Adapting P-k-C* Model in Mediterranean Climate for Organic Removal Performance in Horizontal Treatment Wetlands

D. Ventura, F. Licciardello, L. Sciuto, M. Milani, S. Barbagallo, and G. L. Cirelli

Abstract The P-k-C* is considered as the most suitable in modeling treatment wetland (TW) performance providing a good compromise between accuracy and computational simplicity to assess the degradation processes for selected pollutants. However, there is a need to test the model in different climate conditions due to its high sensitivity to temperature. This study aims at demonstrating the applicability of P-k-C* model to describe the response of horizontal TWs (H-TWs) for domestic and agro-industrial wastewater treatment, and evaluating key design parameters for the model optimization in Mediterranean semi-arid conditions. In particular, kA20 (m year−1) and θ values were assessed in two H-TWs in Eastern Sicily, characterized by different organic loads and hydraulic and design features. The model was evaluated for simulating BOD5 and COD effluent concentrations at the outlet of the H-TW units. Calibration parameters, kA20 and θ, were found by summing and minimizing the squared differences between measured and modeled data, obtained by simultaneous adjustment of kA20 and θ for all samples ($25 < n < 27$). The coefficient of determination, R2, the Nash–Sutcliffe efficiency, NSE, and the root mean square error, RMSE, were used as statistical performance measures. Results showed a good reliability of the model to describe water quality response in terms of BOD5 and COD effluent concentrations. Most important finding was that a $\theta < 1$ should be used from practitioners to optimize H-TW design in Mediterranean conditions.

Keywords Horizontal treatment wetland · P-k-C* model · Semi-arid climate

1 Introduction

Treatment wetlands (TWs) are systems increasingly used worldwide to treat different types of wastewaters by removing mineral and organic pollutants. These systems are

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particularly suited to remove organic matter (i.e. COD and BOD_5) and, in general, chemical compounds such as nitrate, ammonia, phosphate, etc., and microbiological organism through a natural combination of miscellaneous processes contributing to enhance the wastewater (WW) quality. In order to understand and identify the main removal mechanisms acting in the TWs, several models have been proposed by literature [2], to simulate, among others, NO_3^-, COD and microbiological removal. For a comprehensive understanding of TWs treatment processes, concurrent pollutant degradation and hydraulic behavior require to be considered. To this aim the relaxed version of TIS (tank-in-series) model [4], also known as PTIS or P-k-C* model, seems to be the most suitable in representing TWs performance [2], Dotro et al., 2017). Up-to-date, there are several studies on P-k-C* application worldwide [1, 2, 4–6], while there is a lack of information about its applicability in Mediterranean area, especially utilizing observed data from TWs treating different type of WW. Therefore, the aim of this study is to demonstrate the applicability of the model to describe the response of horizontal TWs (H-TWs) treating different type of WW in Mediterranean climate conditions and to validate it by assessing main design parameters. In particular, k_{A20} (m $year^{-1}$), θ and P values were assessed in two H-TWs, respectively 5 an 9 years-operating, treating WW produced by a winery and a farmhouse, both located in Eastern Sicily (Italy).

2 Material and Methods

2.1 Case Studies

Marabino Winery TW. The Marabino winery WW (about 3 m^3 day^{-1}) are treated by a coarse screening, an Imhoff tank, an equalization tank (5 m^3) and a multistage TW (Milani et al., 2020). The TW (Fig. 1) has a total surface area of about 230 m^2 and is made of a vertical subsurface flow (VF) bed, followed by a horizontal subsurface flow (HF) bed and then by a free water (FW) system. Every four hours, a timer activates a pump installed in the equalization tank for a cycle of five minutes to distribute the WW on the top of VF bed. The HF and FW TWs have a nominal hydraulic retention time (HRT) of about 110 and 90 h, respectively. The TW was planted with: *Pragmites australis* (VF), *Cyperus Papirus var. Siculus* and *Canna Indica* (HF), *Iris pseudacorus*, *Nymphaea alba* and *Scirpus lacustris* (FWS).

