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Modelling of nickel dynamics in vertical subsurface flow constructed wetlands using a System Thinking Environment

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Abstract: The application of modelling approaches for simulating and designing of constructed wetlands is still a challenge in environmental science. A mathematical model was developed in STELLA software to simulate Ni dynamics (adsorption, plant uptake and effluent concentrations) from synthetic wastewaters loaded with Ni 0.5 ppm and treated in vertical subsurface flow constructed wetlands vegetated with *Phragmites Karka* on gravel beds. Plant and water samples were collected, pre-treated in the laboratory, digested with diacid and their Ni concentrations were determined using atomic absorption spectrophotometer (AAS), after filtrating the samples on Whatman paper No. 42. A graphical model was developed in STELLA and the data recorded from the experiment were used to calibrate and validate the related mathematical model in the software. Results showed a good agreement between experimental and simulated data indicated by the Wilcoxon Signed Ranks Test p values > 0.05 for Ni adsorbed in gravel, uptake in plant and Ni effluent concentrations. The overall removal analysis showed the following distribution pattern: Experimental data (Total Removal Percentage (%): 84.2; adsorption percentage (%): 50.6; plant uptake percentage (%): 33.6). Simulated data (Total Removal Percentage (%): 83.5; adsorption percentage (%): 52.8; plant uptake percentage (%): 30.6). Thus the adsorption played a major role the removal of Ni from wastewater compare to plant uptake and the overall constructed wetland showed its high removal performance in eliminating Ni from wastewater.

Key words: Process-based models, STELLA software, Wilcoxon Signed Ranks Test, Model validation

1. INTRODUCTION

In recent decades, constructed wetland models were developed for predicting their behaviour over extended period of time in wastewater treatment processes. Available constructed wetland models are primarily of two types: black box types and process based models (Kumar and Zhao, 2011). Instead of developing relationship between input and output of constructed wetlands as considered in "black-box" approach modelling, process-based models show up the increased understanding of the processes involved in the pollutants transfer in constructed wetlands (Langergraber, 2007, Garcia *et al.,* 2010, Meyer *et al.,* 2015). Kumar and Zhao (2011) further stated that these models can provide insight into the "black-box" and give indulgent information which helps highly for the design purpose. Among the existing models, very few models (in numbers, not in quality) were developed for simulating pollutant dynamics in vertical subsurface flow constructed wetlands. Additionally, most of these models were developed for only assessing nutrient and organic pollutant removal in constructed wetlands. Thus very limited modelling efforts were devoted for the simulation of metal removal dynamics in vertical subsurface flow constructed wetlands. The purpose of this study is to develop a mathematical model in STELLA software to simulate Ni dynamics (adsorption, plant uptake and effluent concentrations) from synthetic wastewaters loaded with Ni 0.5 ppm and treated in vertical subsurface flow constructed wetlands vegetated with *Phragmites Karka* on gravel beds.

2. MATERIALS AND METHODS

In this study, STELLA software was used to simulate nickel removal from artificial wastewater.

STELLA is an object-oriented, graphical modelling environment developed by High Performance Systems, Inc. (HPS) (Bullen et al., 2011) and is specifically functional for highly dynamic and independent systems.

2.1 Experimental set up and data collection

The experimental setup consisted of vertical subsurface flow constructed wetlands (VSSF CW) in form of wetland microcosm (50 litres plastic container) at Indian Agricultural Research Institute, in New Delhi, India. Each wetland microcosms had a cylindrical shape, a diameter of 35 cm and a height equals to 50 cm. The wetland microcosms were filled with gravel (size ranging from 1 to 3 mm for fine gravel and from 5 mm to 25 mm for coarse gravel and a total weight of 60.1 kg per wetland) to a depth of 35 cm and planted with *Phragmites Karka*. These plant species had similar age and height at a spacing of 2-5 cm. The experiment was replicated thrice. To find the relative contribution of vegetation, the unvegetated wetland microcosm (containing only gravel) was also used for each treatment (this time without replication). These microcosms were irrigated with Ni, at one strength (0.5 ppm). The levels of concentrations (low) were designed to mimic their current concentration levels (low) found in sewage water. Solutions containing concentration levels of Ni at 0.5 ppm were prepared using salts of Ni $(NO_3)_2 \cdot 6H_2O$. The use of nitrates was justified by the fact that these ions do not form ion pair with metal ions. A total of 4 wetland microcosms were used for the whole experiment. Plant and wastewater samples were analysed in the laboratory to determine their Ni content according to standard procedures (digestion with diacid and Ni determination using atomic absorption spectrophotometer after filtration) (Houba et al., 1989).

