

Article

Effects of Plant and Substrate Types on Turbidity Removal in Constructed Wetlands: Experimental and w-C* Model Validation

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Abstract

Constructed wetlands are nature-based technologies widely used for the treatment of wastewater and contaminated surface water. This study evaluated the efficiency of free water surface (FWS) and horizontal subsurface flow (HSSF) constructed wetlands in reducing the turbidity of mine spoil rainwater using the w-C* model. Different hydraulic retention times (2, 4, and 6 days) were tested, and the influence of macrophyte type and substrate on the w parameter was investigated. Model calibration was performed based on correlation coefficients (R), coefficient of determination (R^2), Nash–Sutcliffe efficiency (NSE), and root mean square error (RMSE). The results indicated a 99% reduction in turbidity, with average values of $R = 0.87 \pm 0.05$ (FWS) and 0.87 ± 0.03 (HSSF), and NSE of 0.76 ± 0.04 (FWS) and 0.74 ± 0.07 (HSSF), demonstrating good agreement between observed and predicted data. The settling rate (w) ranged from 0.16 to 0.40 $\text{m} \cdot \text{d}^{-1}$ in FWS and from 0.20 to 0.70 $\text{m} \cdot \text{d}^{-1}$ in HSSF, with the lowest value recorded in the control (0.09 $\text{m} \cdot \text{d}^{-1}$). The best performances were observed in FWS-P with *Pistia stratiotes* (0.40 $\text{m} \cdot \text{d}^{-1}$) and HSSF with *Typha domingensis* (0.70 $\text{m} \cdot \text{d}^{-1}$), demonstrating that vegetation, combined with the use of medium-grain substrate (9.5–19.0 mm), enhances turbidity removal. The w-C* model proved to be a robust tool for describing the kinetics of suspended colloidal particle removal in constructed wetlands, providing valuable insights for optimizing hydraulic parameters and design criteria for full-scale application.

Keywords: constructed wetlands; w-C* model; turbidity; surface runoff; mine spoil rainwater



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1. Introduction

Constructed wetlands are nature-based technologies that have been widely used for wastewater treatment due to their low cost, ease of operation and maintenance, and effectiveness [1,2]. Studies have shown their potential as an efficient solution for the treatment of industrial and sanitary wastewater, especially in the removal of organic contaminants [3]. In areas of intensive mine activity, the rainfall events in eroded areas of mining sites result in the transport of soil particles from exposed surfaces, carrying contaminants to nearby receiving environments, contributing to increase turbidity levels and environment impacts to the aquatic biota [4]. The runoff generated at the mine site is referred to as mine spoil rainwater, which requires proper treatment. A recent study evaluated the performance of constructed wetlands in reducing high turbidity levels in mine spoil rainwater with an initial turbidity of 1614 ± 357 NTU; it showed that vegetated

constructed wetlands were able to reduce turbidity by up to 99%, with a hydraulic retention time of 4 days [5].

The numerical modelling of these systems has attracted increasing interest in recent research mainly due to its potential to improve the treatment of different types of wastewaters and to optimise the design parameters [6,7]. This modelling makes it possible to predict the system's performance and facilitates large-scale design and sizing [8]. The modified first-order model, the $k\text{-C}^*$ model of Kadlec et al. [9], is widely recognised for its accuracy in predicting pollutant degradation in constructed wetlands [10]. Based on this model, Kadlec et al. [9] adapted two- and three-dimensional sediment transport models in estuaries to the wetland context using the $w\text{-C}^*$ model, where the variable w refers to the settling velocity expressed in $\text{m}\cdot\text{d}^{-1}$.

Recent studies have used advanced numerical simulations to evaluate and improve the performance of constructed wetlands, resulting in more effective pollutant removal strategies [7,11]. Proper calibration through numerical simulations can optimise design parameters, improve pollutant removal rates, and ensure compliance with environmental standards [7]. Several authors have evaluated the performance of constructed wetlands using different modelling methods. However, while modelling for the removal of other pollutants has been widely applied, the use of models for turbidity removal is still relatively scarce in the published literature.

These systems are designed to simulate natural processes and integrate plants as essential components. They perform ecological functions such as the growth of aquatic microbiota, the removal of pollutants, and the sequestration and storage of carbon in their biomass. Macrophytes contribute to the removal of metals and pollutants through mechanisms such as phytoextraction, phytodegradation, and rhizofiltration, as well as promoting turbidity reduction by filtering colloidal material through their roots [12,13]. The interaction between plant root systems and substrates plays a crucial role in enhancing water quality by effectively removing suspended solids through physical entrapment [14]. Plant roots create a dense network, with the substrate providing a larger contact area, acting as a natural filter for suspended particles [15].

Turbidity can be an effective and low-cost proxy for estimating total suspended solids (TSS) concentrations in aquatic systems. Recent datasets confirm the correlation between TSS ($202\text{--}1212\text{ mg}\cdot\text{L}^{-1}$) and turbidity ($63\text{--}501\text{ NTU}$), indicating that turbidity measurements can be used to monitor suspended solids in rivers and to estimate the flow of particulate-associated pollutants such as heavy metals (Ni, Pb, Cd, Cu, Zn, Co, As) and metalloids. These results reinforce the importance of turbidity as an accessible and practical parameter for environmental monitoring in river basins [16].

Water pollution is a growing concern in regions with intensive mining activity. The advancement of this industry, in line with UN Sustainable Development Goals (SDGs) 6 and 14, highlights the urgency of strict control and monitoring of water quality. Open pit mining exposes large areas of land, where the transport of fine particles to the receiving waters can occur, particularly during periods of rainfall [16]. The presence of suspended particles in water affects quality parameters such as total suspended solids and turbidity, which are mainly caused by particles of silt, clay, and organic matter [17].

Therefore, the operating parameters of constructed wetlands are fundamental to ensure efficient wastewater treatment. The main parameters include the wetland typology based on the flow direction, which can be surface (FWS) or subsurface (HF), the hydraulic loading rate (HLR), the hydraulic retention time (HRT), the depth of the system, the composition of the support material, and the vegetation species [8,18,19].

Given these perspectives, the aim of this study was to determine the suitability of the first-order kinetic model $w\text{-C}^*$ describing the response of turbidity reduction in surface and

subsurface horizontal flow constructed wetlands, vegetated with different macrophytes and substrate, and to demonstrate its application as a tool for defining design criteria. Beyond model applicability, this study highlights the practical relevance of using turbidity as a key parameter in the evaluation of water quality, especially for wastewaters or runoff effluents with high particulate content, supporting more effective treatment system design and monitoring strategies.

2. Materials and Methods

2.1. Study Site and Experimental Design

The pilot-scale experiment was carried out at the Federal University of Ouro Preto, Ouro Preto, Minas Gerais, Brazil, in a region with a Cwb climate classified according to the Köppen classification. This is a moderately humid subtropical climate with an average annual temperature between 17 and 18.5 °C and average rainfall between 1450 and 1800 mm, mainly in summer [20]. In the experimental area of the Environmental Sanitation Laboratory, pilot systems of horizontal flow constructed wetlands have been constructed, including two types, surface flow (FWS) and subsurface flow (HSSF).

