Unsteady state series CSTR modeling of removal of ammonia nitrogen from domestic wastewater treated in a vertical flow constructed wetland

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ABSTRACT

This work shows simulation results for subsurface vertical flow constructed wetland (VFCW) using a series CSTR model. The VFCW considered received the outflow from a domestic wastewater treatment plant. In addition, it was planted with Cyperus sp. and filter media was unsaturated. The model was based on an unsteady state mass balance for ammonia, nitrites, and nitrates, using one to three series CSTRs. Nitrogen transformation mechanisms considered were ammonification, nitrification, plant uptake and denitrification. The following effects were evaluated: the number of reacting CSTRs from one to three; the occurrence of the reaction in second and third CSTRs for the case that three CSTRs hold; the use of either equal or different values of reaction rate parameters between CSTRs; and the discretization of the reaction rate parameters. The inflow and outflow measurements of ammonium, nitrites, and nitrates were used for model calibration. The estimated parameters included the reaction rate coefficients and reactor water volume. The coefficient of determination (R²) evidenced a satisfactory capability of simulating outlet pollutant concentrations. Two and three reacting CSTRs achieved similar R² value (0.54–0.55), whereas one reacting CSTR achieved an R² of 0.39, and three CSTRs with reaction only in the first tank achieved an R² of 0.42. Discretization of the nitrification rate for the case of two reacting CSTRs led to an R² of 0.94. The parameter sensitivity analysis revealed a significant effect of model parameters on the R² value.

Keywords:
Nitrogen removal
Series CSTR
VFCW modelling
Wetland modelling

1. INTRODUCTION

Discharge of nitrogen-rich effluents into surface water can result in severe eutrophication and other impacts on aquatic life and water use [1, 2]. Constructed wetlands (CWs) are capable of removing nitrogen and are suitable for small communities where conventional treatment systems are not affordable [2]. In particular, vertical subsurface flow constructed wetlands (VFCWs) are effective in the removal of organic matter and NH₄-N, what is favored by aerobic conditions [3, 4]. However, denitrification is limited [5-7].

The wetland models allow the prediction of pollutant removal and the estimation of the effective area. In fact, they correlate inlet and outlet pollutant concentrations, and they allow determining the land of full-scale wetlands that is required for attaining the target outlet concentration of different pollutants [8-10].
Tracer studies for VFCW indicate that flow pattern is between plug flow and complete mixing rather than ideal flow behavior. Also, this is confirmed by the qualitative shape of the effluent curve which involves a peak and a long flat tail [11-13]. The argument of such behavior is that the direction of the flow of wastewater at each point of the trajectory through the packing media diverges from the downward bulk flow direction [8]. In addition, the uniformity of the flow inside the filter bed is influenced by the degree of saturation, as indicated by the dimensionless variance. Indeed, the degree of local mixing increases as the saturation of the bed decreases. In the case of unsaturated conditions, local mixing is enhanced by the occurrence of different flow paths [14].

A rigorous mechanistic approach to modeling VFCWs considers plug flow with longitudinal dispersion and variably saturated conditions. It has been used for both VFCW and subsurface horizontal flow constructed wetland (HFCW), achieving accurate predictions [11, 15]. Nevertheless, the resulting model involves complex partial differential equations in terms of time and vertical direction, which limits its application for CW design [14, 16].

In contrast, series CSTRs modeling approach allows for practicable handling, and also a detailed description of the different processes. It has proved suitable for describing nonideal plug flow in VFCWs, achieving accurate simulations, even for the case of large-scale [17]. It has been used for different degrees of VFCW bed saturation; unsaturation [18], 21 and 42% saturation [13] and full saturation [16]. In [19] tracer experiments were performed on a pilot scale VFCW, with bed saturation and artificial aeration, and loading in both continuous and intermittent mode. The calibration of the gamma distribution model yielded one CSTR. In [13] tracer experiments were conducted on a pilot-scale VFCW with intermittent loading and at 21% and 41% bed saturation. The model used comprised series-parallel CSTRs under non-stationary conditions: two CSTRs were connected in series, the last one being connected to a side CSTR. This configuration aimed at addressing the shape of the tracer response curve: the series CSTRs account for the peak, whereas the side CSTR accounts for the long flat tail.

Detailed modeling involves the sorption process and the effect of temperature, pH, heterotrophic biomass and dissolved oxygen, resulting in a large number of parameters. To determine them, the following strategies are commonly utilized: i) to take some parameters from literature, so that they correspond to different conditions, thus limiting the model fitting accuracy; ii) to determine some of the parameters from in situ measurements, for instance, adsorption isotherm parameters [20, 21]. As this limits the model applicability, it is recommended that the model has the lowest number of parameters as possible [22].

