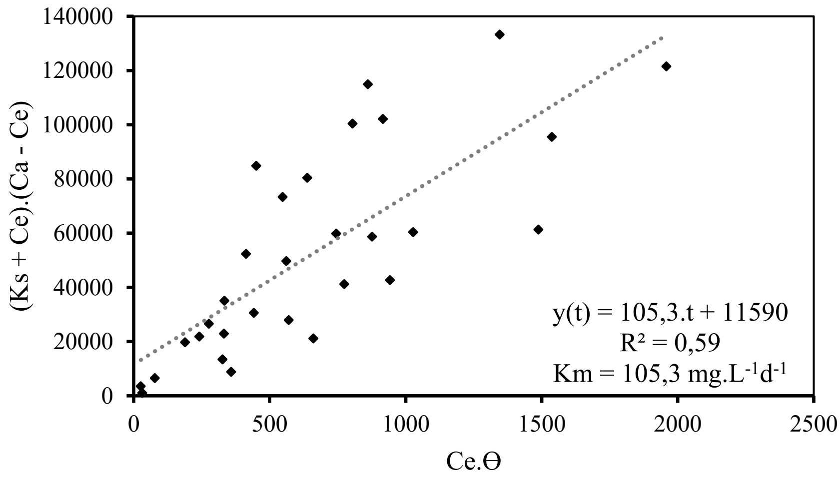

Figure 2. Example of the linearization process of the Monod-CSTR model (according to COD behaviour) to obtain the pollutant degradation kinetics (Km).

Results and discussion

According Table 6, organic matter concentration (BOD and COD) in raw sewage (RS) presented similar values present in literature for fresh domestic sewage. Pre-treatment performed by septic tank (and possibly the sewage aeration caused by pumping well) showed average treatment efficiency of 48.4 and 38.9%, for BOD and COD, respectively. Also, those performance values are similar to those observed in literature for septic tank treatment (generally around 20-50% for organic matter removal) (Metcalf & Eddy, 2013).

Table 6. Statistical values of sewage for BOD and COD in CWs.

Parameter	BOD ($mg\ L^{-1}$)				COD ($mg\ L^{-1}$)			
	RS	I-VSS	O-VSS	O-HSS	RS	I-VSS	O-VSS	O-HSS
Mean	202,7	104,5	32,2	13,0	751,9	459,8	220,8	104,4
Median	217,2	86,1	27,4	10,1	486,7	451,6	183,3	90,7
Maximum	329,5	245,2	66,0	40,9	2586,7	773,3	553,3	248,0
Minimum	150,7	51,9	8,2	1,1	370,0	137,8	5,0	5,0
SD	107,1	49,4	14,6	10,7	816,1	179,8	155,2	76,2
n	10	22	22	22	10	33	33	33

Note: n = number of samples; SD = Standard deviation; RS = raw sewage; I-VSS = inflow sewage of vertical subsurface flow constructed wetland; O-VSS = outflow sewage of vertical subsurface flow constructed wetland; O-HSS = outflow sewage of horizontal subsurface flow constructed wetland.

It was noted that the BOD/COD ratio of raw domestic sewage was 0.27, which characterizes it as a wastewater with intermediary biodegradable fraction. The means BOD/COD ratio of I-VSS, O-VSS and O-HSS were 0.23, 0.14 and 0.12, respectively, which indicate that in the VSSF-CW occurred more organic matter biodegradation processes than in the septic tank or HSSF-CW.

About the CWs, mean organic matter removal values, such as BOD and COD, were 69.1 and 52.0% for VSSF-CW and 59.6 and 52.7% for HSSF-CW, respectively, and the total average removal efficiency of CWs system was 87.5 and 77.3% for BOD and COD, respectively. Such results are consistent with those raised by Zhang et al. (2014) in a literature review on the performance of CWs systems to remove organic matter.