The wetlands were constructed in a series of tanks (TIS = 3) made of black polypropylene boxes (Uninjet, São Paulo, Brazil) with a capacity of 56 L (580 × 400 × 340 mm), placed on a pallet structure and partially covered with greenhouse plastic sheeting over a structure of ¾ PVC pipes to avoid interference from rainfall (Figure 1). Each tank was operated with a 2-day HRT, for a total of 6 days of operation, allowing a detailed assessment of each tank and the whole [21–23]. Piezometers were installed to measure the height of the water column in all tanks of the constructed wetlands.

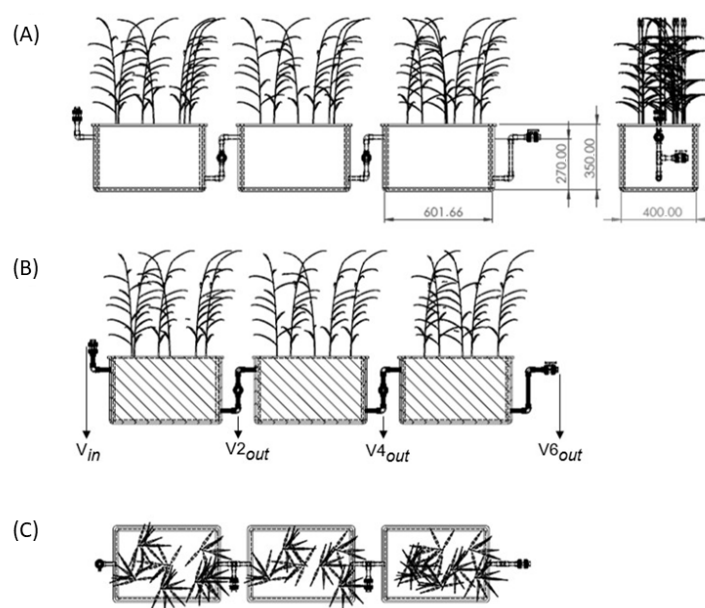


Figure 1. Layout of the constructed wetland systems in series (mm): (A) FWS side view; (B) HSSF side view; (C) FWS and HSSF top view. V_{in} indicates the inlet valve, and V_{out} are the outlet valves based on the HDT applied of V_{2out} (2 days), V_{4out} (4 days), and V_{6out} (6 days).

The operating parameters of the project are shown in Table 1: hydraulic retention time (HRT), flow rate, area, and hydraulic loading rate (HRL). These parameters were defined on the basis of the literature on the treatment of mining waste water types, in order to explore different experimental conditions for the application of the technology [21–23].

Table 1. Operational parameters of the FWS and HSSF wetlands [4].

Unit	HRT (days)	Substrate Volume (L)	Total Volume (L)	Flow Rate (L·h ⁻¹)	Area (m ²)	HLR (L·m ⁻² d ⁻¹)
FWS	2	-	40	0.83	0.18	108.84
FWS	4	-	40	0.83	0.32	68.36
FWS	6	-	40	0.83	0.55	36.53
HSSF	2	20	20	0.42	0.18	54.86
HSSF	4	20	20	0.42	0.32	27.43
HSSF	6	20	20	0.42	0.55	18.27

The constructed wetlands were vegetated with three macrophytes distinguished by their root structures (Figure 2): *Nymphoides humboldtiana*, a native species, and two others widely employed in constructed wetlands systems, *Pistia stratiotes* and *Typha domingensis* [4,12,24–26]. *P. stratiotes* were grown exclusively in FWS systems due to the free water column availability, while *N. humboldtiana* and *T. domingensis* were used in both systems. Vegetation density was approximately 4 rhizomes per m² [27]. Although the total volume differed between the FWS (40 L) and HSSF (20 L) systems, comparability was ensured by maintaining equivalent hydraulic loading rates and surface areas. The higher volume in the FWS system accounts for the additional free water layer required in surface flow wetlands, while the HSSF system relies on saturated media and subsurface flow, requiring less water volume to achieve similar hydraulic retention times. Flow rates were adjusted accordingly to provide comparable hydraulic retention and loading conditions across both systems.

**Figure 2.** Representation of the root architecture of the macrophytes selected during the cultivation period of the experiment: (A) *P. stratiotes*; (B) *N. humboldtiana*; (C) *T. domingensis* [4].

The main criteria for the selection of the substrate were availability, cost, and physical and chemical properties [28]. The selected materials and their respective grain sizes were blast furnace slag (9.5–25.0 mm), dolomitic gravel #2 (19.0–25.0 mm), and dolomitic gravel #1 (9.5–19.0 mm) [29,30]. The specific porosity of materials depends on various factors such as origin, granulometry, and processing. Research by de Matos [31] found that blast furnace slag with a grain size of $d_{10} = 19.1$ mm has a porosity of $0.40 \text{ m}^3 \text{ m}^{-3}$, and for gravel with grain size 2 ($d_{10} = 14.2$ mm), the porosity was $0.45 \text{ m}^3 \text{ m}^{-3}$, and for gravel 1 ($d_{10} = 9.4$ mm), the porosity was $0.43 \text{ m}^3 \text{ m}^{-3}$.

Figure 3 shows the wetlands according to the type of wetland, the selected macrophytes, and the substrate of each wetland cell of the system. The FWS system consists of FWS control (FWS-C), FWS *P. stratiotes* (FWS-P), FWS *N. humboldtiana* (FWS-N), and FWS *T. domingensis* (FWS-T) (Figure 3A). The HSSF conditions include HSSF in dolomitic gravel #1 (HFD1), HSSF in dolomitic gravel #1 and *N. humboldtiana* (HFD1-N), HSSF in dolomitic gravel #1 and *T. domingensis* (HFD1-T) (Figure 3B). Figure 3C shows HSSF in dolomitic gravel #2 (HFD2), HSSF in dolomitic gravel #2 and *N. humboldtiana* (HFD2-N), and HSSF in dolomitic gravel #2 and *T. domingensis* (HFD2-T); Figure 3D shows HSSF in blast-furnace

slag (HFS), HSSF in blast-furnace slag and *N. humboldtiana* (HFS-N), HSSF in blast-furnace slag and *T. domingensis* (HFS-T).