Valle dei Margi (VDM) Farmhouse TW. The TW was designed for the secondary treatment of WW produced by toilets, food area and wellness centre of the VDM farmhouse, with a maximum flow rate of about 30 m^3 day^{-1}. The preliminary and primary treatment plant is made of two parallel lines, each one consisting of a degreaser unit and an Imhoff tank (Fig. 2). TW includes an HF bed followed by a FW unit, with a surface area of about 350 m^2 and 180 m^2, respectively. The nominal HRT is about 64 h in HF and 115 h in FW TW. The HF bed was vegetated with *Canna*

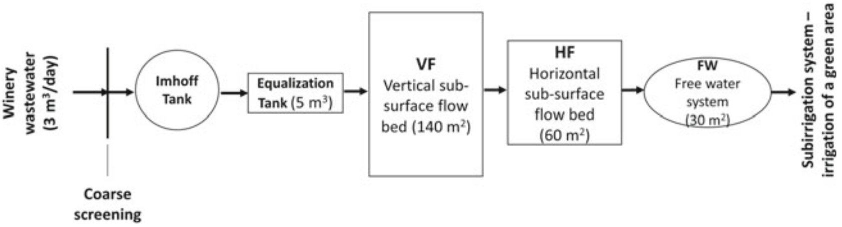

Fig. 1 Layout of wastewater treatment plant in *Marabino* winery

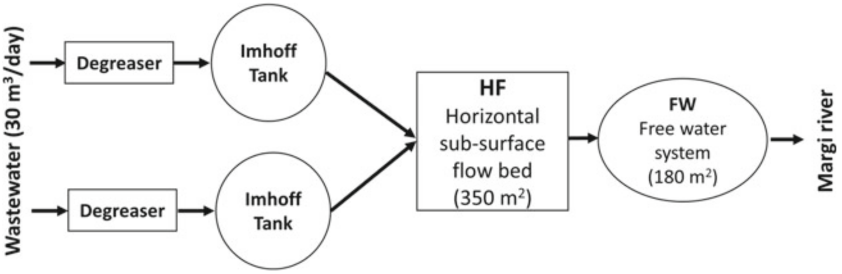

Fig. 2 Layout of wastewater treatment plant in *Valle dei Margi* farmhouse

Indica, Cyperus papyrus and *Iris pseudacorus* while the FW banks was planted with *Phragmites australis.*

Study sites are located in a semi-arid climate area characterized by an average annual precipitation of about 500 mm, and summer air temperature values reaching 40 °C. The climatic data, for two sample years, respectively for Marabino and VDM sites, showed a similar temperature trend with the highest values in July–August (with some peaks in September and the lowest in December-March (data not shown). Temperature values varied from a minimum of -1.6 at VDM (mid-February) °C and -1.7 at Marabino (mid-January) to a maximum of 42 °C at Marabino (beginning of August) and 41.6 at VDM (mid-August). As expected, rain is concentrated in the period September-March with a maximum value of around 40 mm day^{-1} observed in November. The water temperature of collected samples was close to the daily average air temperature due to the high thermic capacity of the water (data not shown).

2.2 Water Quality Database

The simulation procedure was conducted for COD and BOD_5 data collected in 2018–2020 in the Marabino TW (n = 25 samples) and in 2019–2020 in the VDM TW (n = 27 samples). The sampling points were located at the inflow and outflow of each TW using manual water samplers. WW samples were collected in 500 mL plastic bottles and stored at 4 °C during the transport to the laboratory. Analyses were carried out according to Standard Methods (APHA 1998; APHA-AWWA-WEF, 2005). A portable water quality probe (Multiparametric Hanna probe, USA) was used to measure temperature and electrical conductivity (EC). The flow was recorded by an on-site flowmeter. Meteorological variables, such as rainfall and air temperature, were provided by the SIAS (Sicilian Agro-meteorological Informative System) reference stations. For each TW configuration, the loading mass rate (LR) and mass removal rate (MR) parameters were calculated [2], as also reported by [1].

