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Article:

1 **Modelling heavy metals transformation in vertical flow constructed wetlands**

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10 Abstract

11 Constructed wetlands are dynamic ecosystems for which we generally have poor predictive

12 capabilities of the succession relationships between the interdependent components and the

13 processes. In this study a dynamic simulation model that can evaluate the transport and fate

14 of heavy metals in vertical flow constructed wetland systems was developed using a dynam-

15 ic software program: Structural Thinking Experiential Learning Laboratory with Animation

16 (STELLA) v9.0.2. The key heavy metals transformation processes considered in the study

17 were adsorption and plant uptake; whilst the forcing functions considered were wastewater

18 volume, temperature, heavy metals concentration, contact time, flow rate and adsorbent

19 media. The model results indicate that up to 89%, 91% and 91% of Pb, Cr and Cd respec-

20 tively, can be removed through adsorption process; whereas uptake by plants was 6%, 5.1%

21 and 5.2% based on mass balance calculations. Sensitivity analysis also showed that the

22 most sensitive areas in the model coincide with the adsorption parameter (the heterogeneity

23 factor (n) and the Freundlich constant (K_f)). The results obtained indicates that the model

24 can be used to simulate outflow heavy metal concentrations, and it can also be used to es-

25 timate the amount of heavy metal removed by individual processes in the system.

26 **Keywords:** Constructed wetland, ferric sludge, heavy metals, STELLA.

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

53 The efficiency of CWs for wastewater treatment is often evaluated by a comparison between

54 influent and effluent. However, this is a figurative black- box approach since there is no in-

55 formation on the biological and physicochemical processes occurring in the CWs Modelling

56 of HM removal in CWSs is important with regards to understanding the HM behaviour in the

57 integrated treatment processes. Various modelling tools including FITOVERT, CW2D,

58 PHWAT and CWM1 have been used to understand the processes in CWSs (Kumar and

59 Zhao, 2011). However, all these models have been used to simulate the hydraulic properties

60 or degradation of pollutant. In this study the fate of Pb, Cr and Cd in a vertical flow con-

61 structed wetland (VFCW) was investigated through the development of a mathematical

62 model using the Structural Thinking Experiential Learning Laboratory with Animation (STEL-

63 LA) v9.0.2 software. The key objectives were: (1) to develop a dynamic model for simulating

64 adsorption, plant uptake and plant growth from the VFCW which uses ferric dewatered

65 sludge as main substrate; (2) to calibrate the model using the available experimental data;

66 and (3) to apply the model to simulate the fate of HM in the VFCW.

67 2. Materials and methods

68 2.1. Set-up of vertical flow constructed wetland system

69 A laboratory scale VFCW system was set up outdoor using perspex columns that were 100

70 mm in diameter and 1000 mm in height. Each column was filled with 22±3 mm of round

71 gravel to a depth of 150 mm from the bottom, which served as a drainage layer (see Figure

72 1). Air-dried ferric dewatered sludge with a particle size of 1-3 mm was used as the primary

73 media layer (350 mm), followed by 7±2 mm washed gravel for a depth of 150 mm, giving an

74 average porosity of 0.43. The ferric dewatered sludge consisted of Fe (193.85 mg g^{-1}); its

75 detailed physicochemical properties have been published elsewhere (Mohammed et al.,

76 2016). In brief, the specific surface area was 132 m^2 g^{-1} and the iron oxalate content was

77 162 mg g^{-1} which confirmed the amorphous nature of the ferric dewatered sludge. Each col-

78 umn experienced cyclic wet and dry period with the artificial landfill leachate. These periods

79 were generated by peristaltic pumps. Each wet cycle was completed in three hours and fifty

80   minutes, giving each column 3:50 h of wastewater-media contact per cycle. Common reed,

81   Phragmites australis, was planted on the top layer of the stage.

82   Experiments were carried out in two periods, namely Period 1 and 2. The initial purpose of

83   the experiments was to investigate the removal rate of HM from landfill leachate. However,

84   significant removal was not found in the performances of individual CW stages during Period

85   1. Accordingly, alterations to the experiment were made in Period 2. Only one CW stage (re-

86   ferred to as 'A' in Figure 1) was used in Period 1, whereas in Period 2 two CW stages (A +

87   B), which were arranged in parallel, were used.

88   To simulate young landfill leachate, $CdSO_4.H_2O$ salt, $Cr(SO_4)_2.12H_2O$ salt and $PbCl_2$ salt,

89   respectively for cadmium (Cd), chromium (Cr) and lead (Pb) were used to synthesise artifi-

90   cial landfill leachate in the laboratory. The initial concentrations of HM were (230 µg L^{-1}- 630

91   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.

