A Dynamic Model of Cadmium Removal in Free Water Surface Constructed Wetlands

Presented in 12th International Conference on Integrated Diffuse Pollution Management (IWA DIPCON 2008). Research Center for Environmental and Hazardous Substance Management (EHSM)

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Abstract

A mathematical model was developed for the cadmium removal process in the free water surface (FWS) constructed wetlands using a dynamic software program STELLA. Earlier, laboratory-scale experiments were conducted at the Suranaree University of Technology Campus in Northeastern Thailand to investigate the effect of high cadmium loading on the performance of FWS constructed wetlands under different environmental conditions. The predicted values of cadmium concentrations in effluents as well as in various components of the FWS constructed wetlands system, as simulated by the developed and calibrated model, had a good agreement with the experimental results. Thus, the mathematical model developed in this study could be used to explain the cadmium removal process in the FWS constructed wetlands. Hence, it could also be used to predict the fate of cadmium in the industrial effluents treated in FWS constructed wetlands system.

Keywords: Cadmium, Constructed wetlands, Free water surface, Mathematical modeling, STELLA program.

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Introduction

Mathematical modeling techniques can be used to aid in predicting the quality and sequence of relationships between interdependent components and processes in a system. A mathematical model is an idealization of a real situation, in which the most important components are identified and their interactions are described and used as a tool to solve problems (Jorgensen, 1986) and (Daigger and Grady, 1982). A model can be regarded as an assembly of concepts in the form of one or more mathematical equations that approximate the behavior of a natural system or phenomena. Simulation models address the formulation of a mathematical model that simulates a specific situation, with the development of mathematical relationships and solution through a structured and valid process (Treerattanaporn, 1999). Many experimental studies have been conducted on the use of constructed wetlands for heavy metals removal from the wastewater effluents (Polprasert, 1996; Mungur, 1997) and (Pimpan and Jindal, 2007). However, only little work has been reported on the mathematical modeling of the constructed wetland processes for wastewater treatment (Kayombo, 2004), and (Wang, 2000).

The present work was aimed at developing a dynamic mathematical model for describing the fate of cadmium in wastewater treated in a free water surface (FWS) constructed wetlands system. The developed model was validated with the results of the laboratory–scale experiments conducted earlier.

Methodology

A mathematical model was developed for the cadmium removal process in the FWS constructed wetlands using STELLA program. STELLA is a graphical programming language developed by HPS (Nirmalakhandan, 2002) specifically for system dynamics study. As a graphical programming language, it allows a modeler using the program’s graphical tools and functions to build dynamic models. Models can be configured to run independently with set inputs (either numerically or graphically specified) or in an interactive “flight simulator” mode. Model output can be observed via numerical readouts, tables, and graphs (Nirmalakhandan, 2002) (Keerativiriyaporn, 1998).
Laboratory-scale experiments were conducted earlier at the Suranaree University of Technology Campus in Northeastern Thailand to investigate the effect of high cadmium loading on the performance of FWS constructed wetlands under different environmental conditions. The experimental setup consisted of five laboratory-scale FWS constructed wetland units fed synthetic wastewater with CdCl$_2$•H$_2$O at concentrations of 5, 10, 25, and 50 mg/L. The four simultaneous experiments in the wetland units during the three runs (HRT to 5, 7, and 10 days) were designated as R11, R12, R13, R14, R15; R21, R22, R23, R24, R25; and R31, R32, R33, R34, R35, respectively (Pimpan and Jindal, 2007).