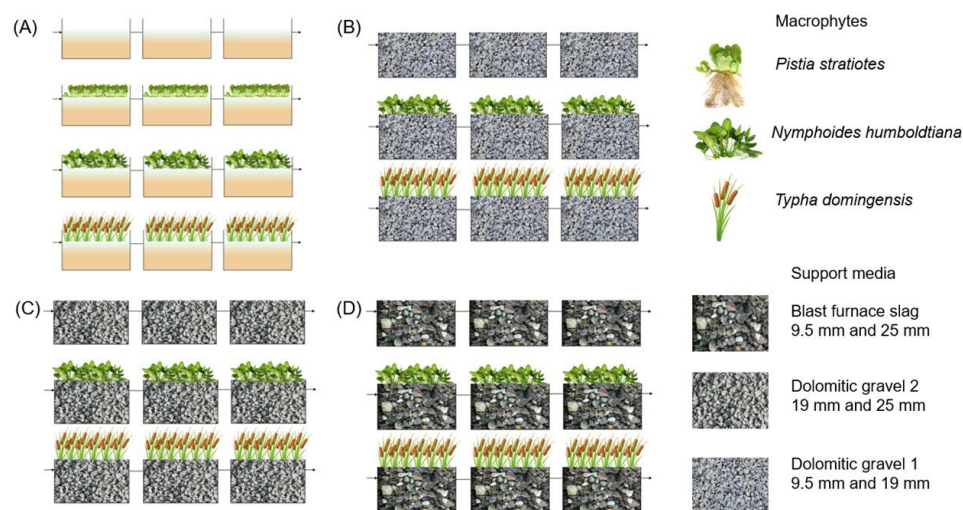


Figure 3. Design of the FWS and HSSF wetlands in the experiment: (A) FWS and the macrophytes; (B) HSSF in dolomitic gravel #1; (C) HSSF in dolomitic gravel #2; and (D) HSSF in blast-furnace slag.

The wetlands were fed with synthetic mine spoil rainwater (SMSR), which has the characteristics of mine spoil rainwater produced according to the methodology described by Gomes et al. [4]. To produce the effluent, solid material from a mining area was scalped, dry sieved, wet milled, and wet sieved, resulting in a pulp of colloidal particles of silt and clay with particle sizes less than $2.6 \mu\text{m}$ (50% of the particles), composed mainly of hematite (Fe_2O_3) and alumina (Al_2O_3) [4].

The pulp obtained by wet screening was dispersed in river water collected from the Piracicaba River, which is located in an intense mining activity region from the Iron Quadrangle in the state of Minas Gerais, Brazil. The SMSR was mixed in a 2000 L agitator tank (Eco Mix 1000 1HP4P/ Ecotecnologia/ Brazil) with constant agitation at a speed of 102.9 rpm throughout the experiment. The SMSR was distributed to the system by peristaltic pumps (DF4a/ ProMinent/ Germany) with a capacity of $1.5 \text{ L} \cdot \text{h}^{-1}$, and the average inlet turbidity value was $1614 \pm 357 \text{ NTU}$ ($n = 60$). Turbidity is considered a reliable proxy for suspended solids by causing light to be scattered and thus providing a correlation between both parameters [15]. These are essential parameters for evaluating water quality based on physical quality of the water, and turbidity is easy and cheap to measure.

The experiment was monitored for 144 days between January and July 2023. Samples were collected three times a week in the morning. The volume collected represented less than 5% of the total volume of each wetland, and the sampling points were located at the inlet and outlet collection valves of each wetland. Analyses followed the protocols described in the standard methods [32], as detailed in Table 2. The samples were stored in plastic containers and analysed at the Environmental Sanitation Laboratory (UFOP).

Table 2. Mean concentrations characterizing the SMSR ($n = 60$).

Parameters	Unit	Mean e sd
Turbidity	NTU	1614 ± 357
Hydrogen Potential	-	7 ± 0.2
Temperature	$^{\circ}\text{C}$	20 ± 3
Dissolved Oxygen	$\text{mg} \cdot \text{L}^{-1}$	7
Oxirreduction Potential	mV	-24 ± 11
Conductivity	$\mu\text{S} \cdot \text{cm}^{-1}$	66 ± 24

2.2. Validation of the Applicability of the First-Order Kinetic Decay Model of the w - C^* Model

The removal of pollutants can be described by a first-order linear decay equation as a function of a background concentration (C^*) that is measured over the course of the treatment [33]. According to Wong [33], the k - C^* model proposed by Kadlec et al. [8] can be used to demonstrate the removal of various pollutants, including turbidity. The k - C^* model has been calibrated and verified in hybrid constructed wetland systems for the treatment of industrial effluents, showing satisfactory fits with the observed data, which helps to predict the behaviour of the system under different operating parameters [7]. The study by Ventura et al. [34] evaluated the applicability of the P - k - C^* model in horizontal flow constructed wetlands in a Mediterranean climate, showing good performance of the calibration and validation data, as well as in the evaluation of the R^2 , NSE, and RMSE metrics.

Studies by Kadlec et al. [8] adapted the 2- and 3-D models of sediment transport in estuaries to the wetland scenario, where w refers to the sedimentation velocity, expressed in $\text{m}\cdot\text{d}^{-1}$. Therefore, the first-order model applied to TIS was chosen to describe the dynamics of turbidity reduction based on the removal of total suspended solids, which are the main cause of turbidity. This w - C^* model is robust for the typologies evaluated in this study (FWS and HSSF) in reduced HRTs, where the sedimentation mechanism is not completed [8].

Thus, the w - C^* model correlates the initial and final turbidity values with the HRT, the number of tanks in series (N), the height of the water column (h), settling velocity (w) and the minimum non-zero turbidity (C^*). The model equation is expressed by Equation (1):

$$\frac{(C_o - C^*)}{(C_i - C^*)} = \left(1 + \frac{w\tau}{Nh}\right)^{-N} \quad (1)$$

where C_o = final turbidity (NTU), C_i = initial turbidity (NTU), C^* = minimum observed turbidity (NTU), w = settling rate ($\text{m}\cdot\text{d}^{-1}$), τ = hydraulic retention time (HRT), N = number of tanks in series, and h = height of water column (m).

For calibration, the C^* value was set at 1 NTU, a value considered adequate due to the efficiency observed in reducing turbidity at the end of the 6 days of HRT. The N value was set at 3, as three cells were used in series in all wetland systems. C_i was measured as described in Section 2.1. The τ was pre-determined at 2, 4, and 6 days, corresponding to the different HRTs evaluated in the experiment ($\tau = Q/V$), where Q = flow rate and V = volume. The h was measured continuously throughout the experiment by piezometers installed at the inlet and outlet of each wetland, and the mean value was used in the calculations.

The Generalised Reduced Gradient method was used to optimise a non-linear problem with the aim of minimising the sum of squared errors. The Excel software Solver plug-in (version 2505) was used to adjust the model parameters according to the established criteria, and Equation (1) was adjusted to calculate the final turbidity concentration (C_o) based on the experimental data.

The Excel Solver was first used to fit the w parameter, looking for the best fit between the observed and simulated final turbidity data. There were no limitations to the use of the Solver plug-in, but it is recommended to check the limitations of the algorithm for non-linear functions.

The experimental data were divided into two sets for modelling, with the calibration set comprising 70% of the data and the validation set comprising the remaining 30%. The data were randomly selected for each set using the Python (version 3.13.2) language in the Thonny development environment [35], using the random module, which generates pseudorandom samples from a pseudorandom number generator based on the Mersenne Twister algorithm. The model was validated by applying the calibrated values of w to the validation data.

To assess the accuracy of the model developed in this study, statistical metrics widely used in constructed wetland research were used, including Pearson's correlation (R), coefficient of determination (R^2), Nash–Sutcliffe efficiency (NSE), and Root Mean Square Error (RMSE). These metrics were used to analyse the predictive power of the model and its ability to reproduce the data observed during the experiment [36,37]. The statistical coefficients of Pearson's correlation (R) and determination (R^2) are widely used to assess the collinearity between the observed values and those estimated by the model [38]. These coefficients vary between -1 and 1 and indicate positive or negative linearity, with values closer to the extremes indicating a strong linear relationship between the variables analysed [38].