In [16] a model was proposed for domestic wastewater treatment in a VFCW. The water flows upwards so that the filter media remains saturated. The filter media consisted of three layers: an upper layer involving plant growth; a medium layer involving pollution removal, and a lower layer for flow distribution. The flow rate and pollutant concentrations were measured at wetland inflow, wetland outflow and at each layer. The model mass balance considers three unsteady series CSTRs, each CSTR is related to one filter media layer. The transformation mechanisms considered are nitrification, denitrification, plant nutrient uptake, and filter media adsorption. The state variables are the concentrations of organic nitrogen, NH₃-N and (NO₃⁻+NO₂⁻). The reaction rates account for the effect of temperature, pH, dissolved oxygen (DO) and ammonium nitrogen (AN), with a Monod kinetics in terms of AN and DO. The rate of plant growth is assumed constant, as wetland plants had already taken shape. The model parameters are different for each CSTR, and the water volume at each CSTR was separately calculated based on the filter media porosity for the corresponding layer. Each CSTR model was calibrated by using the concentration measurements of the corresponding layer. The main limitation is that the model calibration requires determination of layer porosity, and measurements of flow rate, pollutant concentrations, pH and DO in each layer.

In [22] a model was proposed for a retention soil filter (RSF). The RSF is a VFCW that is combined with a detention basin and is used for treating combined sewage overflow (CSO). The layers of filter media are detention zone, upper gravel layer, sand layer, and drainage layer. Accordingly, the model considers three layers: retention layer, process layer, and drainage layer. The mass balance considers three unsteady series CSTRs; each CSTR is related to one layer. The calculation of volumes and flow rates of each layer is based on the flow infiltration through layers.

In this work, domestic wastewater treated in an unsaturated VFCW is modeled. The model is based on unsteady mass balance for one to three series CSTRs. The state variables are ammonium nitrogen concentration and (NO₃⁻+NO₂⁻) concentration. The model is calibrated by minimization of the sum of the squared errors between model and data. The main contributions of this study are as follows: i) the model is calibrated using concentrations measured at CW inflow and outflow, as concentrations at each filter layer were unknown; ii) all model parameters are estimated by minimization and none is borrowed from other studies; iii) the volumes of the series CSTRs are estimated instead of being determined from direct CW measurements; iv) the parameter sensitivity is determined for each parameter, as the effect of model parameters on the coefficient of determination. Also, the coefficient of determination is evaluated for
the effect of the following model features: the number of reacting CSTRs from one to three; the occurrence of reaction in second and third CSTRs for the case that three CSTRs hold; the use of either equal or different values of reaction rate parameters between CSTRs; and finally the discretization of the reaction rate parameters.

2. METHODS

2.1. A brief review of pollutant removal in SSFCWs

Nitrogen removal in CWs encompasses a number of complex processes, including ammonification, nitrification-denitrification, adsorption, uptake by plants and uptake by microorganisms [2]. Nutrient removal in SSFCWs comprises a limited effect of plant absorption in comparison to biological degradation. Indeed, in the case of high nutrient loadings, plant uptake is negligible in comparison to microbially-mediated removal [19]. The amount of nitrogen plant uptake depends on the plant’s growth requirements rather than nitrogen loading [23, 24].

The nitrogen removal in SSFCWs depends on hydraulic retention time (HRT), temperature, vegetation type and the filter media [25]. Biological nitrification and denitrification are regarded as the main processes for the removal of ammonia in subsurface flow constructed wetlands (SSFCWs) [2]. It has been noted that nitrification is the limiting step for nitrogen removal. Nitrification is strictly aerobic, and it only occurs if DO is available [26]. It is dependent on dissolved oxygen, pH and temperature. The nitrification rate is significantly affected by DO and pH, whereas temperature has a lower effect [16]. Aeration significantly enhances nitrification, whereas low oxygen concentration and temperature have a decreasing effect [27, 28]. The optimum pH range is 7.0 - 9.0; whereas pH below 7.0 has an adverse effect [16]. A high content of organics leads to nitrification inhibition because heterotrophic organic degradation depletes the dissolved oxygen [29, 30].

In [25] nitrogen and organics removal efficiencies were reported for VFCWs in tropical and subtropical regions. Therein, NH$_4^+$-N removal percentages range from 45% to 99% (average of 66%), and outflow NH$_4^+$-N is below 52.0 mg/L with average of 18.0 mg/L, whereas BOD removal efficiencies average 88%. In [31] nitrification rates in VFCWs were reported, which ranged from 0.01 to 2.15 g N/(m$^2$·day), with an average of 0.048 g N/(m$^2$·day). It has been observed that background concentration for ammonia removal is nearly zero [24].