Organic matter removal – COD

VSSF-CW

The statistical estimators and removal kinetic constants (K) for COD behaviour in VSSF-CW, according to kinetic-hydrodynamic models and scenarios evaluated in CSTR flow reactors, are presented below in Table 7.

Table 7. Statistical estimators and kinetic constants of the models evaluated in VSSF-CW for COD removal.

Flow	Kinetics	Without climate influence			With climate influence			Test	
		R^2	RMSER	K*	R^2	RMSER	K*	F	t
CSTR	First Order	0,02	0,69	1,64 d^{-1}	0,01	0,88	14,2 d^{-1}	NS	NS
	Grau Second Order	0,11	0,74	769,2 d^{-1}	0,00	1,60	0,01 d^{-1}	NS	NS
	Monod	0,59	0,44	105,3 mg L^{-1} d^{-1}	0,70	0,49	139,8 mg L^{-1} d^{-1}	SD	SD
	Monod Multi	0,69	0,41	204,1 mg L^{-1} d^{-1}	0,78	0,48	274,5 mg L^{-1} d^{-1}	SD	SD
	Stover-Kincannon	0,66	0,27	217,6 mg L^{-1} d^{-1}	0,53	0,33	315,2 mg L^{-1} d^{-1}	SD	SD

Note: K* Kinetic constants (Kv = First Order or Grau Second Order; K_m = Monod, Monod Multi or Stover-Kincannon); NS = no statistical significance; SD = statistical difference; R^2 = Pearson coeficient; RMSER = relative mean square error root; F = Fisher; t = Student.

As we can realise, Monod Multi (climate-influenced) kinetic model was the most suitable (R^2 = 0,78 e RMSER = 0,48) to representate COD removal processes in relation to the other models considered, and Monod Multi kinetics considered organic matter (COD) and DO as the two limiting (and representative) substrates of the organic matter transformation process. Monod and Stover-Kincannon kinetics showed a slightly smaller statistical adjustment (R^2 < 0.70). However, the First Order and Grau Second Order models were not adequate to represent the COD removal in VSSF-CW, confirming that indicated by Kadlec (2000), which states that First Order kinetics, although widely used, is not adequate to describe the removal of organic matter in CWs. Furthermore, first Order models are associated with idealized hydrodynamics, i.e., they do not perfectly represent the behavior of the wastewater in the treatment system, as they are not able to simulate any anomalies in wastewater flow. Such models also do not portray the reduction of effluent biodegradability throughout the treatment, and finally, they do not consider the fraction of the effluent that is residual, recalcitrant, or not removable (Matos, Matos, Costa, & von Sperling, 2018; Ferreira, Borges, & Rosa, 2021).

Of all the models evaluated, only the First Order and Grau Second Order kinetics did not present different statistical significance (NS) considering the aspects with and without the climatic effects, and for the most representative models, Monod and Monod Multi, the indirect insertion of Ra and EPT in the equations increased their effectiveness. Models such as Monod and Monod Multi approximately represent zero and one order kinetics, as well as the transition between them, depending on the concentration of the limiting substrate in it. The great advantage of these models is their structure, which makes it possible to continuously represent the range of variation between the extremes of scarcity and abundance of the pollutant in the environment, especially for the removal of heterogeneous organic material. In general, the Monod and Monod Multi models, for example, may be responsible for "correcting" the concentrations of pollutants resulting from evapotranspiration in the SAC's, as well as representing reversible reactions in the treatment process, in addition to considering more than one limiting substrate (case of Monod Multi) in the treatment (Kadlec, 2000; Von Sperling, 2014).

Nguyen et al. (2018) observed that First Order and Monod models showed an intermediate correlation (R^2 = 0.51 and 0.60, respectively) in the COD representation in VSSF-CW. On the other hand, Zhao, Hu, Zhao, and Kumar (2018) observed that the Monod-CSTR model did not present a satisfactory representation (R^2 = 0.41) of COD removal processes in VSSF-CW. The study carried out by Saeed and Sun (2011) also concluded that Monod's kinetic model was more effective (R^2 = 0.7 and RMSER = 0.8) in representing COD removal in VSSF-CW than First Order kinetics. However, Monod Multi kinetics showed the best fit (R^2 = 0,8 e RMSER = 0,9).