The NSE, with values ranging from 0 to 1 , quantifies the accuracy of the model in comparing the observed data with the simulated data, with values close to 1 indicating a high degree of agreement within a range considered acceptable ($1:1$) [39]. The RMSE is a widely used statistical metric to quantify the magnitude of the error between the observed values and those simulated by a model [40]. This index assesses the dispersion of the residuals and is expressed in the same unit as the variables analysed. Lower RMSE values indicate greater accuracy and better model performance in reproducing the observed data [40].

2.3. Statistical Analysis

The analysis was carried out using the `ggscatter` function of the `ggpubr` package in the RStudio programming software (2024.04.1). This function was used to calculate the correlations between the observed turbidity dependent variable and the simulated turbidity independent variable. The purpose of the fitted regression was to visualise the trend of the data in relation to the proposed model. In interpreting the results, the correlation coefficient (R) and the coefficient of determination (R^2) were evaluated. In addition, the value of statistical significance (p -value) was assessed, with $p < 0.05$ being considered significant. The analysis was performed using R software (version 2024.04.1) [41].

3. Results and Discussion

3.1. Water Quality Monitoring

Table 3 presents the means and standard deviations of the physical and chemical parameters of water quality observed in the inlet (SMSR) and in the different constructed wetland systems after 6-days of HRT. The compliance of the final effluent quality with the regulatory standards of the Brazilian environmental legislation was verified by monitoring the parameters as turbidity, pH, conductivity, dissolved oxygen, and oxidation-reduction potential of the post-treatment wetlands.

The FWS-P, FWS-T, HFS, HFS-N, HFS-T, HFD2-N, HFD1, HFD1-N, and HFD1-T wetlands were found to have effluent with a turbidity of less than 40 NTU, indicating that, after treatment, this water had properties equivalent to those of Class 1 water, according to the parameters established by Brazilian legislation CONAMA 357/2005. On the other hand, the FWS-N and HFD2 wetlands had effluents with turbidity of less than 100 NTU, meeting the quality standards for Class 2 and 3 waters under the same legislation. However, the sedimentation tank did not provide effective treatment, as the effluent could not be classified in any mentioned categories (Table 3). These results indicate that most of the evaluated wetlands effectively treated the effluent and achieved turbidity level standards compatible with those found in high-quality water bodies. The sedimentation tank (FWS C), used to simulate an untreated environment, represents a natural environment without the influence of macrophytes and support material, making it possible to assess the impact of these components on the performance of the studied wetland systems. The study

provides insights into both the role of vegetation and the potential of substrate to optimise wastewater treatment. However, further analysis is required for a greater comparison between the different configurations and their effectiveness in controlling turbidity.

Table 3. Mean values and standard deviations of the physical and chemical parameters measured in the inlet and in the different constructed wetlands on the surface (FWS C, FWS P, FWS N, and FWS T) and underground (HFS, HFS-N, HFS-T, HFD2, HFD2-N, HFD2-T, HFD1, HFD1-N, and HFD1-T).

Wetlands	Turbidity (NTU)	Temperature (°C)	Potential Hydrogen -	Conductivity ($\mu\text{S cm}$)	Dissolved Oxygen ($\text{mg}\cdot\text{L}^{-1}$)	Oxidation- Reduction Potential (mV)
Inlet	1614 $\pm$ 357	19.0 $\pm$ 0	7.3 $\pm$ 0.1	57.6 $\pm$ 0.8	8.1 $\pm$ 0.2	−29.7 $\pm$ 4.2
FWS C	230 $\pm$ 67	19.0 $\pm$ 3.0	7.4 $\pm$ 0.4	101.6 $\pm$ 40.7	7.3 $\pm$ 0.3	−36.9 $\pm$ 20.6
FWS P	11 $\pm$ 5	19.1 $\pm$ 3.1	7.3 $\pm$ 0.3	159.5 $\pm$ 54.5	6.4 $\pm$ 0.5	−28.1 $\pm$ 14.0
FWS N	87 $\pm$ 32	18.9 $\pm$ 3.1	7.3 $\pm$ 0.3	127.1 $\pm$ 42.5	6.9 $\pm$ 0.4	−31.5 $\pm$ 14.7
FWS T	26 $\pm$ 9	18.9 $\pm$ 2.9	7.3 $\pm$ 0.3	160.3 $\pm$ 36.8	6.5 $\pm$ 0.6	−30.6 $\pm$ 18.7
HFS	23 $\pm$ 12	19.0 $\pm$ 3.0	8.7 $\pm$ 0.2	101.7 $\pm$ 23.9	6.3 $\pm$ 0.5	−120.2 $\pm$ 7.8
HFS-N	6 $\pm$ 5	19.1 $\pm$ 2.9	8.2 $\pm$ 0.3	152.1 $\pm$ 44.0	6.3 $\pm$ 0.5	−77.1 $\pm$ 15.3
HFS-T	4 $\pm$ 3	19.1 $\pm$ 3.0	8.1 $\pm$ 0.2	163.0 $\pm$ 36.4	6.3 $\pm$ 0.5	−78.0 $\pm$ 7.9
HFD2	51 $\pm$ 24	19.1 $\pm$ 3.0	8.1 $\pm$ 0.2	110.1 $\pm$ 33.9	7.1 $\pm$ 0.3	−74.4 $\pm$ 10.7
HFD2-N	14 $\pm$ 10	19.1 $\pm$ 3.0	7.8 $\pm$ 0.2	193.0 $\pm$ 47.6	6.9 $\pm$ 0.4	−53.9 $\pm$ 6.1
HFD2-T	3 $\pm$ 1	19.1 $\pm$ 3.0	7.6 $\pm$ 0.2	221.5 $\pm$ 52.7	6.4 $\pm$ 0.5	−46.2 $\pm$ 6.9
HFD1	22 $\pm$ 13	19.3 $\pm$ 3.0	7.8 $\pm$ 0.2	114.0 $\pm$ 29.8	7.1 $\pm$ 0.4	−57.0 $\pm$ 8.1
HFD1-N	4 $\pm$ 3	19.2 $\pm$ 3.0	7.6 $\pm$ 0.2	229.0 $\pm$ 46.8	6.8 $\pm$ 0.4	−46.0 $\pm$ 6.3
HFD1-T	2 $\pm$ 1	19.5 $\pm$ 2.9	7.6 $\pm$ 0.2	243.8 $\pm$ 54.5	6.7 $\pm$ 0.5	−45.4 $\pm$ 6.3

The same Resolution states that waters from Classes 1, 2, and 3 present a pH level between 6 and 9. The evaluated wetlands found that turbidity reduction did not result in significant pH changes of the treated effluent. The FWS wetlands showed pH values between 7.3 and 7.4, indicating stability within the regulatory limits. In the HSSF wetlands containing dolomitic gravel #1 and #2, the pH values were slightly higher, ranging from 7.8 to 7.6, and the highest pH was observed in the system filled with blast-furnace slag, from 8.1 to 8.7, which is possibly related to the mineralogical composition of the substrate. Increased pH values can lead to the precipitation of metals, reducing their mobility and bioavailability [42].