2.2. System description

In this study, the VFCW experiment reported by [32] is considered. The system is located at Pereira (Colombia) and planted with Cyperus sp. It receives the outflow from a domestic wastewater treatment plant, which includes a septic tank and an upflow anaerobic filter. The length, width, and depth of the VFCW are 8.65 m, 5.0 m, and 0.80 m respectively, resulting in a surface area of 43.25m$^2$. The porous media consists of medium and thick size gravel. The data were taken on a weekly basis over ten weeks, starting in March 2012. The inflow was intermittent downflow, with three pulses per hour. The average inflow discharge was 314 L/h, and the hydraulic loading rate was 17.4 cm/d. The inflow pH ranged from 7.4 to 7.6 (average of 7.5), whereas the outflow pH ranged from 7.46 to 7.61 (average of 7.5). The inflow water temperature ranged from 24.0 to 26.0°C (average of 25°C), and the outflow temperature ranged from 25.0 to 27.0°C (average of 26°C). The inflow COD ranged from 208.7 to 318.8 mg/L (average of 249.1 mg/L) and the inflow NO$_3^-$ ranged from 3.9 to 7.9 mg/L (average of 5.0 mg/L). The outflow NO$_3^-$ ranged from 3.9 to 48.8 mg/L (average of 27.8 mg/L).

The inflow BOD ranged from 72.4 to 203.0 mg/L (average of 118.2 mg/L) and the BOD loading averaged 20.6 g/(m$^2$·d), whereas the outflow BOD ranged from 7.01 to 45.6 mg/L (average of 21.5 mg/L, and 81.8 % removal). This removal percentage (81.8%) is below the average (88%) reported by [25]. The inflow NH$_4^+$-N ranged from 170.9 to 206.0 mg/L (average of 192.1 mg/L), the outflow NH$_4^+$-N ranged from 93.6 to 145.1 mg/L (average of 121.7 mg/L), with 36.6% average removal. This removal percentage (36.6%) is below the range (45 to 99%), and the average (66%) reported by [25], whereas the average outflow NH$_4^+$-N is above the highest value (52.0 mg/L) reported therein.

The high outflow concentrations of nitrite and nitrates are due to the low denitrification capability, what is typical of properly aerated VFCWs. The time courses of outflow ammonium and (NO$_3^-$+NO$_2^-$) involved unexpected effects, mainly abrupt changes. Outflow ammonia exhibited an initial increase and an abrupt decrease after ca. 35 days, whereas outflow (NO$_3^-$+NO$_2^-$) exhibited a significant increase from 5 mg/L at the initial time, to ca. 60 mg/L in the last ten days. These abrupt changes are attributable to the adaptation of the wetland to the incoming wastewater during the start-up process. This is concluded because wetland adaptation to wastewater lasted only one month [32], and similar effects are exhibited by the HFCW start-up described by [24].
CWs start-up involves the establishment of sorption process and adaptation of the microbial community to the loading and aeration. These effects can occur for many months, thus affecting the removal percentage [23, 24]. An example of nitrogen performance in HFCW start-up is shown by [24]. The time course of ammonia outflow concentration involves an increase, a smooth decrease, and an abrupt decrease, such that the corresponding removal percentage comprises a decrease, an increase, and an abrupt increase.

In contrast, the outflow nitrate concentration departs from zero, follows a smooth bell-shaped curve along the timeline and vanishes at the end.

2.3. Mass balance model

Consider ammonification, nitrification, plant uptake and denitrification as being the primary nitrogen removal and formation pathways, and assume: i) ammonium is converted to nitrite and nitrate in one step; ii) plant growth rate is constant. Thus, the mass balance for nitrogen concentrations across a single CSTR gives [16, 33].

\[
\frac{d\text{ON}}{dt} = \frac{Q}{V} (\text{ON}_{\text{in}} - \text{ON}) - r_a \\
\frac{d\text{NH}_4}{dt} = \frac{Q}{V} (\text{NH}_4_{\text{in}} - \text{NH}_4) + r_a - r_n - r_d \\
\frac{d(\text{NO}_2^+ + \text{NO}_3^-)}{dt} = \frac{Q}{V} [(\text{NO}_2^- + \text{NO}_3^-)_{\text{in}} - (\text{NO}_2^- + \text{NO}_3^-)] + r_n - r_d \\
\]

\[r_a = k_a \text{ON} \]
\[r_n = k_n C_T C_p \mu \frac{DO}{K_{DO} + DO} \frac{NH_4}{(\text{NO}_2^- + \text{NO}_3^-)} \]
\[r_d = k_d \theta^{-20} \frac{V}{k_d} \frac{\text{NH}_4}{(\text{NO}_2^- + \text{NO}_3^-)} \]
\[r_p = k_p \]