We can note that the First Order kinetics model is not the most efficient in describing the process of degradation of organic matter in CWs (Kadlec, 2000), on the other hand, it has advantages such as the reduced amount of variables used and the ease of estimating the value of Kv. Those are the main reasons why this kinetics is widely used in CW sizing in Brazil (Sezerino et al., 2015). However, considering such removal kinetic model in CWs sizing, there is a risk of process inefficiency, then, as we can see the First Order kinetic models have some limitations: they are more sensitive to variations in the concentration of pollutants being treated over time; consider that irreversible reactions occur in sewage treatment processes; consider only one single limiting substrate (with homogeneous characteristics) in the treatment process.

On evaluating COD removal efficiency in VSSF-CW of this paper, we see that it is a highly reducing environment, anaerobic reactions prevailed, which may have been responsible for the low treatment efficiency. A priori, the studied VSSF-CW was dimensioned taking into account the First Order kinetic model, which, in this research, was unsatisfactory in the representation of the process. Also, this error may have been responsible for the reduced efficiency (52.0%) of COD removal in the studied CW, and the hypothesis that the largest biodegradable fraction was removed in the previous treatment units, and consequently reducing the removal efficiency in the CWs, may also be true.

Considering the model that presented the best suitability (Monod Multi-CSTR), the maximum COD removal kinetic rate (Km) in VSSF-CW obtained in this study was estimated in 274.5 mg COD L^{-1} d^{-1} (considering the climate influence). Saeed and Sun (2011) estimated the Km value in 12.1 mg L^{-1} d^{-1} and 14.2 mg $L^{-1}.d^{-1}$ for the Monod Multi and Monod kinetics, respectively, lower than those found in the present research. This result can be explained due to the size of the reactors used by Saeed and Sun (2011) (laboratory scale) and the type of wastewater used (synthetic wastewater with very low organic load) in their research.

HSSF-CW

Table 8 shows statistical estimators and kinetic parameters of COD reaction in HSSF-CW, according to kinetics, hydrodynamics, and scenarios evaluated in CSTR and PFR reactors.

Table 8. Statistical estimators and kinetic constants of models evaluated in HSSF-CW for COD transformation.

Flow	Kinetics	Without climate influence			With climate influence			Test	
		R^2	RMSER	K*	R^2	RMSER	K*	F	t
CSTR	First Order	0,15	0,87	0,44 d^{-1}	0,05	0,81	7,14 d^{-1}	NS	NS
	Grau Second Order	0,19	2,00	17,8 d^{-1}	0,05	2,86	10,63 d^{-1}	SD	SD
	Monod	0,04	0,89	99,8 mg L^{-1} d^{-1}	0,03	0,80	56,9 mg L^{-1} d^{-1}	NS	NS
	Monod Multi	0,06	0,97	88,3 mg L^{-1} d^{-1}	0,63	0,98	88,1 mg L^{-1} d^{-1}	SD	SD
	Stover-Kincannon	0,75	0,34	78,7 mg L^{-1} d^{-1}	0,68	0,41	66,7 mg L^{-1} d^{-1}	NS	NS
PFR	First Order	0,03	0,79	1,50 d^{-1}	0,04	1,24	1,08 d^{-1}	NS	NS
	Grau Second Order	0,02	0,79	2,39 d^{-1}	0,01	0,95	5,1 d^{-1}	NS	NS
	Monod	0,08	0,79	99,1 mg L^{-1} d^{-1}	0,09	0,94	167,3 mg L^{-1} d^{-1}	NS	NS
	Stover-Kincannon	0,22	0,62	98,7 mg L^{-1} d^{-1}	0,40	0,59	152,3 mg L^{-1} d^{-1}	SD	SD

Note: K* Kinetic constants (Kv = First Order or Grau Second Order; K_m = Monod, Monod Multi or Stover-Kincannon); NS = no statistical significance; SD = statistical difference; R^2 = Pearson coeficient; RMSER = relative mean square error root; F = Fisher; t = Student.