2.3 *P-k-C* Model Application*

The fundamentals of the P-k-C* model are based on first order removal rate coefficients (k-rates), non-zero background concentrations (C*), and non-ideal hydraulics [2], while assuming steady-state conditions: no infiltration, no evapotranspiration, and constant flow in the system. The pollutant concentration at outlet (C_o calculated) was calculated by Eq. 1.

$$C_{o\,calculated} = C^* + \frac{C_i - C^*}{\left(1 + \frac{k_{A20}\theta^{(T-20)}}{Pq}\right)^P} \tag{1}$$

The first order areal removal rate constant (k_A) indicates how fast the pollutant degradation process is and depends on water temperature through the theta factor (θ) [2], deriving from the Arrhenius equation. The non-zero background concentration C* [7] represents the lowest effluent concentration (i.e. regarding certain pollutant loads) at the TW outlet. Moreover, P is a fitted parameter that accounts for apparent tanks-in-series, since it merges both, the hydraulic efficiency of the reactor (number of tanks in series, N) and the pollutants "weathering". The parameters P, k_{A20} and θ (Eq. 1) were optimized to minimize the sum of the square of the errors (SSE) between C_o observed and calculated [3–5]. The minimization process was carried out following [1]. Calibration and validation goodness of *P-k-C** kinetic equation was evaluated by calculating the root mean squared error, RMSE ($mg\ L^{-1}$), the coefficient of determination, R^2, and Nash–Sutcliffe efficiency, NSE, between calculated and measured concentration values (for each quality parameter and in individual TWs). With the aim to demonstrate the applicability of the model in the Mediterranean climate to design and to manage TWs for different WW, NSE and RMSE were evaluated for all TWs together.

3 Results

3.1 TWs Characterization and Model Fit Parameters

Mean quality parameter concentrations measured at the inlet (C_i, mg L^{-1}) and at the outlet of TW systems (C_o, mg L^{-1}) and flow rates at the inlet (q_i, m d^{-1}) are reported in Table 1. Evapotranspiration (ET), evaluated as in Consoli et al. (2018), reduced the flow at the inlet (q_i) of about 4% on average in both TWs (with a minimum value of 1% in winter. and a maximum 20% in summer). Mean mass removal rates, considering COD and BOD_5 for each TW were equal to 51% and 50% for Marabino TW and 85% and 86% for VDM TW (Table 1).

Model fitting (reaction rate) parameters, K_{A20} and θ, optimized for the calibration dataset of COD and BOD_5 in each TW are summarized in Table 2. The apparent number of TIS (P) was set equal to 8.3, a median value derived by 35 studies [2] for both COD and BOD_5 and both TWs; the calibration process of this parameter did not improve the simulations.

Mean and standard deviation EC values observed in different periods of the year for the TWs are reported on Table 3. Mean EC values showed an increase of about 15% between April-September (summer season) and October - March (winter season) probably due to the higher ET in the hottest period.

Table 1 Number of samples, mean quality parameters concentration measured at the inlet and outlet of TW systems and their standard deviation (SD), and flow rates at the inlet (q_i, m day^{-1}). C* was fixed as the lowest outlet concentration observed

TWs	n	Parameter	C_i (mg L^{-1})		C_o (mg L^{-1})		C^* (mg L^{-1})	q_i (m day^{-1}) Nominal	MR (%)
			Mean	SE	Mean	SE			
Marabino	25	BOD_5	121	7	38	2	3	0.05	50
	25	COD	221	12	74	4	3		51
VDM	21	BOD_5	513	8	77	3	3	0.09	86
	27	COD	712	10	107	3	3		85

Table 2 Model fit parameters k_{A20} and θ (m $year^{-1}$) for BOD_5 and COD measured in each TW

TWs	COD k_{A20} (m $year^{-1}$)	θ	BOD_5 k_{A20} (m $year^{-1}$)	θ
Marabino	169.7	0.744	132.2	0.803
VDM	59.9	0.965	41.4	1.018
Mean	114.8	0.855	86.8	0.910

Table 3 Electrical conductivity (EC) measured in HF effluents in different seasons