The minimum dissolved oxygen values standard for Class 1 rivers is 6.0 $\text{mg}\cdot\text{L}^{-1}$. The evaluated wetlands showed a similar level of dissolved oxygen to those observed in Class 1 water bodies, pointing out that the systems were effective in maintaining oxygenation of the treated effluent. The temperature of the wetlands showed average values of less than 20 °C, also corroborating the compliance with the standards for Class 1 waters. This result shows the efficiency of wetlands and highlights their importance for water quality and ecological balance.

3.2. Calibration and Validation of the *w-C** Model in Constructed Wetlands

The R^2 in the FWS wetlands indicated that the model had a high ability to predict the data, being able to predict over 77% of the data with statistical significance between the observed and simulated data. The data for statistical metrics for all FWS wetland results are shown in Table 4.

Analysis of the calibrated and validated data showed that the obtained R^2 for the calibration data ranged from 0.70 to 0.82 and for the validation data from 0.77 to 0.82. This metric showed a satisfactory fit of the model for turbidity reduction for the different macrophytes evaluated. Figure 4 shows the simulation results for the FWS constructed wetlands.

Table 4. Statistical evaluations of the w-C* model: w, R^2 , R, p value, NSE, and RMSE for the FWS wetlands non-vegetated (FWS-C), vegetated with *P. stratiotes* (FWS-P), *N. humboldtiana* (FWS-N), and *T. domingensis* (FWS-T).

Wetland	w (m·d ⁻¹)	R^2		R	p Value	NSE		RMSE	
		cal	val			cal	val	cal	val
FWS-C	0.09	0.70	0.80	0.89	$<2.2 \times 10^{-16}$	0.70	0.72	196.40	180.73
FWS-P	0.40	0.72	0.77	0.88	$<7.7 \times 10^{-16}$	0.71	0.77	37.23	39.45
FWS-N	0.16	0.82	0.79	0.79	$<2.2 \times 10^{-16}$	0.82	0.74	90.91	139.06
FWS-T	0.25	0.77	0.82	0.91	$<2.2 \times 10^{-16}$	0.76	0.82	76.10	55.37

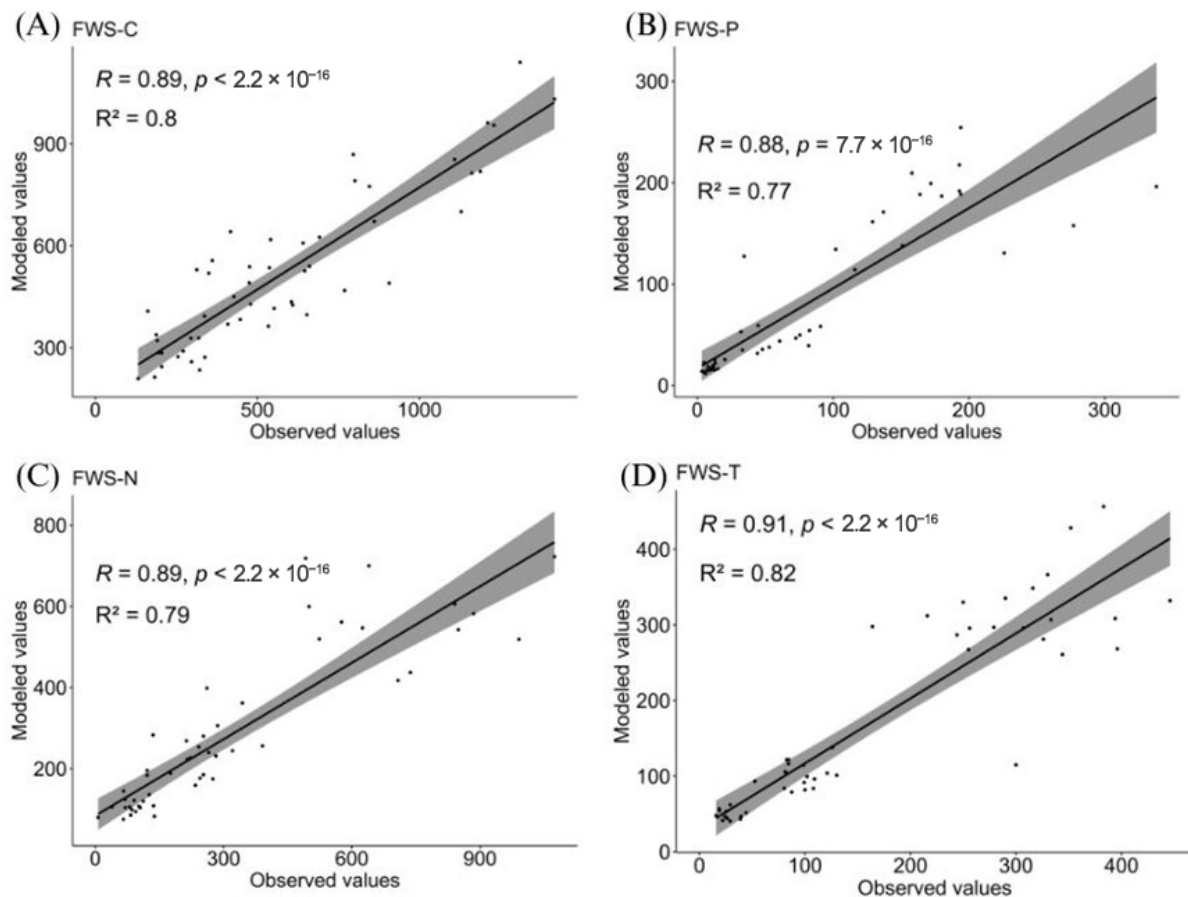


Figure 4. Modelled and observed turbidity values in the constructed wetland systems: (A) FWS-C, (B) FWS-P, (C) FWS-N, and (D) FWS-T.

The results from the analysis in the w-C* model were evaluated by relating the observed and simulated data using the R^2 , R, and p -value coefficients ($p < 0.05$). These parameters were chosen by the ability of confirming the model fit quality and the statistical significance between simulated and observed data. The results are significant for the FWS wetlands.

For the FWS-C validation data, high R^2 values of 0.80 and R values of 0.89 were observed, with a significant p -value ($p < 0.05$), indicating statistical significance between observed and simulated data (Figure 4A). For FWS-P, the R^2 values also showed a well-adjusted fit to the model, with $R^2 = 0.77$ and $R = 0.88$ ($p < 0.05$) (Figure 4B). The fit of the FWS-N wetland to the model was satisfactory, where the values are statistically significant for $R^2 = 0.79$ and $R = 0.79$ (Figure 4C). The FWS-T showed $R^2 = 0.82$ and $R = 0.91$ values, indicating a good fit to the model (p -value < 0.05) (Figure 4D).

NSE and RMSE performance metrics were carried out on the calibrated and validated model data, showing the high predictive capacity of the w-C* model for the performance of constructed wetlands in reducing turbidity (Table 4).