Where ON is the organic nitrogen concentration, DO is the dissolved oxygen concentration, Q is the flow rate, V is the effective volume, which is the product of volume and porosity of each CSTR; NH\textsubscript{4}\text{in} is the inflow NH\textsubscript{4} concentration; r\textsubscript{a} is the ammonification rate, r\textsubscript{n} is the nitrification rate, r\textsubscript{d} is the plant uptake rate, and r\textsubscript{p} is the denitrification rate. The model parameters are k\textsubscript{a}, k\textsubscript{n}, K\textsubscript{DO}, k\textsubscript{AN}, k\textsubscript{d}, k\textsubscript{p}. C\textsubscript{T} is a linear function of pH and C\textsubscript{p} is an exponential function of temperature. Both Monod and first-order expressions can be used to describe ammonia removal in wetlands [24]. When Monod kinetics exhibit values of the half-saturation constant significantly higher than pollutant concentration (C\textsubscript{K}<<K), a first order expression is more suitable [34]. Thus, in this study both first order and Monod kinetics in terms of NH\textsubscript{4} concentration are evaluated for the nitrification rate. It is worth mentioning that NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} are produced by nitrification and are consumed by denitrification [16]. In this study, experimental data evidenced a significant formation of (NO\textsubscript{2}\textsuperscript{-}+NO\textsubscript{3}\textsuperscript{-}).

Therefore, the (NO\textsubscript{2}\textsuperscript{-}+NO\textsubscript{3}\textsuperscript{-}) mass balance is considered in this study, in order to simulate its formation.

The following features of the VFCW are considered: i) available VFCW measurements included neither concentrations of organic nitrogen nor dissolved oxygen; ii) the water temperature remained approximately constant, wherein the outflow values ranged from 25.0°C to 27.0°C and averaged 26.0°C; iii) pH variations were negligible, as outflow pH ranged from 7.46 to 7.61 and averaged 7.5. Therefore, the following simplifications are made: i) the temperature and concentrations of organic nitrogen and DO are assumed constant; ii) the term (r\textsubscript{a}-r\textsubscript{p}) is assumed to be constant in the NH\textsubscript{4} concentration mass balance (r\textsubscript{a}-r\textsubscript{p}=k\textsubscript{m}); iii) the term r\textsubscript{n} is simplified as

\[r_n = k_n \frac{\text{NH}_4^+}{K_{KS} + \text{NH}_4^+}; \text{ or } r_n = k_n \text{NH}_4^+ \]

iv) the denitrification rate r\textsubscript{d} is simplified as

\[r_d = k_d \frac{(\text{NO}_2^- + \text{NO}_3^-)}{K_{DENO} + (\text{NO}_2^- + \text{NO}_3^-)}; \text{ or } r_d = k_d \]

Incorporating these simplifications and arranging the notation, gives

\[\frac{d\text{NH}_4}{dt} = \frac{Q}{V} (\text{NH}_4_{\text{in}} - \text{NH}_4) - r_n + r_p \]
\[\frac{d\text{NO}_2^- + \text{NO}_3^-}{dt} = \frac{Q}{V} \left(\text{NO}_3^-_{\text{in}} - \text{NO}_3^-\right) + r_n - r_d \]
\[ r_n = k_{nmx} \frac{NH}{k_{s5+NH}} \text{ or } r_n = k_n NH; r_{ap} = k_{ap}; r_d = k_{dmx} \frac{NO}{k_{dSN0+NO}} \text{ or } r_d = k_{dmx} \]

Where NH\textsubscript{in} and NH are the inflow and outflow NH\textsubscript{4}\textsuperscript{+}-N concentrations, respectively, whereas NO\textsubscript{in} and NO are the inflow and outflow (NO\textsubscript{2}+NO\textsubscript{3}) concentrations, respectively.

Now, we consider three series CSTRs, to account for non-ideal flow mixing through the VFCW. Parameter values are considered to be different between CSTRs, in order to account for the fact that removal efficiencies and reactions rates are different between filter media layers. Also, different CSTR volumes are used in order to account for different media porosities. This is in accordance with [35], who found that NH\textsubscript{4}\textsuperscript{+}-N and NO\textsubscript{3}-N removal in VFCWs is different along the filter bed, and with [16], who used different parameter values between CSTRs, where each CSTR corresponded to one filter media layer. The subscript \(i\) = \{1,2,3\} indicates the \(i\)-th CSTR. The mass balance for the concentrations of NH\textsubscript{4}\textsuperscript{+} and (NO\textsubscript{2}+NO\textsubscript{3}) across the three reacting CSTRs gives