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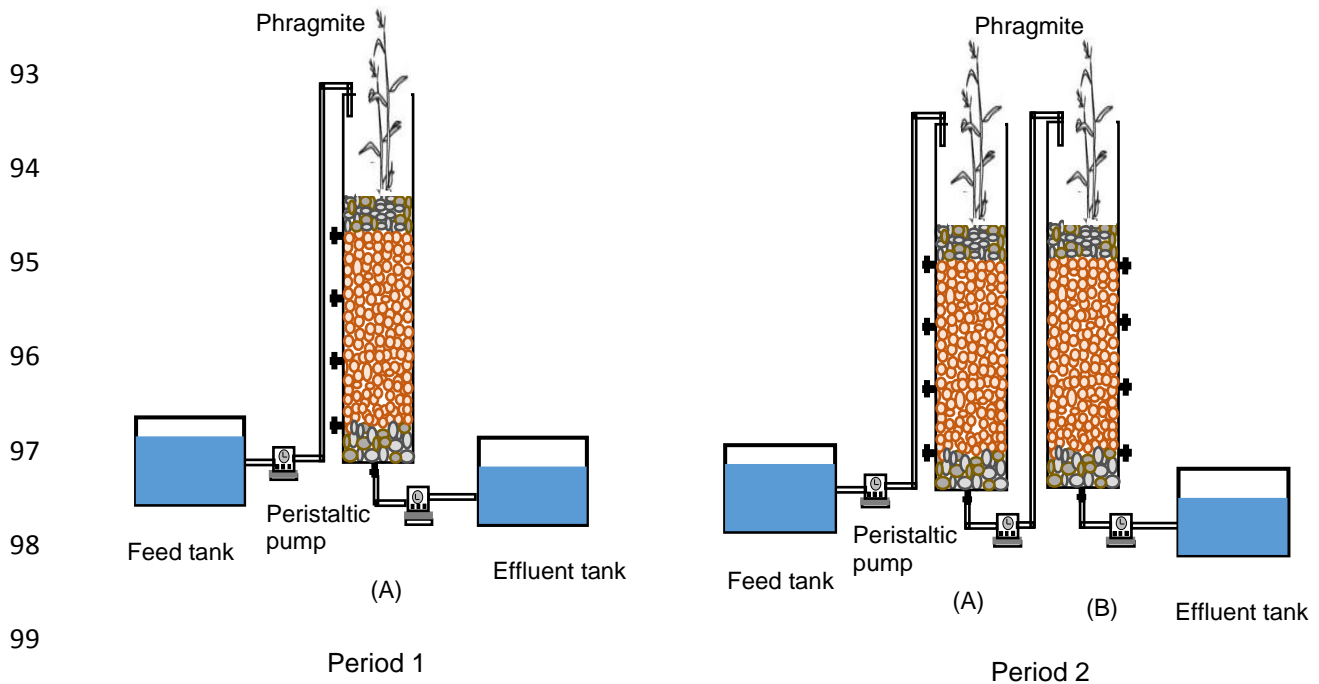
101   Figure 1. Schematic description of the constructed wetland system in Period 1 (left) and Period 2

102   (right).

103

104   2.2. Batch analysis

105   Batch experiments were used to investigate the kinetic of the adsorption process and

106   examine the kinetics of heavy metal adsorption by the ferric dewatered sludge. To

107   investigate the effects of sludge dosage and equilibration time, different masses of the

108   sludge sample (0.1, 0.5 and 1.0 g) were equilibrated with 100 ml each of heavy metal

109   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

110   250 ml polyethylene bottles for 1–96 h using a rotary shaker. At specified time points, the

111   mixture was withdrawn, filtered and analysed for each heavy metal using an Optima 210 DV

112   ICP OES, and the uptake of those metals was determined using Eq. (1).

113

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

115

116   Here, C_o and C_e (both in mg L^{-1}) are the initial (t=0) and final heavy metals concentrations at

117   equilibrium (q_e), respectively; q_e is the mass of heavy metal adsorbed on the adsorbent

118   (sludge) at equilibrium (mg g^{-1}); v is the volume of the solution (L); and m is the mass of

119   ferric dewatered sludge used (g).

120   2.3. Description of the STELLA model

121   According to Jay Forrester's systems dynamics language, STELLA is a software for graphic

122   and dynamic simulation. The use of iconographic modelling techniques makes the model a

123   flexible simulation tool with an easy user interface for making change and calibrate. The user

124   can immediately view the effects of the changes, which reduces the time required to develop

125   the model (Jørgensen and Fath, 2011).