Stover-Kincannon (with and without climate influence) and Monod Multi (with climate influence) kinetic models, both for CSTR flow, showed a intermediate linear correlation ($R^2 > 0.62$), indicating those which were reasonably adequate in explaining COD behavior in HSSF-CW. The other models and scenarios were totally inadequate ($R^2 < 0.40$), possibly because the best hydrodynamic model for the case is the dispersed flow (as a preliminary hydrodynamic traced test suggest). CSTR flow presented a better description of COD behaviour in HSSF-CW than PFR flow, which brings the hypothesis that the presence of volumetric hydrometers in the system increases the dispersion of sewage flow across CWs.

Again, the use of pollutant loading instead of concentration, thus considering the influence of Ra and EPT on sewage treatment processes, was more appropriate or with no statistical difference. High rates of Ra can dilute (reduce the concentration) wastewater pollutants in CWs, and on the other hand, high rates of EPT can cause an increase in the concentration of pollutants. Both situations can modify the hydrodynamics of the flow of pollutants and the kinetics of degradation of organic matter, for example. Percentage rates of water loss by EPT in CWs vary greatly depending on climate (higher rates in warmer climates), type of vegetation, among other factors. Studies show values of water losses by EPT greater than 50%, which reinforces the importance of EPT in CW projects (Bialowiec, Albuquerque, & Randerson, 2014; Silva Júnior, Almeida, Rodrigues, & Silva, 2015).

Stover-Kincannon kinetics already consider the pollutant load (La) input to its equation, a fact that may explain the statistical insignificance in the relationship of models with and without influence of Ra and EPT. Rangel-Peraza et al. (2017), in surface-flow CW, obtained R^2 of 0.79 for the First Order kinetic model, on the other hand, the Stover-Kincannon and Grau Second Order kinetic models were more appropriate ($R^2 = 0.99$) in the representation of the COD removal phenomenon studied by the authors.

Evaluating the best fit (Stover-Kincannon-CSTR, with and without climate influence) kinetic models to COD behavior in HSSF-CW, the maximum removal rates (Km) obtained in this research were 78.7 and 66.7

mg COD.L^{-1}.d^{-1}, respectively, lower than kinetics rate obtained in VSSF-CW, indicating that the most easily biodegradable fraction of organic matter was consumed in the previous treatment units. Rangel-Peraza et al. (2017) obtained Km of 2,500.0 mg COD.L^{-1}.d^{-1}, but without previous treatment of sewage of university origin, also, the same mechanisms of COD removal predominant in VSSF-CW, anaerobic reactions (methanogenesis and sulfetogenesis), besides denitrification, are indicated as the possible responsible for the reduction in COD concentration in HSSF-CW.

Organic matter removal – BOD

VSSF-CW

Table 9 shows statistical estimators that indicate the suitability of the studied models and their kinetic reaction rates for BOD behaviour in VSSF-CW, considering CSTR flow.

Table 9. Statistical estimators and kinetic constants of VSSF-CW models evaluated for BOD transformation.