\[
\begin{align*}
\frac{dNH_1}{dt} & = \frac{Q}{V_1} (NH_{in} - NH_1) - r_{n1} + r_{ap1} \\
\frac{dNO_1}{dt} & = \frac{Q}{V_1} (NO_{in} - NO_1) + r_{d1} - r_{d1} \\
\frac{dNH_2}{dt} & = \frac{Q}{V_2} (NH_{in} - NH_2) - r_{n2} + r_{ap2} \\
\frac{dNO_2}{dt} & = \frac{Q}{V_2} (NO_{in} - NO_2) + r_{d2} - r_{d2} \\
\frac{dNH_3}{dt} & = \frac{Q}{V_3} (NH_{in} - NH_3) - r_{n3} + r_{ap3} \\
\frac{dNO_3}{dt} & = \frac{Q}{V_3} (NO_{in} - NO_3) + r_{d3} - r_{d3}
\end{align*}
\]

Where NH\textsubscript{1}, NH\textsubscript{2}, NH\textsubscript{3} are the NH\textsubscript{4}\textsuperscript{+}-N outflow concentrations in first, second and third CSTRs, respectively, whereas NO\textsubscript{1}, NO\textsubscript{2}, and NO\textsubscript{3} are the outflow concentration of (NO\textsubscript{2}+NO\textsubscript{3}) in first, second and third CSTRs, respectively. The general modeling structure is presented in Figure 1.

![Diagram](image-url)

**Figure 1.** General structure of the series CSTR modeling concerning NH\textsubscript{4}\textsuperscript{+}-N removal and (NO\textsubscript{2}+NO\textsubscript{3}) formation in VFCW
Remark 1. The mass balances for each CSTR correlate pollutant concentrations at CSTR outflow with concentrations at CSTR inflow. The joint mass balances correlate pollutant concentrations at last CSTR outflow (NH, NO) with concentrations at the first CSTR inflow (NH_{in}, NO_{in}), which correspond to VFCW outflow and VFCW inflow, respectively.

2.4. Model calibration and simulation

Model calibration used the dataset corresponding to the VFCW experiments reported by [32] and described above. The overall flowrate and the concentrations of NH_{4^+}, (NO_{2^-}+NO_{3^-}) at VFCW outflow and inflow are available, but concentrations at intermediate bed locations were not. Therefore, the model output of last CSTR is compared to the VFCW outflow, but comparison of first and intermediate CSTRs to intermediate bed measurements is not possible. In order to simulate the VFCW performance, the proposed model is calibrated by minimization of the sum of the squared errors between the model output and the experimental data, using the least squares criterion (see Appendix A). Matlab 2014 software (the MathWorks Inc., Natick, Mass.) with the 'fmincon' subroutine was used to perform minimization, with the ode113 command for integration of differential equations. The aforementioned staged behavior of ammonium nitrogen removal hampers accurate simulation; hence discrete parameter values are used. Reaction rates can be modeled by using coefficients that take on discrete values over time, in order to account for time-dependent changes [36]. Examples of this type of parameters for batch biological reaction are presented by [37, 38]. Thus, in this study an additional model calibration case is performed, which involves discrete values for the ammonium nitrogen model parameters.

The prediction capability of the model was assessed by the coefficient of determination (R^2) (see Appendix B). The coefficient of determination was evaluated for the effect of the following model features: number of reacting CSTRs from one to three; the occurrence of reaction in second and third CSTRs for the case that three CSTRs hold; the use of either equal or different values of reaction rate parameters between CSTRs; and the discretization of the reaction rate parameters as shown in Table 1.

In summary, the main features of simulation and parameter estimation are:
- Model calibration compared pollutant concentrations at the last CSTR with concentrations at VFCW outflow.
- All model coefficients were estimated by sum-of-squares minimization, and none of them was borrowed from other studies; the volumes of the three CSTR were different, and they were estimated by sum-of-squares minimization.
- The coefficient of determination was evaluated for the effect of several model features, including number of reacting CSTRs, reaction occurrence, equal/different model parameters between CSTRs, as shown in Table 1.
- An additional model calibration was performed which involved discretized values of the ammonium nitrogen model parameters.

Also, the capability of the used models for simulating VFCW outflow concentrations of NH_{4^+} and (NO_{2^-}+NO_{3^-}) was assessed by drawing the predicted concentrations as a function of observed VFCW outflow concentrations. The precision of the estimated parameters was assessed by the sensitivity analysis used by [39]. It comprised the effect of each estimate on the coefficient of determination, with only one estimate varied at a time, and a -50 to 50% variation range.