2.2. Model development

For simulation, the data collected (experimental data on Ni adsorption, plant uptake and effluent) were used to perform linear models which the coefficients (Table 1) were applied as inputs in the STELLA graphical model (Figure 1) to calibrate the developed mathematical model and to produce simulated outputs. Figure 1 illustrates the components of the models (building blocks), connections and influences between stocks, flows and convertors.

The models were run repetitively by adjusting its parameters using trial and error until the simulated and experimental values showed good agreement.

3. RESULTS AND DISCUSSION

3.1 Determination of adsorption and plant uptake coefficients using linear models

3.1.1 Testing of normality of data

To ensure the normality of data trend before development of regression equations, the Shapiro-Wilk test (Razali and Wah, 2011) was performed using the data acquired from experiment. It was observed that the parameter W and p-value obtained from Shapiro-Wilk normality test were 0.957 and 0.0672, which were closed to one and greater than 0.05, respectively. These parameters were well within the adjudged range and corroborated that all datasets followed the normal distribution.

3.1.2 Plant Uptake and gravel adsorption coefficients for Ni in VSSF CWs

It was observed that the p values of different models were < 0.001, for the regression analysis performed (plant uptake and gravel adsorption). The coefficient of determination value (R^2) of the linear model was 0.91. Therefore, these high values of R^2, coupled with positive values of regression coefficients (RC) indicated that there existed a linear relationships between Ni uptake in plant and the Ni influent concentrations. The regression equations developed between the amount of Ni (mg/kg) adsorbed in gravel (predicted variable) and the Ni influent concentration (mg/L) (regressor) showed a good fit between these variables, indicated by $R^2 = 0.72$ for Ni 0.5 ppm.

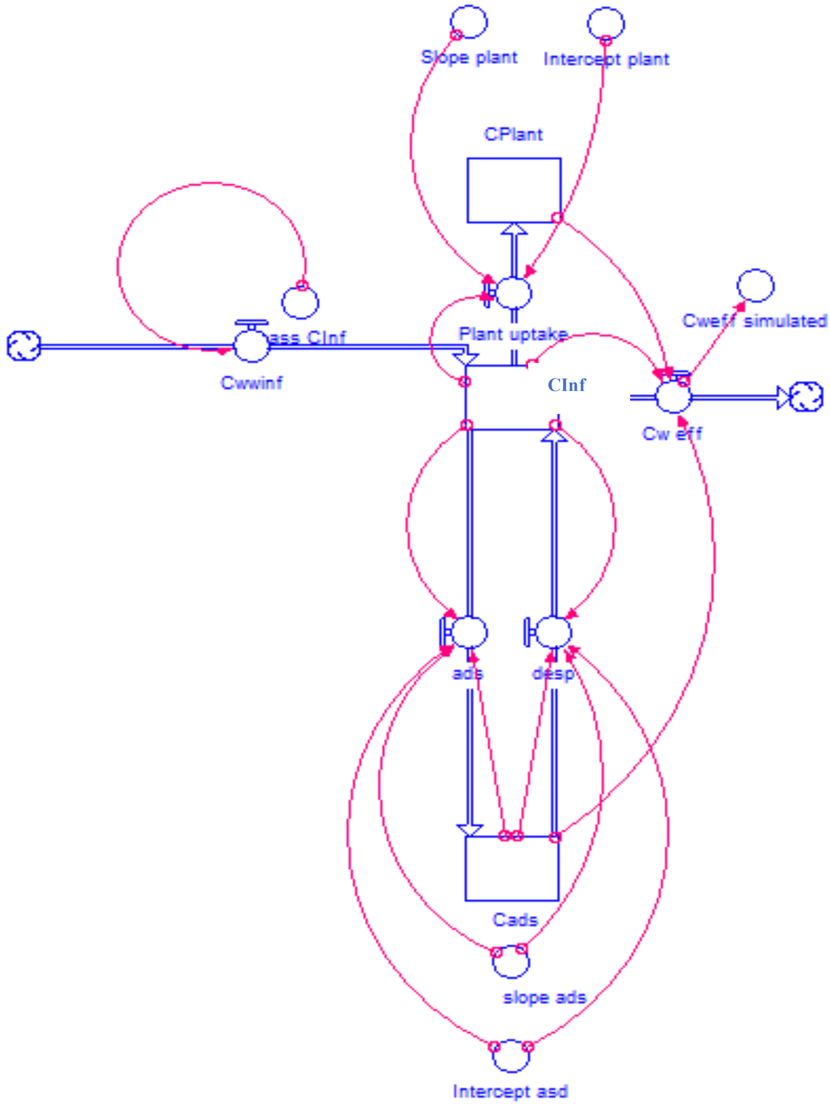

Figure 1. Graphical model of heavy metal dynamics in subsurface flow constructed wetland [ads = adsorption, desp = desorption, Cads = Ni concentration adsorbed on the substrate (mg), Cw effluent = mass (mg) of Ni in the effluent water, CInf = amount of Ni in the influent (mg); Cplant = mass of Ni uptake in the dry weight of plant tissues (mg)]