Wastewater samples were collected daily from the influent and effluent points and analyzed for soluble chemical oxygen demand (S-COD) concentration until quasi-steady-state conditions were reached. Subsequently, four parameters were analyzed in the influent and effluent streams including: pH, dissolved oxygen (DO), S-COD, and cadmium. The wetland was divided into four compartments along the reactor length: 1, 2, 3 and 4. Each compartment representing 1/4 of the reactor volume had Cd removal in three components of wetlands: plants, wastewater, and soil. Samples of wastewater and top soil at 5 sampling points (including inlet and outlet) along the reactor length of the wetland, and four samples of stems, one each from four compartments were taken. At the end of each run, soil samples were taken at the five locations along the lengths and at the depths of 0, 15, 30 and 45 cm from the top of the soil bed. The plants’ samples, both roots and stems, one each from the four compartments were also collected. All samples were analyzed for Cd concentration by flame atomic adsorption spectrometry (FAAS).

**Model development**

**Conceptual Model**

The conceptual model for cadmium removal in FWS constructed wetland is shown in Figure 1. The Cd present in the three components of wetland was expressed by three parameters; cadmium in plants (Cd$_{dp}$), cadmium in wastewater (Cd$_{ww}$), and cadmium in soil (Cd$_{s}$). Flow diagram of cadmium removal in FWS constructed wetland using STELLA simulation program is presented in Figure 2. For Cd$_{dp}$, Cd$_{ww}$ and Cd$_{s}$ parameters, the suffices 1, 2, 3, and 4 were used for the first, second, third, and fourth compartment, respectively.

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**Figure 1.** General conceptual model of cadmium removal in FWS constructed wetland.

**Figure 2.** Flow diagram of cadmium removal in FWS constructed wetland using STELLA simulation program.
Model Equations

A simplified Freundlich equation was chosen to describe the adsorption process in the FWS constructed wetland as shown below:

\[ C_{ds} = K_{Cd} + b \quad (1) \]

where \( K_{Cd} \) is Adsorption coefficient (slope) and \( b \) is a constant (intercept).

The results of regression analysis between Cd accumulation in soil (\( C_{ds} \)) and Cd concentration in wastewater (\( C_{Cdww} \)) for each compartment is shown as below:

\[ C_{ds}(mg) = \frac{V_{water}(L)^3.678(L/kg_{Cdww})}{4} + \frac{17.621(mg/kg_{Cdww})^4}{4} \quad (2) \]

The basic model equation for cadmium accumulation in soil was transformed from flow diagram as follows:

\[ \frac{3.678(L/kg_{Cdww})}{4} \frac{Ms(kgdw)}{V_{water}(L)^3.678(L/kg_{Cdww})} C_{ds}(mg) + \frac{17.621(mg/kg_{Cdww})^4}{4} \frac{Ms(kgdw)}{4} \quad (2) \]

The basic model equation for cadmium accumulation in soil was transformed from flow diagram as follows:

\[ CdS(t) = CdS(t - dt) + (Adsorption - Desorption) * dt \quad (3) \]

The plants uptake is described by the following equation (Kayombo, 2004):

\[ C_{dp} = f \times C_{Cdww} \times mp + c \quad (4) \]

where \( f \) is a multiplication factor (slope); \( mp \) is the dry weight of plants, kgdw and \( c \) is a constant (intercept).

The relationship between Cd uptake by plants (\( C_{dp} \)) and Cd concentration in wastewater (\( C_{Cdww} \)) for each compartment as shown below:

\[ Cd_{dp1-4}(mg) = \frac{140.801(L/kgdw)^2}{V_{water}(L)} (mp_{1-4}(kgdw))^2 C_{Cdww}(mg) + 346.813(mg/kg_{dp1-4}) mp_{1-4}(kgdw) \quad (5) \]

where \( p_{1-4}, f_{1-4}, \) and \( mp_{1-4} \) represent the values for the four compartments (1–4).