Flow	Kinetics	Without climate influence			With climate influence			Test	
		R^2	RMSER	K*	R^2	RMSER	K*	F	t
CSTR	First Order	0,40	0,78	0,51 d^{-1}	0,06	0,95	15,9 d^{-1}	SD	SD
	Grau Second Order	0,00	0,96	2500,0 d^{-1}	0,00	1,25	0,02 d^{-1}	NS	NS
	Monod	0,36	0,76	39,0 mg L^{-1} d^{-1}	0,37	0,75	45,1 mg L^{-1} d^{-1}	NS	NS
	Monod Multi	0,35	0,87	88,5 mg L^{-1} d^{-1}	0,84	0,53	94,1 mg L^{-1} d^{-1}	SD	SD
	Stover-Kincannon	0,95	0,34	75,1 mg L^{-1} d^{-1}	0,64	0,66	97,4 mg L^{-1} d^{-1}	SD	SD

Note: K* Kinetic constants (Kv = First Order or Grau Second Order; K_m = Monod, Monod Multi or Stover-Kincannon); NS = no statistical significance; SD = statistical difference; R^2 = Pearson coeficient; RMSER = relative mean square error root; F = Fisher; t = Student.

Stover-Kincannon kinetic model (without climate influence) was the most appropriate (R^2 = 0.95 and RMSER = 0.34) in the representation of BOD removal processes in relation to the other models considered. Monod Multi kinetics, adopting the effects of Ra and EPT, also showed good statistical adjustment (R^2 = 0.84) in the description of organic matter removal (BOD) in VSSF-CW. Other models and scenarios evaluated showed low linear fit (R^2 < 0.40).

Again, Fisrt Order model was not adequate to represent organic matter removal in VSSF-CW. Nguyen et al. (2018) showed that none of the models considered (First Order or Monod) presented adequate representation (R^2 < 0.30) of BOD removal in the studied VSSF-CW. Zhao et al. (2018) found an intermediate statistical correlation (R^2 < 0.68) for the Monod model associated with CSTR flow in the description of BOD removal in VSSF-CW.

Gholizadeh, Gholami, Davoudi, Rastegar, and Miri (2015), through BOD analysis, also observed that the Stover-Kincannon model was more appropriate (R^2 = 0.95) than First Order and Monod kinetics in describing the processes of organic matter removal in HSSF-CW, and that indicates that the Stover-Kincannon kinetics is suitable for describing BOD removal phenomena regardless of the type of hydrodynamic flow adopted.

According to the kinetic model that showed the best suitability (Stover-Kincannon without climate influence) to BOD decay in VSSF-CW, the maximum removal rate (Km) obtained in this research was 75.1 mg BOD L^{-1}. d^{-1}. Km value obtained by Zhao et al. (2018) in the Monod removal kinetics for BOD in VSSF-CW was 303.7 mg BOD L^{-1} d^{-1}, but for high organic load swine wastewater (58.0 – 146.0 g BOD m^{-2} d^{-1}).

Of all models evaluated, First Order, Monod Multi and Stover-Kincannon kinetics were the ones that presented statistical significance considering the scenarios with and without climatic effects, and Monod Multi model was favorable to the use of climate variables in the representation of organic matter (BOD) removal, unlike the First Order and Stover-Kincannon kinetics.

HSSF-CW

Table 10 describes the values of the statistical estimators that indicate the suitability of the studied models and their reaction kinetic rates for BOD behaviour in HSSF-CW, considering the CSTR and PFR flows.

As presented above, the Monod Multi kinetic model, considering the climatic influence and CSTR flow, was the most appropriate in the representation of BOD removal processes, with good correlation of the variables (R^2 = 0.82 and RMSER = 0.40). The other kinetics and scenarios evaluated had intermediate or low representativeness of reality (R^2 < 0.64).

Table 10. Statistical estimators and kinetic constants of models evaluated in HSSF-CW for BOD transformation.