3. RESULTS AND DISCUSSION

3.1. Model fitting

The cases of two and three reacting CSTRs (models A1 and A2) achieved similar fitting quality, being higher than in the following cases: one reacting CSTR followed by a non-reacting CSTR (model B1); a single reacting CSTR (model A3); two reacting CSTRs, with model parameters being the same between CSTRs (model C1). These results are in agreement with the VFCW study of [16], where three reacting series CSTRs were used with model parameters being different between CSTRs.

The coefficient of determination for NH_{4^+} simulations is shown in Table 1. Taking the case of two reacting CSTRs (model A2) as the reference model (R^2 of 0.54), the following is concluded: i) two series CSTRs, with reaction only in the first one (model B1) yields a slight decrease of R^2, from 0.54 to 0.51; ii) two series reacting CSTRs, with the same model parameters excepting volume (model C1) yielded a significant decrease of R^2, from 0.54 to 0.33. Furthermore, the discrete estimation of nitrification coefficients (model A2b) resulted in an increase of the coefficient of determination from 0.54 to 0.94. Hence, the model comprising two series reacting CSTRs with different model parameters and discrete parameters is suitable. The observed VFCW outflow concentrations of NH_{4^+} and the A2 and A2b model simulations are shown in Figure 2 to Figure 5, confirming its correlation.
Table 1. Evaluation of the coefficient of determination for NH$_4^+$ simulation, as function of model

| Evaluated effects | Model                                                                 | Number of parameters | Coefficient of determination ($R^2$) for NH$_4^+$ simulation |
|-------------------|------------------------------------------------------------------------|----------------------|-------------------------------------------------------------|
| Number of reacting CSTRs. | Model A1: three reacting CSTRs hold. Model parameters are different between CSTRs. | 12                   | 0.549                                                       |
|                    | Model A2: two reacting CSTRs hold. Model parameters are different between CSTRs. | 8                    | 0.540                                                       |
|                    | Model A2b: two reacting CSTRs hold. Model parameters are different between CSTRs and vary with time. | 8                   | 0.94                                                        |
| Reaction occurrence for two CSTRs. | Model A3: one CSTR with reaction holds. Model parameters are different between CSTRs. | 4                    | 0.391                                                       |
|                    | Model B1: two CSTRs hold, the reaction occurs only in the first one. Model parameters are different between CSTRs. | 5                    | 0.512                                                       |
| Use of the same model parameters between CSTRs, except volume. | Model C1: two reacting CSTRs hold. The model parameters are the same between CSTRs. Model performance is compared with model A2. | 5                    | 0.331                                                       |
| Reaction occurrence for three CSTRs. | Model D1: three CSTRs hold; reaction only occurs in the first and second ones. Model parameters are different between CSTRs. Model performance is compared with model A1. | 9                    | 0.555                                                       |
|                    | Model D2: three CSTRs hold; reaction only occurs in the first one. Model parameters are different between CSTRs. Model performance is compared with model A1. | 6                    | 0.42                                                        |

Figure 2. VFCW outflow concentrations of NH$_4^+$ and A2 model simulations (Model A2 comprises two reacting CSTRs). Experimental values (symbols) and model calculations (solid line)

Figure 3. Comparison of NH$_4^+$ concentrations at VFCW outflow and A2 model simulations

Figure 4. VFCW outflow concentrations of NH$_4^+$ and A2b model simulations (A2b model comprises two reacting CSTRs and time-varying parameters)

Figure 5. Comparison of the NH$_4^+$ concentrations at VFCW outflow and A2b model simulations
Estimated parameters of models A2, A2b, and B1 for NH₄⁺ simulation are shown in Table 2. For model A2b, only parameter $k_{ap}$ exhibited time-varying behavior. The VFCW outflow concentrations of (NO₂⁻+NO₃⁻) and the A2 and A2b model simulations are shown in Figure 6 to Figure 8, confirming its correlation.