126   Conceptual diagrams of the adsorption processes, plant uptake and plant growth for Pb, Cr

127   and Cd are shown in the STELLA diagrams below (Figures 2-4). The major mechanisms for

128   HM dynamics in CWS considered in this study were adsorption and plant uptake. The

129   removal of heavy metals in CWs is widely attributed to adsorption and plant uptake

130   (Kosolapov et al., 2004; Marchand et al., 2010). The developed models have five state

131   variables including dissolved HM (DISHM), plant HM (PLHM), which means the heavy

132   metals that are available for plant uptake are those that are present as soluble components

133   in the soil solution or those that are easily solubilized by root exudates, Although plants

134   require certain heavy metals for their growth and upkeep so that the third state is plant

135   biomass (PLBHM), detritus HM (DETHM) and adsorption (ADSHM), all expressed in mg of

136   HM per day. Adsorbent HM concentration and contact time are considered to be major

137   forcing functions in the model, since the adsorption process is highly related to the retention

138   capacity of substrates over time (Marchand et al., 2010). The state variables, processes,

139   parameters and auxiliary variables used in the model are shown in Table 1. Detailed

140   descriptions of each mechanism responsible for removal and HM dynamics are presented

141   below.

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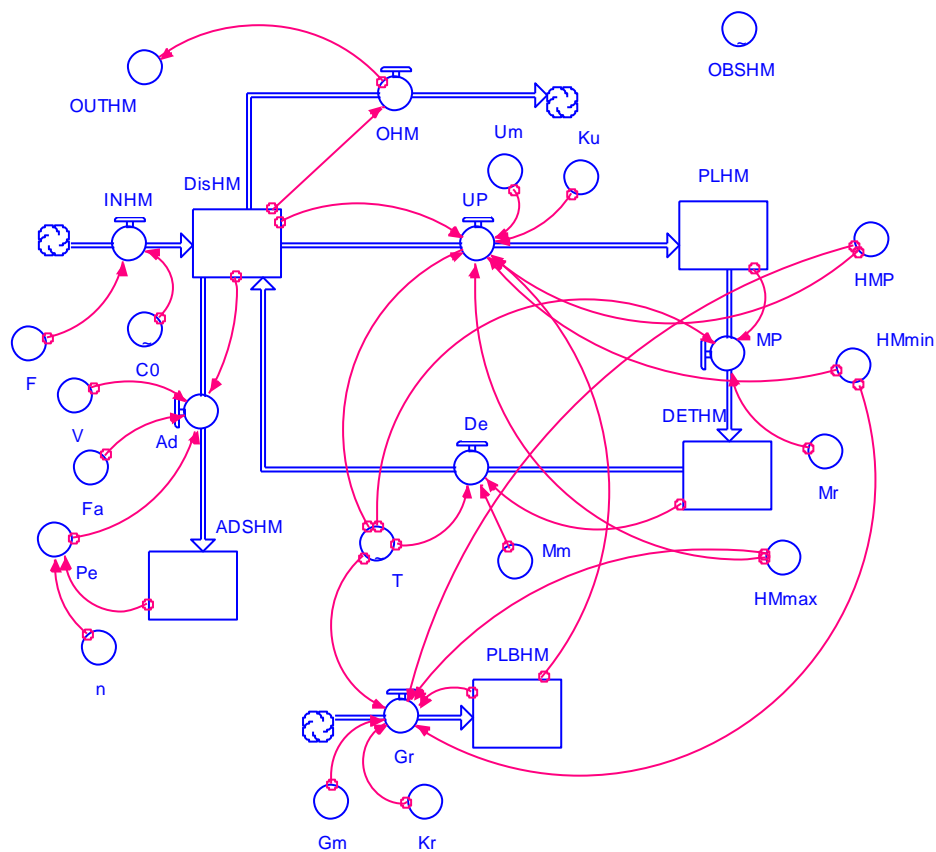
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144   Figure 2. A STELLA diagram of the HM model.

145

146   2.3.1. Process equations

147   The adsorption process was described by the equilibrium between HM in water and HM in

148   the adsorbent. Unlike other processes, this process is fast and reaches equilibrium in hours,

149   based on the batch results (Figure 9). Therefore, 0.02 delta time (DT) was selected as the

150   time step. DT refers to the time interval between calculations in STELLA software. In addi-

151   tion, the adsorption process was multiplied by a factor (Fa) of 2.5, 5 and 3, respectively for

152   Pb, Cr and Cd for column A, and 3.5, 14 and 5, respectively for Pb, Cr and Cd for column B.

153   These factors were based on experimental results, and it is expected that they will vary ac-

154   cording to the type of media, HM concentrations, type of pollutant, type of CWs, etc.