The NSE values varied between 0.70 and 0.82 for the calibration data and between 0.72 and 0.82 for the validation data. This metric performance indicates a good fit between observed and simulated turbidity values, and the results were close to 1 [39]. It was observed that the NSE was slightly lower than the R^2 in the FWS-C and FWS-N wetlands, suggesting that the model may overestimate certain values but still effectively represents the general tendency, as indicated by the R^2 value [43].

The RMSE observed in the FWS-C wetland showed the highest value of 196.40 in the calibration and 180.73 in the validation. FWS-P, -N, and -T vegetated systems had a RMSE of 37.23. The RMSE indicated that vegetated FWS showed a better fit to the model compared to FWS-C, considered a control that simulates a natural sedimentation tank.

The w value proved to be sensitive to the macrophyte species, as shown in Table 4. The highest value was recorded in the wetland FWS-P ($0.40 \text{ m} \cdot \text{d}^{-1}$) at 19.1°C , while the lowest value was observed in the FWS-C ($0.09 \text{ m} \cdot \text{d}^{-1}$) at 19.0°C . These results indicate that the settling rate was 4.4 times higher in the FWS-P compared to FWS-C and can be attributed to the presence of *Pistia stratiotes*, which plays a crucial role in enhancing sedimentation processes. The plant's dense root system increases surface roughness and reduces water flow velocity, creating favourable conditions for suspended particles to settle, and the roots provide a large surface area for biofilm development, which can trap and aggregate fine particles, facilitating their removal, resulting in a 99% reduction in turbidity. Higher values than the FWS-C were observed for the FWS-T and FWS-N systems of $0.25 \text{ m} \cdot \text{d}^{-1}$ at 18.9°C and $0.16 \text{ m} \cdot \text{d}^{-1}$ at 18.9°C , respectively. The turbidity reduction percentages found in these systems were 99% in FWS-T and 95% in FWS-N.

This can be explained by the dense root structure of *P. stratiotes* (FWS-P) that increased the surface contact, consequently increasing the suspended particle settling rate, resulting in a greater turbidity reduction level and high w values for vegetated FWS wetlands [44]. The free roots zone in the water column of this floating macrophyte resulted in a settling rate that was 1.6 times faster than the wetland vegetated with *T. domingensis* (FWS-T), which is classified as an emergent rooted macrophyte, where only the stems were in contact to the water column, leading to reduced surface contact for suspended and dissolved solids retention and interception [45]. Furthermore, the w observed for FWS-P (*P. stratiotes*) was 2.5 times faster than FWS-N (*N. humboldtiana*) due to a low root structure compared to the other evaluated macrophytes, resulting in a reduced area for contact and, therefore, decreasing the settling rate [4].

The results of this study suggest the use of floating macrophytes for FWS systems, such as *P. stratiotes*, highlighting that the root's structure dispersed in the water column provides an effective surface area to retain and intercept the suspended solids, resulting in a higher particle settling rate.

For HSSF wetlands, the results were analysed according to the wetland substrate blast-furnace slag, #2 dolomitic gravel, and #1 dolomitic gravel.

The w-C* model showed satisfactory predictive ability, and the R^2 ranged from 64% to 81% for the validation data. According to Table 5, the HFS system achieved an R^2 of 0.84 in calibration and 0.76 in validation. For HFS-N, the results were similar, with an R^2 of 0.75 (calibration) and 0.81 (validation). HFS-T achieved an R^2 of 0.78 in calibration and 0.64 in validation, as shown in Table 5.

Table 5. Statistical evaluations of the w-C* model: w, R², R, p value, NSE, and RMSE in wetlands filled with blast furnace slag, non-vegetated (HFS), and vegetated by *N. humboldtiana* (HFS-N) and by *T. domingensis* (HFS-T).

Wetland	w (m·d ⁻¹)	R ²		R	p Value	NSE		RMSE	
		cal	val			cal	val	cal	val
HFS	0.38	0.84	0.76	0.87	$<2.2 \times 10^{-16}$	0.83	0.74	25.30	37.23
HFS-N	0.44	0.75	0.81	0.90	$<2.2 \times 10^{-16}$	0.75	0.78	29.85	36.97
HFS-T	0.61	0.78	0.64	0.80	$<6.7 \times 10^{-16}$	0.77	0.56	14.78	28.19

NSE and RMSE performance metrics were performed on the calibrated and validated data of the model (Table 6). The NSE values ranged from 0.75 to 0.83 for the calibration data and from 0.56 to 0.78 for the validation data. Considering that this metric is considered effective when the values are close to 1, the proposed model fitted the data satisfactorily, with a tendency to overestimate the simulated values in all the wetlands evaluated: HFS, HFS-N, and HFS-T [46].

Table 6. Statistical evaluations of the w-C* model: w, R², R, p value, NSE, and RMSE in wetlands filled with #2 dolomitic gravel, non-vegetated (HFD2), and vegetated by *N. humboldtiana* (HFD2-N) and by *T. domingensis* (HFD2-T).

Wetland	w (m·d ⁻¹)	R ²		R	p Value	NSE		RMSE	
		cal	val			cal	val	cal	val
HFD2	0.20	0.83	0.82	0.91	$<2.2 \times 10^{-16}$	0.82	0.82	64.99	62.81
HFD2-N	0.29	0.85	0.81	0.90	$<2.2 \times 10^{-16}$	0.84	0.79	46.29	56.22
HFD2-T	0.39	0.86	0.80	0.90	$<2.2 \times 10^{-16}$	0.83	0.77	27.26	27.56

The RMSE observed in these wetlands ranged from 14.78 to 29.85 in calibration and from 28.19 to 37.23 in data validation, indicating the suitability of the model to the data [40].

The results of the R², R, and p-value coefficients of the w-C* model analysis between the observed and simulated data evaluated in the wetlands are shown in Figure 5. (A) HFS, (B) HFS-N, and (C) HFS-T. In the HSF, high values of R² = 0.84 and R = 0.84 were observed, indicating statistical significance between the observed and simulated data (Figure 5A). In HFS-N, the R² values also showed a good fit to the model, with R² = 0.75 and R = 0.90 ($p < 0.05$) (Figure 5B). The fit of the HFS-T wetland to the model was satisfactory, and statistically significant values of R² = 0.78 and R = 0.80 were obtained (Figure 5C).

The settling rate (w) observed in Table 5 for the HFS-T system was 0.61 m·d⁻¹ at 19.1 °C, followed by HFS-N (0.44 m·d⁻¹) at 19.1 °C, while the HFS non-vegetated had the lowest rate (0.38 m·d⁻¹) at 19.0 °C. Vegetation increased the settling by 1.6 times (HFS-T) and 1.15 times (HFS-N) compared to the non-vegetated system (HFS). Vegetation plays a key role in the removal of suspended sediment through submerged structures such as rhizomes, roots, and stems [14]. *T. domingensis* has a better developed and dispersed root system, contributing to greater retention of suspended solids compared to *N. humboldtiana*, which has a small root structure [4].

