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Modelling heavy metals transformation in vertical flow constructed wetlands

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ABSTRACT

Constructed wetlands are dynamic ecosystems for which we generally have poor predictive capabilities of the succession relationships between the interdependent components and the processes. In this study, a dynamic simulation model that can evaluate the transport and fate of heavy metals in vertical flow constructed wetland systems was developed using a dynamic software program: Structural Thinking Experiential Learning Laboratory with Animation (STELLA) v9.0.2. The key heavy metals transformation processes considered in the study were adsorption and plant uptake; whilst the forcing functions considered were wastewater volume, temperature, heavy metals concentration, contact time, flow rate and adsorbent media. The model results indicate that up to 89%, 91% and 91% of Pb, Cr and Cd respectively, can be removed through adsorption process; whereas uptake by plants was 6%, 5.1% and 5.2% based on mass balance calculations. Sensitivity analysis also showed that the most sensitive areas in the model coincide with the adsorption parameter (the heterogeneity factor (n) and the Freundlich constant (Kf)). The results obtained indicates that the model can be used to simulate outflow heavy metal concentrations, and it can also be used to estimate the amount of heavy metal removed by individual processes in the system.

1. Introduction

Constructed wetland systems (CWs) have become a popular technical alternative worldwide for the treatment of various wastewaters. (Kadlec and Wallace, 2008). They are used not only to degrade organic substances and nutrients from wastewaters (Sun and Austin, 2007; Sun et al., 2005), but also to remove metals from several industrial wastewaters (Cheng et al., 2002; Zhao et al., 2009).

Unlike organic pollutants, heavy metals (HM) cannot be degraded through biological processes. Understanding the mechanism of HM removal has expanded concurrently with increased adoption and usage of treatment wetlands (Kosolapov et al., 2004). Marchand et al. (2010) indicated that there are four main processes of metals removal in CWs. These include adsorption to fine textured sediments and organic matter; precipitation as insoluble salts (mainly sulphides and oxyhydroxides); absorption and induced changes in biogeochemical cycles by plants and bacteria; and deposition of suspended solids due to low flow rates.

However, adsorption represents an important mechanism for removal of metals in CWs. Therefore, to ensure efficient HM removal, it is important to use substrates with high HM removal capacity and suitable physiochemical properties. A low-cost material that can enhance HM removal is ferric dewatered sludge (Mohammed et al., 2016). It is available worldwide and is mostly landfilled at huge costs since it is regarded as a waste with little known reuse value. However, the physicochemical properties of ferric dewatered sludge give it a highly reactive surface and a strong affinity for phosphorous and HM (Al-Tahmazi and Babatunde, 2016; Mohammed et al., 2016).

Plants also play an important role in CWs for the removal of pollutants. They take up nutrients and they are also able to adsorb and accumulate metals (Cheng et al., 2002). Moreover, *Phragmites australis*, known as common reed, is widely used in CWs for treatment

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of urban and industrial wastewaters containing metals (Bonanno and Lo Giudice, 2010).

The efficiency of CWs for wastewater treatment is often evaluated by a comparison between influent and effluent. However, this is a figurative black- box approach since there is no information on the biological and physicochemical processes occurring in the CWs. Modelling of HM removal in CWSs is important with regards to understanding the HM behaviour in the integrated treatment processes. Various modelling tools including FITOVERT, CW2D, PHWAT and CWM1 have been used to understand the processes in CWSs (Kumar and Zhao, 2011). However, all these models have been used to simulate the hydraulic properties or degradation of the pollutants. In this study, the fate of Pb, Cr and Cd in a vertical flow constructed wetland (VFCW) was investigated through the development of a mathematical model using the Structural Thinking Experiential Learning Laboratory with Animation (STELLA) v9.0.2 software. The key objectives were: (1) to develop a dynamic model for simulating adsorption, plant uptake and plant growth from the VFCW which uses ferric dewatered sludge as main substrate; (2) to calibrate the model using the available experimental data; and (3) to apply the model to simulate the fate of HM in the VFCW.

2. Materials and methods

2.1. Set-up of vertical flow constructed wetland system

A laboratory scale VFCW system was set up outdoor using perspex columns which were 100 mm in diameter and 1000 mm in height. Each column was filled with 22 ± 3 mm of round gravel to a depth of 150 mm from the bottom, which served as a drainage layer (see Fig. 1). Air-dried ferric dewatered sludge with a particle size of 1–3 mm was used as the primary media layer (350 mm), followed by 7 ± 2 mm washed gravel for a depth of 150 mm, giving an average porosity of 0.43. The ferric dewatered sludge consisted of Fe (193.85 mg g^{-1}); its detailed physicochemical properties have been published elsewhere (Mohammed et al., 2016). In brief, the specific surface area was 132 m^2 g^{-1} and the iron oxalate content was 162 mg g^{-1} which confirmed the amorphous nature of the ferric dewatered sludge. Each column experienced cyclic wet and dry period with the artificial landfill leachate. These periods were generated by peristaltic pumps. Each wet cycle was completed in three hours and fifty minutes, giving each column 3 h and 50 min of wastewater-media contact per cycle. Common reed, *Phragmites australis*, was planted on the top layer of the stage.