TWs	EC (µS cm^{-1})		EC (µS cm^{-1})		Difference
	October - March		April – September		
	Mean	SD	Mean	SD	
Marabino	885.6	50.1	1049.5	29.2	18.5
VDM	2765.2	40.3	3101.0	20.7	12.1
Mean	1825.4		2075.3		15.3

Table 4 Calibration Statistical Evaluations: R^2, NSE, RMSE (mg L^{-1})

TWs	COD				BOD_5			
	n	R^2	NSE	RMSE	n	R^2	NSE	RMSE
Marabino	15	0.93	0.91	32.1	15	0.85	0.80	22.0
VDM	16	0.71	0.54	50.6	13	0.84	0.81	29.1

Table 5 Validation Statistical Evaluations: R^2, NSE, RMSE (mg L^{-1})

TWs	COD				BOD_5			
	n	R^2	NSE	RMSE	n	R^2	NSE	RMSE
Marabino	10	0.96	0.67	66.3	10	0.91	0.48	39.3
VDM	11	0.51	0.32	56.9	8	0.92	0.71	24.6

3.2 *Calibration and Validation Results*

Statistical evaluations were carried out for calibration and validation datasets for each pollutant and TW (Tables 4 and 5, respectively).

Mean R^2 values (considering both TWs) varied between 0.73 (COD) and 0.92 (BOD_5) for both calibration and validation dataset. Mean NSE values (considering both TWs) varied from 0.59 to 0.81 (respectively for validation and calibration set of BOD_5) and from 0.73 to 0.82 (respectively for validation and calibration set of COD). Mean RMSE values varied between 32.0 (BOD_5) and 61.6 (COD) for both calibration and validation dataset. After calibration/validation process carried out separately for each TW, the observed/predicted values were recompiled for an overall calculation of RMSE and NSE. The statistical metrics of both TWs for each pollutant are summarized in Table 6. As expected, model prediction strength varied between calibration and validation, being for the first dataset higher (between 0.76 and 0.86 for COD and BOD_5 respectively) than the second one (between 0.58 and 0.63 for BOD_5 and COD respectively).

Table 6 Statistical metrics for pollutants observed in all TWs

Pollutant	Calibration (both H-TWs)			Validation (both H-TWs)		
	n	NSE	RMSE (mg L^{-1})	n	NSE	RMSE (mg L^{-1})
COD	31	0.76	56.54	21	0.63	72.84
BOD_5	28	0.86	30.21	18	0.58	39.52

4 Discussion

The calibration/validation procedure confirmed the ability of the P-k-C*model to represent BOD_5 and COD kinetic degradation in different H-TWs operating in semi-arid Mediterranean climate. After the calibration of k_{A20} and θ parameters for COD and BOD_5, accordingly with [8], the performance of the model evaluated for all the TWs together was very good for the calibration step, good for the validation set. [9], following a similar model calibration approach (first for a single TW and then considering all TWs together), found similar NSE values (0–72-0.91). k_{A20} optimized values ranging from 41.4 to 169.7 m $year^{-1}$, considering the two investigated pollutants (COD and BOD_5) in the present study, are in the range of those found in literature [2],they are higher than those generally found in temperate areas [3, 6] and very similar to those found in another study in semi-arid areas [1]. The fact that θ was < 1 in most cases (with the exception of BOD_5 for VdM) was found in literature for a study carried out in Ethiopian arid climate [5] besides another one carried out in Sicily [1]. In particular, optimized K_{A20} and θ parameters allowed the following considerations. A value of $\theta < 1$, means that temperature increases in the summer season caused a reduction in the K_{A20} and the kinetic degradation in all the cases, as observed by [5] under African arid conditions, and by [1] under Sicilian semi-arid conditions.