### Table 2. Model calibration results for NH₄⁺ simulation

| Model | Estimated parameters |
|-------|----------------------|
| A2. Monod expression is used for nitrification in first CSTR, whereas first-order kinetics is used in second CSTR, (R² of 0.54) | First CSTR (Monod expression is used for nitrification)  
$V_f$=679538 L  
$K_{nmx1}$=21000 mg/(Ld)  
$K_{ns1}$=1×10⁶ mg/L  
$K_{ap1}$=-0.295 mg/(Ld)  
Second CSTR (first-order expression is used for nitrification)  
$V_f$=150000 L  
$K_{nmx2}$=0.00722 d⁻¹  
$K_{ap2}$=1.89 mg/(Ld) |
| A2b. Monod expression is used for nitrification in first CSTR, whereas first order kinetics is used in second CSTR (parameters are time varying) (R² of 0.94) | First CSTR (Monod expression is used for nitrification):  
$V_f$=679538 L  
$K_{nmx1}$=21000 mg/(Ld)  
$K_{ns1}$=1×10⁶ mg/L  
$K_{ap1}$=4.83 mg/(Ld) for $t<33.8$ d; -1.79 mg/(Ld) for $t \in [33.8, 40.8]$ d, -0.245 mg/(Ld) for $t \geq 40.77$ d  
Second CSTR (first order expression is used for nitrification):  
$V_f$=150000 L  
$K_{n2}$=0.000341 mg/(Ld)  
$K_{ap2}$=-1.53 mg/(Ld) for $t<33.8$ d; -9.43 mg/(Ld) for $t \in [33.8, 40.8]$ d, -0.440 mg/(Ld) for $t \geq 40.77$ d |
| B1 (R² of 0.51) | First CSTR  
$V_f$=679538 L  
$K_{nmx1}$=21000 mg/(Ld)  
$K_{ns1}$=1×10⁶ mg/L  
$K_{ap1}$=0.735 mg/(Ld)  
Second CSTR  
$V_f$=150000 L |

Figure 6. VFCW outflow concentrations of (NO₂⁻+NO₃⁻) and A2 model simulations (Model A2 comprises two reacting CSTRs; Monod and first-order expressions are used for nitrification in first and second CSTRs, respectively). Experimental values (symbols) and model calculations (solid line)  
Figure 7. VFCW outflow concentrations of (NO₂⁻+NO₃⁻) and A2b model simulations (Model A2b comprises two reacting CSTRs and time-varying nitrification parameters; Monod and first-order kinetics are used for nitrification in first and second CSTR, respectively). Experimental values (symbols) and model calculations (solid line)
Figure 8. Comparison of the VFCW outflow concentrations of (NO\textsubscript{2}+NO\textsubscript{3}) and A2b model output

Estimated parameters of the denitrification rate for models A2, A2b and B1 are shown in Table 3. Using time-varying coefficients of \( r_n \) and \( r_ap \) yielded a slight decrease in the coefficient of determination for (NO\textsubscript{2}+NO\textsubscript{3}) from 0.79 to 0.70.

Table 3. Model calibration results for (NO\textsubscript{2}+NO\textsubscript{3}) formation

| Model and denitrification reaction rate | Estimated parameters for denitrification rate | Coefficient of determination \((R^2)\) for (NO\textsubscript{2}+NO\textsubscript{3}) simulation |
|----------------------------------------|-----------------------------------------------|--------------------------------------------------|
| A2 (two series reacting CSTRs; \( r_n=k_{dix} \) \((K_{dix1} \text{ and } K_{dix2} \text{ constrained to positive values})\) | First CSTR(Monod kinetics is used for nitrification) \(K_{dix1}=0.167 \text{ mg/(Ld)}\); Second CSTR(First order kinetics is used for nitrification) \(K_{dix2}=5.7 \times 10^{-6} \text{ mg/(Ld)}\) | 0.79 |
| A2b (involves time varying parameters); \( r_n=k_{dix} \) | First CSTR (Monod kinetics is used for nitrification) \(K_{dix1}=1.067 \text{ mg/(Ld)}\); Second CSTR (First order kinetics is used for nitrification) \(K_{dix2}=0.473 \text{ mg/(Ld)}\) | 0.70 |
| B1 (two series CSTRs, with reaction occurring in the first one); \( r_n=k_{dix} \) | First CSTR \(K_{dix1}=0.752 \text{ mg/(Ld)}\) | 0.67 |

3.2. Sensitivity of estimated parameters

Sensitivity analysis for model A2 parameters is shown in Figure 9 (refer Appendix C), consisting of the effect of parameters on the coefficient of determination related to NH\textsubscript{4} simulation. The order of parameters, from higher to lower effect on the coefficient of determination is \( k_{ns1}, k_{nmx1}, V_2, k_{ap2}, V_1, k_{nmx2}, k_{ap1} \). Hence, the estimated \( k_{ap1} \) has the lowest accuracy, whereas estimated \( k_{ns1} \) has the highest accuracy. Sensitivity analysis for model A2b parameters and BOD simulation is shown in Figure 10 (refer Appendix C). The order of parameters, from higher to lower effect on the coefficient of determination is \( k_{ns1}, k_{nmx1}, k_{ap1}, k_{ap2}, V_2, V_1, k_{n2} \). Hence, the estimated \( k_{ap2} \) has the lowest accuracy, whereas estimated \( k_{ns1} \) has the highest accuracy.