Experiments were carried out in two periods, namely Period 1 and 2. The initial purpose of the experiments was to investigate the removal rate of HM from landfill leachate. However, significant removal was not found in the performances of individual CW stages during Period 1. Accordingly, alterations to the experiment were made in Period 2. Only one CW stage (referred to as 'A' in Fig. 1) was used in Period 1, whereas in Period 2 two CW stages (A + B), which were arranged in parallel, were used.

To simulate young landfill leachate, $CdSO_4{\cdot}H_2O$ salt, $Cr(SO_4)_2{\cdot}12H_2O$ salt and $PbCl_2$ salt, respectively for cadmium (Cd), chromium (Cr) and lead (Pb) were used to synthesise artificial landfill leachate in the laboratory. The initial concentrations of HM were (230 μg L^{-1}–630 μg L^{-1}), (240 μg L^{-1}–650 μg L^{-1}) and (240 μg L^{-1}–810 μg L^{-1}) for Pb, Cr and Cd, respectively.

2.2. Batch analysis

Batch experiments were used to investigate the kinetics of the adsorption process and heavy metal adsorption by the ferric dewatered sludge. To investigate the effects of sludge dosage and equilibration time, different masses of the sludge sample (0.1, 0.5 and 1.0 g) were equilibrated with 100 ml each of heavy metal solutions (0.5 mg L^{-1} for Pb, 1 mg L^{-1} for Cr and 5 mg L^{-1} for Cd), which were contained in 250 ml polyethylene bottles for 1–96 h using a rotary shaker. At specified time points, the mixture was withdrawn, filtered and analysed for each heavy metal using an Optima 210 DV ICP OES, and the uptake of those metals was determined using Eq. (1).

$$q_e = \frac{(c_o - c_e)}{m} v \quad (1)$$

Where, C_o and C_e (both in mg L^{-1}) are the initial (t = 0) and final heavy metals concentrations at equilibrium (q_e), respectively; q_e is the mass of heavy metal adsorbed on the adsorbent (sludge) at equilibrium (mg g^{-1}); v is the volume of the solution (L); and m is the mass of ferric dewatered sludge used (g).

2.3. Description of the STELLA model

According to Jay Forrester's systems dynamics language (Forrester, 1997), STELLA is a software for graphic and dynamic simulation. The use of iconographic modelling techniques makes the model a flexible simulation tool with an easy user interface for making change and calibrate. The user can immediately view the effects of the changes, which reduces the time required to develop the model (Jørgensen and Fath, 2011).

Conceptual diagrams of the adsorption processes, plant uptake and plant growth for Pb, Cr and Cd are shown in the STELLA diagrams below (Figs. 2–4). The major mechanisms for HM dynamics in CWs considered in this study were adsorption and plant uptake. The removal of heavy metals in CWs is widely attributed to adsorption and plant uptake (Kosolapov et al., 2004; Marchand et al., 2010). In addition, the system was operated to be fully saturated for 3 h and 50 min and unsaturated for 10 min. Such high HRT allow for higher contact between wastewater and HH sludge and enhance adsorption process (Stefanakis et al., 2014). The developed models have five state variables including dissolved HM (DISHM), plant HM (PLHM), which means the heavy metals that are available for plant uptake and those that are present as soluble components in the soil solution, biomass (PLBHM) which means a certain heavy metals require for plant growth and upkeep, detritus HM (DETHM) is the HM bond to the organic material with a wide range of biodegradable and adsorption (ADSHM), all expressed in mg of HM per day. Adsorbent HM concentration and contact time are considered to be major forcing functions in the model, since the adsorption process is highly related to the retention capacity of substrates over time (Marchand et al., 2010). The state variables, processes, parameters and auxiliary variables used in the model are shown in Table 1. Detailed descriptions of each mechanism responsible for removal and HM dynamics are presented below.

2.3.1. Process equations

The adsorption process was described by the equilibrium between HM in water and HM in the adsorbent. Unlike other processes, this process is fast and reaches equilibrium in hours, based on the batch results (Fig. 9). Therefore, 0.02 delta time (DT) was selected as the time step. DT refers to the time interval between calculations in STELLA software. In addition, the adsorption process was multiplied by a factor (*Fa*) of 2.5, 5 and 3, respectively for Pb, Cr and Cd for column A, and 3.5, 14 and 5, respectively for Pb, Cr and Cd for column B. These factors were based on experimental results, and it is expected that they will vary according to the type of media, HM concentrations, type of pollutant, type of CWs, etc.

Adsorption process can be describe using equation 2, where, *Fa* is a factor, *DISHM* is dissolve HM (either Pb, Cr or Cd) (mg day^{-1}), P_e