Table 1. Plant uptake and gravel adsorption coefficients and intercepts for Ni linear models

Ni (ppm)	Variables	Phragmites	Gravel adsorption
0.5	P value	5.92E-08	1.06E-05
	Intercept	0.003	0.10
	Coefficient	0.779 ***	0.69 ***
	R^2	0.913	0.72

3.2 Ni adsorption/desorption models on gravel

The results of model calibration for Ni accumulation in the gravel medium using the concentration of 0.8 mg/L of Ni, hence 19.58 mg of Ni in influent over a period of 15 months are presented below.

The adsorption and desorption equations performed in the Stella model is shown in the following equation:

$$\text{Adsorption} = \text{IF (Cads} < 1.30*\text{CInf} - 6.09) \text{ THEN } (1.30*\text{CInf} - (6.09+\text{ads})) \text{ ELSE } (0);\ R^2 = 0.79. \quad (1)$$

While the desorption equation is:

$$\text{Desorption} = \text{IF (Cads}>1.30*\text{CInf} -6.09)\text{THEN}((\text{Cads}-(-6.09)/1.30-\text{CInf})\text{ELSE}(0) \quad (2)$$

The instantaneous values of Ni adsorbed are given by a mathematical model as follows:

$$\text{Cads (t)} = \text{Cads (t - dt)} + (\text{adsorption - desorption}) * dt \quad (3)$$

$$\text{INITIAL Cads} = 0 \text{ mg} \quad (4)$$

3.3 Ni plant uptake model

The plant uptake equation performed in the Stella model is shown in the following equation:

$$\text{Plant\_uptake} = (0.067295*\text{CInf}+0.502241),\ R^2=0.72 \quad (5)$$

The values of Ni in effluent are given by the linear model computed in STELLA program.

$$\text{Cw\_effluent} = (\text{CInf-CPlant-Cads}) \quad (6)$$

3.4 Model validation and mass balance

A relative comparison between experimental and simulated data of Ni in gravel, plant, influent and effluent during experimental period are shown in Figure 2. The Ni from wastewater was accumulated in gravel by the adsorption process. A fraction of Ni adsorbed was released in pore water through the desorption process. Ni accumulated in plant (plant uptake) constituted an important part in the removal process, despite the fact that the decomposed plant mass could return in the reactor and release the metal previously removed. To minimize this impact in the system, the dead plants were regularly harvested.

The simulated and experimental Ni 0.5 ppm removal efficiencies in the VSSF CWs during the study are presented in Table 2 for relative comparison.

Table 2. Mass balance (%) comparing simulated and experimental data for Ni

Ni 0.5 ppm	Designation	Efficiency %	*Phragmites Karka*
	Simulated	RE	83.5
		Ads	52.8
		Plant	30.6
	Experimental	RE	84.2
		Ads	50.6
		Plant	33.6

The overall removal efficiencies (RE in %) of Ni in VSSF CWs were ranged between 83.5 % for simulated data and between 84.0 % for observed data, indicating a good performance of the system.

Amongst them, 52.8 % of Ni were adsorbed in gravel regarding simulated data while there was 50.6 % of adsorption for observed data. For plant uptake, simulated removal efficiencies were 30.6 % for simulated data while it was 33.6 % for experimental data. Therefore, it appeared that the adsorption efficiencies were higher than plant uptake in the overall system for the level of concentration Ni 0.5 ppm. Gravel played a major role in the removal of Ni 0.5 ppm in VSSF CWs, while plant species played secondary role.