According to Table 6, the model showed a high predictive ability, with an R² above 80% for the subsurface wetlands filled with #2 dolomitic gravel. HFD2 had an R² of 0.83 in calibration and 0.82 in w-C* validation, showing strong consistency between the stages. HFD2-N had an R² of 0.85 in calibration and 0.81 in validation, while HFD2-T had 0.86 and 0.80, respectively, both high values.

For the calibration of the data, the NSE values were between 0.82 and 0.84, indicating good model performance. For the validation data, the NSE values ranged from 0.77 to 0.82, confirming the consistency of the model [39].

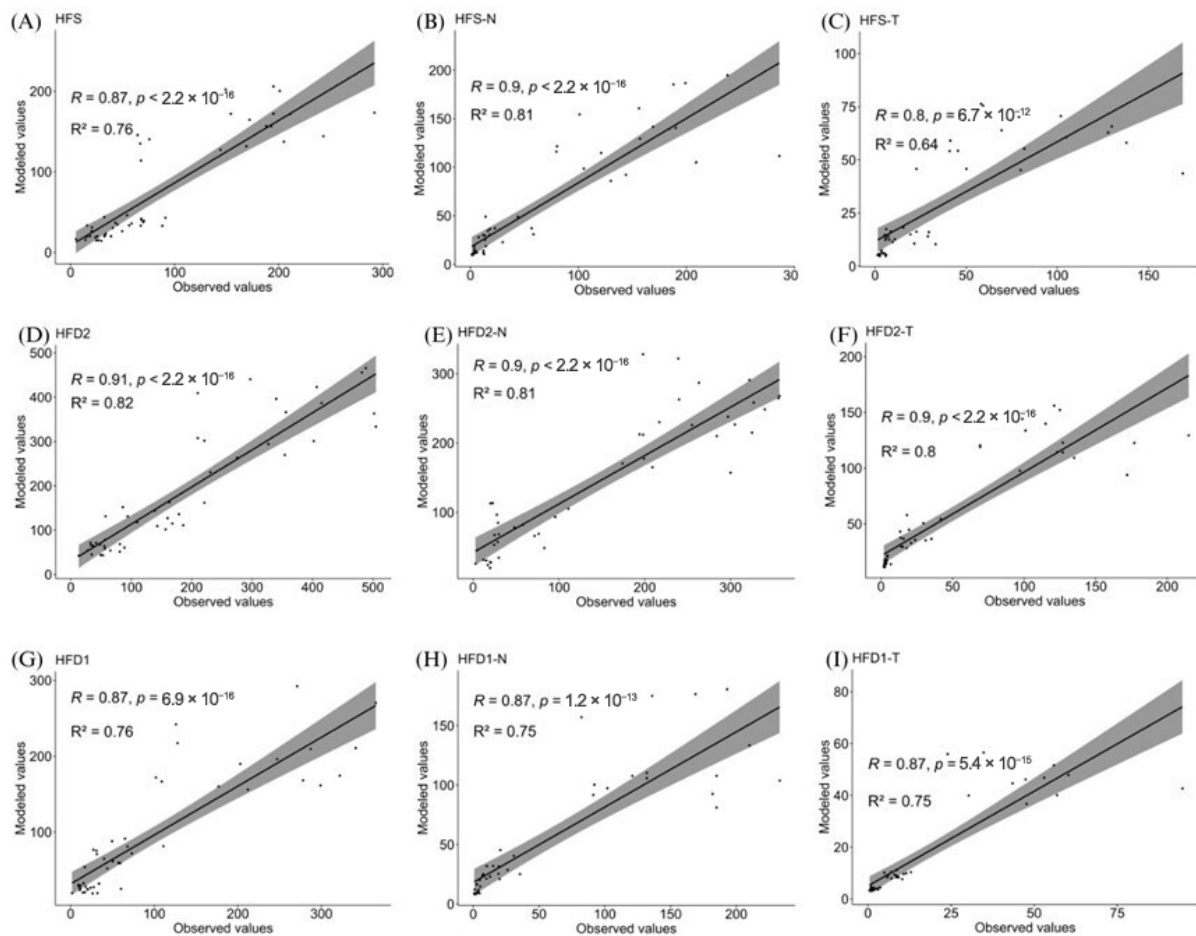


Figure 5. Modelled and observed turbidity values in the constructed wetland HSSF: (A) HFS, (B) HFS-N, (C) HFS-T, (D) HFD2, (E) HFD2-N, (F) HFD2-T, (G) HFD1, (H) HFD1-N, and (I) HFD1-T.

The RMSE values ranged from 27.26 to 64.99 during calibration and from 27.56 to 62.81 during validation. These results confirm the adequacy of the model to the experimental data, demonstrating its potential to accurately represent the processes studied in the wetlands [40].

In the wetlands containing dolomitic gravel #2, the high values of the coefficients of determination indicated a satisfactory fit of the model (Figure 5).

For HFD2, $R^2 = 0.82$ and $R = 0.91$ were observed, showing statistical significance between the observed and simulated data (Figure 5D). Similarly, HFD2-N showed an $R^2 = 0.85$ and $R = 0.81$, also with statistical significance ($p < 0.05$; Figure 5E). The performance of HFD2-T was equally satisfactory, with $R^2 = 0.80$ and $R = 0.90$, confirming the suitability of the model to the experimental data (Figure 5F).

Sedimentation velocity was highest in HFD2-T ($0.39 \text{ m} \cdot \text{d}^{-1}$) at 19.1°C , followed by HFD2-N ($0.29 \text{ m} \cdot \text{d}^{-1}$) at 19.1°C , and lowest in the non-vegetated system ($0.20 \text{ m} \cdot \text{d}^{-1}$) at 19.1°C . These results highlight the role of macrophytes in the retention and interception of suspended solids, contributing to the reduction of turbidity [47]. *T. domingensis* (HFD2-T) increased sedimentation velocity by 1.95 times, while *N. humboldtiana* (HFD2-N) promoted an increase of 1.45 times higher compared to the non-vegetated system. However, a general decrease in settling rate was observed when dolomitic gravel #2 was used, possibly due to the larger grain size, which reduced the surface area available for particle interception [30,48].

The modelling of the subsurface wetlands filled with dolomitic gravel #1 showed satisfactory results, and the prediction capacity was over 75% in the validation data. The R^2 values obtained in the calibration and validation phases were close, demonstrating the

robustness and reliability of the model in predicting the behaviour of the wetland system, as described in Table 7.

Table 7. Statistical evaluations of the w-C* model: w, R², R, p value, NSE, and RMSE in wetlands filled with #1 dolomitic gravel, non-vegetated (HFD1), and vegetated by *N. humboldtiana* (HFD1-N) and by *T. domingensis* (HFD1-T).

Wetland	w (m·d ⁻¹)	R ²		R	p Value	NSE		RMSE	
		cal	val			cal	val	cal	val
HFD1	0.30	0.78	0.76	0.87	$<6.9 \times 10^{-16}$	0.78	0.74	48.96	53.32
HFD1-N	0.46	0.70	0.75	0.87	$<1.2 \times 10^{-13}$	0.69	0.73	34.00	37.77
HFD1-T	0.70	0.82	0.75	0.87	$<5.4 \times 10^{-15}$	0.81	0.75	9.78	10.74

For HFD1, the R² values were 0.78 and 0.76, for HFD1-N 0.70 and 0.75, and for HFD1-T 0.82 and 0.75 for the calibration and validation, respectively. These results confirm the consistency of the model and its ability to adequately represent the turbidity reduction processes in the studied wetland systems.