The basic equation of the model for cadmium removal by plants uptake was transformed from flow diagram as follows:

\[ C_{dp}(t) = C_{dp}(t - dt) + (Uptake1) * dt \quad (6) \]

The basic equation of the model for instantaneous cadmium concentration in wastewater at time “\( t \)” for each compartment was transformed from flow diagram as follows (mass balance):

\[ C_{Cdww}(t) = C_{Cdww}(t - dt) + (Inflow + Desorption - Uptake - Adsorption - Outflow) * dt \quad (7) \]

Results and Discussion

Model Calibration

The model was calibrated by using the equations for Cd accumulation in soil, and for plant uptake for three experiments (R14, R24, and R34). For desorption process, a multiplication factor of 0.05 was used in model calibration as shown below:

\[ Adsorption = (3.678 \times C_{Cdww} + 17.621 - C_{ds}) * 0.05 \]

The slope of the regression line for R14 (Figure 3) was close to 0.5 and correlation was close to 0.9, indicating a good agreement between predicted and observed values.
For plants uptake, a multiplication factor of 0.09 was used in calibration as shown below:

\[
\text{Uptake} = \left(\frac{(140.801 \text{ m}^2 \times \text{Cd}_{\text{ww}}) + 346.813 - \text{Cdp}}{64.6875 \text{ L}}\right) \times 0.09
\]

Figure 4, the slope of the regression line for R14 was close to 1, and the correlation was close 0.9, which supports a good model calibration.

![Simulated vs Measured CdP R14](image)

Figure 4. Correlation between simulated and measured cadmium removal by plants uptake for R14.

Model Validation

The model was validated using the data from the remaining nine experiments (R12, R13, R15, R22, R23, R25, R32, R33, and R35) of the first, second, and third run, respectively.

The model validation for Adsorption in soil by using the experimental data for four compartments in reactor 3 of the first run, experiment R13 (Cd = 10 mg/L), is illustrated in Figure 6 a–d.

![Simulated vs Measured CdP R14](image)

Figure 6. Correlation between simulated and measured cadmium accumulation in soil for R13.

The slope of the regression line between the measured and simulated values of cadmium accumulation in soil and removal by plants uptake for R13 (Figures 7 and 8) were close to 0.7 and 0.9. The correlations were both close to 0.9, which also supported a good model validation.
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Figure 6. a–d. Model validation for adsorption of Cd in the soil in four compartments during R13 (mg/d).

Figure 7. Correlation between simulated and measured cadmium accumulation in soil for R13.

Figure 8. Correlation between simulated and measured cadmium removal by plants uptake for R13.

Figure 9. Comparison of predicted and experimental values of outflow in model validation for R13 (mg/d).
The simulated values of cadmium mass fraction ranged between 0.43–38.3% in the effluents, 33.6–76.6% in the soil, 0.3–6.6% in other sink and 21.6–24.9% in plants uptake during three experimental run.

The simulated and measured average Cd removal efficiencies in FWS constructed wetland as shown in Figure 10 were in the range of 61.7–83.3 and 74.6–82.0% for HRT = 5 d, 63.2–94.2 and 87.2–91.0% HRT = 7 d, and 65.4–99.6 and 95.2–96.5% for HRT = 10 d.

The simulated and measured average Cd removal efficiencies were statistically compared for nine experiments selected for model validation (T test). The level of significance in the Levene’s Test for equality of variances was 0.089. Thus, the predicted and measured values of the Cd removal in FWS constructed wetlands were in good agreement.

Conclusions

A mathematical model for describing the cadmium removal process in the FWS constructed wetlands was developed using STELLA program. The simulated values of cadmium concentrations in effluents as well as in various components of the FWS constructed wetlands system had a good agreement with the experimental results.

The simulated and measured average Cd removal efficiencies for 9 experiments, used for model validation (ranging between 61.7–99.6% and 74.6–96.5%, respectively). The predicted and measured values of the Cd removal in FWS constructed wetlands were in good agreement. Therefore, the developed mathematical model in this study could be used to describe the cadmium removal process in the FWS constructed wetlands.

Acknowledgements

This study was supported by the funding from the Royal Golden Jubilee Ph.D. Scholarship Grant (RGJ-Ph.D.) of Thailand Research Fund (TRF), Thailand. The authors also acknowledge the assistance provided by the Suranaree University of Technology (SUT).

References