This behaviour could be explained by two compensation factors, in contrast with the general idea that temperature increases cause K_{A20} increases (Vymazal et al., 2021). First of all, generally, the temperature increase causes the increase of kinetic degradation rate and therefore of k_{A20} value, since "seasonal variations of some biotic and abiotic factors" occur [12]. In spite of this, in summer period in semiarid region, very high temperatures and consequent ET increases can act predominantly causing a higher concentration of effluent pollutants than expected, and so, determining a reduction of k_{A20} [2]. Also, a correlation between the increased water salinity and the TW treatment effectiveness reduction, due to plants and microbial function inhibition, was reported by [11]. In our case, this effect could be contributing as confirmed by higher EC values observed during April–September season. On the other hand, the second compensation condition occurs in winter season, when rain dilutes pollutants concentration in TW outlet, increasing the k_{A20}, being also ET almost neglectable and the effect of temperature not relevant. However, the preponderance of literature (Stein et al., 2006) evidence suggests that BOD_5 removal is not improved with higher wetland water temperatures.

5 Conclusion

The P-k-C* model calibration/validation procedure carried out in the present study, confirms the applicability of the model to describe the simulation of H-TWs treating different type of WW and characterized by different design, and hydraulic and organic load in Mediterranean climate conditions. Very good values of R^2, NSE and RMSE reached in most of cases indicated the good performance of the model. Therefore, optimized data of k_{A20} and θ, confirming those already found in arid and semiarid areas of the world, could be considered a contribute for P-k-C* model application in typical Sicilian climate, and, in general in Mediterranean weather conditions. In particular, the calculated k_{A20} values were generally higher than those showed in the case of TWs located in temperate climate zone and for all the pollutants considered, the θ values were generally lower than 1. This means that temperature increase in the summer reduces the k_{A20} and the kinetic degradation in all cases.

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References

1. Ventura, D., et al.: Application of first-order kinetic removal models on constructed wetlands under Mediterranean climatic conditions. Ecol. Eng. **175**, 106500 (2022)
2. Kadlec, R.H., Wallace, S.D.: Treatment Wetlands, 2nd edn. CRC Press, Boca Raton, Florida (2009)
3. Nivala, J., Knowles, P., Dotro, G., GaraJ., Wallace, S.: Clogging in subsurfaceflow treatment wetlands: measurement, modeling and management. Water Res. **46**(6), 1625–1640 (2012). https://doi.org/10.1016/j.watres.2011.12.051
4. Nivala, J.: Effect of Design on Treatment Performance, Plant Nutrition and Clogging in Subsurface Flow Treatment Wetlands. PhD Thesis. Aarhus University, Department of Bioscience, Aarhus, Denmark (2012)
5. Ayano, K.K.: Effect of Depth and Plants on Pollutant Removal in Horizontal Subsurface Flow Constructed Wetlands and their Application in Ethiopia. PhD Thesis. Berlin University (2014)
6. Vymazal, J.: Is removal of organics and suspended solids in horizontal sub-surface flow constructed wetlands sustainable for twenty and more years? Chem. Eng. J. (2019). https://doi.org/10.1016/j.cej.2019.122117
7. IWA: Constructed Wetlands for Pollution Control. Processes, Performance, Design and Operation (2000). https://www.iwapublishing.com/sites/default/files/ebooks/9781900222051.pdf. Accessed 2 Sept 2021
8. Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Binger, R.L., Harmel, R.D., Veith, T.: Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. Trans. ASABE **50**, 885–900 (2007). https://doi.org/10.13031/2013.23153.

9. Merriman, L.S., Hathaway, J.M., Burchell, M.R., Hunt, W.F.: Adapting the relaxed tanks-in-series model for stormwater wetland water quality performance. Water **9**, 691 (2017). https://doi.org/10.3390/w9090691
10. Ecol. Eng. **26**, 100 –112. https://doi.org/10.1016/j.ecoleng.2005.07.001
11. Liang, Y., et al.: Constructed wetlands for saline wastewater treatment: a review. Ecol. Eng. **98**, 275–285 (2017). https://doi.org/10.1016/j.ecoleng.2016.11.005
12. Zhu, Y., Cui, L., Li, J., Wang, R., Vymazal, J., Li, W., Lei, Y., Zhang, M., Hao, T., Wei, J.: Long-term performance of nutrient removal in an integrated constructed wetland. Sci. Total Environ. **779**, 146268 (2021). https://doi.org/10.1016/j.scitotenv.2021.146268