4. CONCLUSION

The coefficient of determination between VFCW outflow concentrations of NH\textsubscript{4} and (NO\textsubscript{2}+NO\textsubscript{3}) and simulations confirms the CSTR-like behavior of VFCWs stated by [8,18,13]. Also, it enabled the identification of the model features that lead to improved simulations. Indeed, it was found that the model comprising two reacting series CSTRs with parameter values that are different among CSTRs and take on discrete values over time is suitable. The cases of two and three reacting CSTRs have similar fitting quality and are more suitable than a single reacting CSTR. The higher fitting quality obtained for reaction parameters with different values between CSTRs in comparison to the case with the same values is in agreement with the modeling study performed by [16], where different parameter values between CSTRs were used because of the different features of filter media layers.
The lack of pollutant measurements at intermediate bed locations did not avoid using series CSTRs modeling, but posed uncertainty on the setting of the initial time value of pollutant concentrations. Nevertheless, setting this value as the VFCW outflow pollutant concentration at the initial time resulted in proper fitting quality. The estimated coefficients of the nitrification rate indicate that a first-order expression is more suitable than Monod expression. Indeed, the values of Monod half-saturation constant are significantly higher than \( \text{NH}_4^+ \) concentration. The discretization of the coefficients of the reaction rates of the ammonium nitrogen model yielded a significant improvement of fitting quality. This strategy enabled addressing the staged increase of ammonium nitrogen removal.

The parameter sensitivity analysis confirms that the estimates correspond to an optimum \( R^2 \) value, which is attained by using the sum of squares minimization and indicates that most model parameters have a significant effect on the \( R^2 \) value. To use the modeling results for sizing of VFCWs, further experiments with different hydraulic loadings must be conducted. Furthermore, the large scale VFCW must have the same features of the VFCW experiment (for instance bed porosity, vegetation, filter media depth, frequency of intermittent loading), and input data must include inflow rate, inflow concentrations of BOD and \( \text{NH}_4^+ \), and the corresponding target limit concentrations.

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**APPENDIX**

**Appendix A: Sum-of-squares minimization**

The sum-of-squares minimization procedure estimates model parameters by minimizing the differences between measured values and model simulations. The cost function to be minimized is the sum of the squared residuals (RSS) [40]. The cost function for simulation of $NH_4^+$ and $(NO_2^-+NO_3^-)$ is

$$RSS(\theta) = \sum_{i=1}^{N_S} \left( NO_i - NO_i^{\text{exp}} \right)^2$$

$$RSS(\theta) = \sum_{i=1}^{N_S} \left( NH_i - NH_i^{\text{exp}} \right)^2$$

Int J Elec & Comp Eng, Vol. 10, No. 1, February 2020 : 868 - 880
Where $\theta$ is the vector of model parameters; $N$ is the number of data points; $NH_4^{\text{exp}}$ is the observed concentration of NH$_4^+$ at VFCW outflow, $NH_4^{\text{cal}}$ is the NH$_4^+$ model simulation; $NO_3^{\text{exp}}$ is the (NO$_2$+NO$_3^-$) observed concentration at VFCW outflow, $NO_3^{\text{cal}}$ is the (NO$_2$+NO$_3^-$) model simulation.

Appendix B: Coefficient of determination
The definition of the coefficient of determination ($R^2$) provided by [38] is considered in this study. The expression of $R^2$ for the simulation of NH$_4^+$ and (NO$_2$+NO$_3^-$) at VFCW outflow is

$$R^2 = \frac{\sum_{i=1}^{N}(NH_4^{\text{exp}} - NH_4^{\text{cal}})^2}{\sum_{i=1}^{N}(NH_4^{\text{exp}} - \overline{NH})^2} \text{ for NH}_4^+ \text{ simulation}$$

$$R^2 = \frac{\sum_{i=1}^{N}(NO_3^{\text{exp}} - NO_3^{\text{cal}})^2}{\sum_{i=1}^{N}(NO_3^{\text{exp}} - \overline{NO}_3)^2} \text{ for (NO}_2\text{+NO}_3^-) \text{ simulation}$$

Where $N$ is the number of data points, $\overline{NH}$ is the mean of $NH_4^{\text{exp}}$, and $\overline{NO}_3$ is the mean of $NO_3^{\text{exp}}$. Further discussion of the coefficient of determination is given by [38].

Appendix C:

Figure 9. Sensitivity analysis for model A2 parameters and NH$_4^+$ simulation (Model A2 involves reaction occurring in the first and second CSTRs; Monod and first-order kinetics used for nitrification in first and second CSTRs, respectively)

Figure 10. Sensitivity analysis for model A2b parameters and NH$_4^+$ simulation (Model A2b involves reaction occurring in first and second CSTRs; nitrification parameters are time-varying; Monod and first-order kinetics are used for nitrification in first and second CSTR, respectively)
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