Flow	Kinetics	Without climate influence			With climate influence			Test	
		R^2	RMSER	K*	R^2	RMSER	K*	F	t
CSTR	First Order	0,16	0,89	0,36 d^{-1}	0,00	2,12	101,0 d^{-1}	SD	SD
	Grau Second Order	0,08	1,08	50,0 d^{-1}	0,13	0,98	65,6 d^{-1}	NS	NS
	Monod	0,65	0,68	6,20 mg L^{-1} d^{-1}	0,44	0,78	6,90 mg L^{-1} d^{-1}	SD	SD
	Monod Multi	0,47	0,59	12,5 mg L^{-1} d^{-1}	0,82	0,40	15,1 mg L^{-1} d^{-1}	SD	SD
	Stover-Kincannon	0,44	0,68	15,7 mg L^{-1} d^{-1}	0,38	0,69	13,7 mg L^{-1} d^{-1}	NS	NS
PFR	First Order	0,04	1,26	2,04 d^{-1}	0,13	1,02	3,26 d^{-1}	NS	NS
	Grau Second Order	0,00	1,30	5,07 d^{-1}	0,00	0,99	4,56 d^{-1}	NS	NS
	Monod	0,27	0,85	9,66 mg L^{-1} d^{-1}	0,14	0,80	90,0 mg L^{-1} d^{-1}	SD	SD
	Stover-Kincannon	0,57	0,67	15,2 mg L^{-1} d^{-1}	0,31	0,74	11,7 mg L^{-1} d^{-1}	SD	SD

Note: K* Kinetic constants (Kv = First Order or Grau Second Order; K_m = Monod, Monod Multi or Stover-Kincannon); NS = no statistical significance; SD = statistical difference; R^2 = Pearson coeficient; RMSER = relative mean square error root; F = Fisher; t = Student.

Gholizadeh et al. (2015) observed that Stover-Kincannon model was the most suitable (R^2 = 0.95) in describing the processes of organic matter removal in HSSF-CW. However, Sun and Saeed (2009), on evaluating kinetic modeling for 80 HSSF-CW plants in the representation of BOD removal, concluded that Monod-PFR kinetic-hydrodynamic model was the most representative, but with low suitability (R^2 = 0.45 and RMSER = 0.56). It is noteworthy that these authors did not evaluate Stover-Kincannon kinetics in their research, and the first order kinetics was totally inadequate (R^2 < 0.15).

Such information is important, as most HSSF-CW designed in Brazil are sized based on BOD removal for PFR-type reactors and with First Order removal kinetics (Sezerino et al., 2015) and can, therefore, present inadequate efficiency. For BOD in the studied HSSF-CW, using CSTR hydrodinamics, equations that consider climatic influence on the kinetic organic matter removal was the most appropriate for Monod Multi model. The use of CSTR flow also improved, most of the time, the description of BOD behaviour along with pollutant removal kinetics in HSSF-CW.

According to the kinetic model that showed the best suitability (Monod Multi with climatic influence and CSTR flow) to BOD decay representation in HSSF-CW, the maximum removal rate (Km) obtained in this research was 15.1 mg BOD L^{-1} d^{-1}, much lower than that found by Gholizadeh et al. (2015) (50.0 mg BOD L^{-1} d^{-1}). Those authors, however, worked with sanitary sewage without previous biological treatment. In this case, the remaining organic matter is more easily degraded by microorganisms, which implies a higher K value.

We can see that the BOD removal kinetics rate (K) estimated dropped about five times from VSSF-CW to HSSF-CW, according to the best models evaluated, and in the COD transformation kinetics, there was a decrease of three and a half times in kinetics organic matter removal (K), which supports the hypothesis of high biodegradation rates of organic matter in the CWs evaluated.

Conclusion

Finally, in VSSF-CW, Monod Multi - CSTR model was the most suitable (R^2 > 0.71) for COD representation and Stover-Kincannon - CSTR model for BOD behavior (R^2 = 0.95), and the HSSF-CW, Monod Multi - CSTR model was the best fit for BOD description. Stover-Kincannon - CSTR model was the most suitable for HSSF-CW according to COD behaviour.

Thus, we can note that the use of kinetic-hydrodynamic models considering pollutant load, instead of those that use concentration, was more appropriate or without significant statistical difference in most scenarios studied to represent the behaviour of pollutants evaluated. Only for the BOD parameter (in VSSF-CW) the scenario without climate influence was more appropriate.

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