The NSE and RMSE metrics (Table 7) were used to assess the performance of the model. During calibration, the NSE values varied between 0.69 and 0.81, indicating a consistent fit between the observed and simulated data. During validation, the NSE values varied between 0.73 and 0.75, confirming the reliability of the model in different datasets and indicating that the model tended to overestimate the data in these wetlands [46].

For the RMSE, the results showed values between 9.78 and 48.96 in calibration, while in validation the values were in a wider range, from 10.74 to 53.32. These values indicate that the model fits the training data well, suggesting that the parameters were effectively optimised between calibration and validation.

The values of the determination coefficients for the wetlands with dolomitic gravel #1, HFD1, HFD1-N, and HFD1-T are shown in Figure 5. For HFD1, the coefficients R² = 0.76 and R = 0.87 indicated statistical significance (Figure 5G). Similarly, HFD1-N showed R² = 0.75 and R = 0.87 with $p < 0.05$ (Figure 5H), similar to that observed in HFD1-T, with R² = 0.75 and R = 0.87, confirming the adequacy of the model to the experimental data (Figure 5I).

The settling rate varied considerably in the HSSF wetlands with dolomitic gravel #1 (Table 7). The highest settling rate (w) value among the studied wetlands was observed in HFD1-T (0.7 m·d⁻¹) at 19.5 °C. HFD1-N had a w of 0.46 m·d⁻¹ at 19.2 °C, while HFD1 non-vegetated had a value of 0.3 m·d⁻¹ at 19.3 °C. In HFD1-T, the settling rate of *T. domingensis* was 2.33 times higher than that of *N. humboldtiana* (1.5 times higher). The dolomitic gravel #1 has the smaller grain size compared to those previously observed, and it seemed to be a critical factor in settling efficiency, providing a larger surface area for particle trapping [30].

The model was sensitive to the macrophyte and substrate wetland components. Wetlands vegetated with *T. domingensis* in every type of substrate were characterised by a higher settling rate. This suggests that the dense root structure of this macrophyte plays a crucial role in the removal of suspended solids and is an important criterion for optimising the performance of the treatment system. The highest settling rate was observed in the wetland planted with *T. domingensis* on dolomitic gravel #1.

Increasing the particle size of the substrate in wetlands, as with the blast furnace slag and dolomitic gravel #2, had a significant effect on settling rate, mainly due to changes in flow dynamics and particle interaction. As particle size increases, settling rate decreases, which is related to higher flow velocities and a reduced surface contact area for particle interception [4,48].

FWS and HSSF perform the same physical processes for transport and removal of SST in constructed wetlands. The combination of materials with smaller particle sizes and

macrophytes with a highly developed root system improves settling by filtration, where both criteria form a filter bed, improving the performance of constructed wetlands [8]. Kadlec and Wallace Nasrabadi reported a wide range of settling velocities (w), from 0.0076 to $26.3 \text{ m}\cdot\text{d}^{-1}$, based on column settling experiments conducted across various wetlands designed for sediment removal. These results are strongly influenced by the size and type of suspended particles, and it is important to note that colloidal materials settle very slowly, indicating the need for further investigation into their behaviour in treatment wetlands. Although the $w\text{-C}^*$ model developed by Kadlec is widely used to predict pollutant removal in constructed wetlands, there is a noticeable lack of studies that explicitly define or discuss the apparent settling velocity (w) for parameters such as total suspended solids (TSS) and turbidity.

Application of the $w\text{-C}^*$ model by Kadlec and Wallace Nasrabadi demonstrated a settling velocity (w) of $0.29 \text{ m}\cdot\text{d}^{-1}$ for turbidity reduction in a horizontal subsurface flow (HSSF) wetland, under surface loading rates ranging from 8.4 to $20 \text{ m}\cdot\text{d}^{-1}$. These findings are consistent with the w values observed in the present study, which operated under a hydraulic loading rate of $18.27 \text{ L}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, suggesting comparable system dynamics and supporting the reliability of the model for evaluating turbidity removal in similar configurations.

The synergy between vegetation and substrate plays a critical role in enhancing treatment performance. While substrates provide surface area for microbial colonization and promote sedimentation and filtration, plant roots contribute to the physical trapping of particles and stimulate microbial activity through oxygen release and rhizodeposition [47]. The suitability of native macrophytes, such as *N. humboldtiana*, in HSSF flow-through wetlands was demonstrated by the increase in the settling rate for this typology, demonstrating their effectiveness in improving sedimentation and pollutant removal. The integration of native species in constructed wetlands not only improves the water quality but also promotes ecological benefits, reinforcing the importance of assessing local flora for such applications.

The absence of vegetation in constructed wetlands significantly affected settling rates by the reduction of contact area for sediment deposition, which is essential to retain suspended solids [49]. Macrophytes play an important role in increasing sediment trapping and improving water quality, as demonstrated in this study. However, the data presented provide valuable information for the application of the technology in situations where the use of vegetation is not feasible. This trend is consistent with the $w\text{-C}^*$ model, which predicts greater pollutant removal with increased retention time due to enhanced sedimentation and interaction with treatment media. The optimal HRT observed experimentally aligned closely with model predictions, confirming the model's applicability to turbidity dynamics under the tested conditions.

4. Conclusions

This study demonstrated the applicability of the $w\text{-C}^*$ model for predicting turbidity removal in constructed wetlands treating mine spoil rainwater, with strong agreement between observed and modelled data. The model performed robustly across both FWS and HSSF configurations, with higher settling rates and lower prediction errors observed in HSSF systems.

The presence of vegetation and substrate characteristics emerged as key factors influencing removal efficiency. Species with dense, fibrous root systems, such as *T. domingensis* and *N. humboldtiana*, significantly enhanced settling velocities, particularly when combined with substrates of smaller granulometry ($9.5\text{--}19.0 \text{ mm}$). These plant–substrate synergies facilitated greater particle filtration, interception, and deposition, underscoring their relevance in wetland design.

Despite the study being conducted under controlled conditions, the findings offer practical guidance for optimising constructed wetland configurations aimed at turbidity reduction. Further studies should consider the controlled conditions, which may not fully capture the variability of full-scale applications. Additionally, hydraulic retention time was assessed at specific intervals, but long-term seasonal dynamics were not considered. Future research incorporating seasonal variations and real-world operational conditions could enhance the applicability of these findings. Despite these limitations, the TSS removal model proved to be a reliable tool for describing turbidity reduction kinetics, offering crucial insights into hydraulic parameters and design criteria for large-scale implementation.

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Abbreviations

The following abbreviations are used in this manuscript:

HRT	Hydraulic retention time
HRL	Hydraulic loading rate
HSSF	Horizontal subsurface flow
FWS	Free water surface
SMRS	Synthetic mine spoil rainwater
NTU	Nephelometric turbidity unit

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