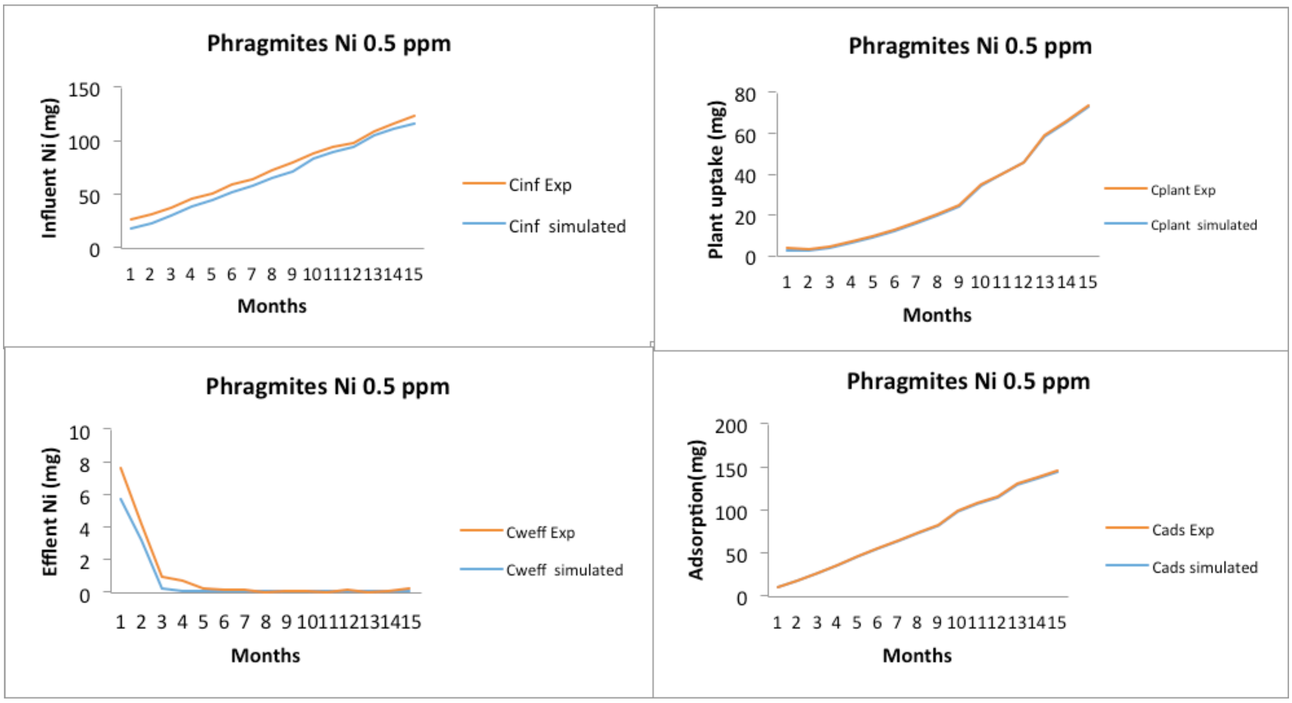

Figure 2. Comparison of simulated and experimental data for influent, adsorption, plant uptake and effluent

For the removal of Ni concentrations studied, a good agreement was observed between experimental and simulated data indicated by large values of Asymp Sig. (p values > 0.156) that were recorded from Wilcoxon Signed Ranks Tests. Therefore, there was no significant difference between experimental and simulated data. The validation of the model showed that there is no significant difference between experimental and simulated data (p value > 0.05) for adsorption, plant uptake, influent and effluent values of Ni studied. Additionally, the Pearson coefficient confirmed the good fit between simulated and experimental values: $R^2 > 0.7$ regardless of the component of the model studied. Similar results were obtained by Bullen et al. (2011) who simulated the removal of cadmium from wastewater in free water surface constructed wetlands. But, the substrate used in constructed wetlands was a soil material.

The mathematical model developed in this paper is a new facility to simulate the behaviour of metal in subsurface flow constructed wetland including, inflow and outflow, adsorption/desorption and plant uptake removal processes.

4. CONCLUSIONS

Constructed Wetlands in recent decades are pointed out by several authors as the effective alternative to conventional system for the treatment of agricultural, industrial and municipal wastewater. Numerous models have been developed to simulating and predicting the behaviour of CWs over extended period of time. These are categorized as black-box and process-based models. In black-box category the first order model is still widely used to design CWs but has numerous inadequacies to predict the outlet contaminant concentrations. Despite the fact that mechanistic models highlight the comprehension of internal processes involving in pollutant dynamics in CWs, is still unable to take in account all the processes and interactions that exist in CWs. Besides this more efforts should be devoted for modelling heavy metal dynamics in CWs and especially more modelling studies should be extended to SSF CWs and hybrid systems for improving their performances in effective wastewater treatment processes in a better way. The application of STELLA Software for developing a mathematical model (STELLA model) to simulate Ni dynamics in subsurface flow constructed showed a good fit (p value > 0.05) between experimental and simulated data (Pearson coefficient $R^2 > 0.70$). The model developed showed a very high performance in the removal of Ni from artificial wastewater, indicated by a removal efficiency of 83.0 %, in agreement with the real system which showed a removal efficiency (RE = 84.0 %). Hence, keeping in view the fact that most modelling approaches developed have concentrated only on hydrodynamics and nutrient cycling and very less efforts devoted for heavy metals dynamics, the developed mathematical model is a significant contribution that is useful to describe the Ni dynamics in different component of a vertical subsurface flow constructed wetland and to simulate and understand its behaviour over an extended period of time.

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