155   Adsorption process can be describe using equation 2, where, Fa is a factor, DISHM is

156   dissolve HM (either Pb, Cr or Cd) (mg day^{-1}), P_e is the equilibrium concentration (mg L^{-1} day^{-1}

157    $^{-1}$) and V is the volume of wastewater (L).

158

159    $$Ad = Fa(DISHM - P_e \times V)\text{...(2)}$$

160

161   P_e can be calculated by using equation 3, where ADSHM is adsorption of HM (either Pb, Cr

162   or Cd) (mg day^{-1}), T_A is the total amount of adsorbent (g), K_F is the Freundlich constant (L g^{-1}

163    $^{-1}$) and n is the heterogeneity factor.

164    $$P_e = \left(\frac{ADSHM}{T_A \times K_F}\right)^n \text{...(3)}$$

165

166   Mohammed et al. (2016) found that the Freundlich adsorption model was well fit to describe

167   the adsorption behaviour of Pb, Cr and Cd, with correlation coefficients of 0.97, 0.98 and

168   0.98 for Pb, Cr and Cd, respectively.

169   The growth of the plant, phragmites australis depends on the amount of HM in the plant and

170   can be described as a function of maximum growth rate at the optimum temperature.

171 Furthermore, the plant's growth can be expressed by Michaelis-Menton equation of

172 dissolved HM. The following equation was used to describe plant growth:

173

174
$$Gr = \frac{G_m \times PLB \times (HM_p - HM_{min}) \times 1.05^{(T-20)}}{K_r \times (HM_{max} - HM_{min})} \dots (4)$$

175

176 Here, G_m and K_r are maximum HM growth rate of the plant and the plant's growth rate

177 (Michaelis-Menton half saturated constant for growth); PLB is plant biomass; HM_P, HM_{min}

178 and HM_{max} are heavy metal in the plant, minimum heavy metal in the plant and maximum

179 heavy metal in the plant, respectively; and T is temperature. Plant uptake (phragmites

180 australis) is defined as a function of maximum uptake rate at the optimum temperature as

181 explained in equation 5, where U_m and K_u are the maximum uptake rates of plants and the

182 uptake rate of HM (Michaelis-Menton half saturated constant for uptake), respectively.

183

184
$$Up = \frac{U_{max} \times PLB \times (HM_{max} - HM_p) \times DISHM \times 1.05^{(T-20)}}{(DISHM - K_u) \times (HM_{max} - HM_{min})} \dots (5)$$

185

186 The first order reaction with Arrhenius function of temperature was used to express the plant

187 mortality and the detritus and as shown below.

188

189
$$MHM = PLHM \times M_r \times 1.07^{(T-20)} \dots (6)$$

190

191
$$De = DETHM \times M_m \times 1.07^{(T-20)} \dots (7)$$

192

193
$$KT = K_{20}\theta^{(T-20)} \dots (8)$$

194

195 Here, M_r and M_m are the mortality rate and maximum HM mineralization, respectively; KT is

196 the removal rate constant at T°C; K_{20} is the removal rate constant at 20°C; θ is

197   dimensionless; and T is the water temperature (∘C). The value of θ is 1.05 for plant growth

198   and plant uptake, whereas the plant's mortality decomposition is more sensitive to

199   temperature changes. Therefore, the θ value ranges from 1.07 to 1.08 (Kumar et al., 2011).

200   2.4. Calibration and sensitivity analysis

201   Before applying the resulting STELLA model to estimate the removal of heavy metals, the

202   model was calibrated and validated using a standard trial and error procedure. In general,

203   model calibration is a process adjusting the selected parameter values to obtain the best fit

204   between the observed data and simulated results. In practical modelling, sensitivity analysis

205   is carried out to aid in model calibration. This is done by changing the parameters and

206   observing the corresponding response on the selected parameter. Thus, the sensitivity (S) of

207   a parameter (P) is defined as follows:

208    $$S = \frac{\delta X / X}{\delta P / P}$$ ....(9)

209

210   Here, X is the model output. The higher the value of S, the more important the parameter

211   (Jørgensen and Fath, 2011). The relative change in the parameter is chosen based on

212   experimental knowledge as to the certainty of the parameters.

213   Table 1. Summary of the state variables, processes, parameters and their associated units in the model development for Pb, Cr and Cd.

Symbol	Description	Value			Unit	Source
State variables						
ADSHM	Amount of HM adsorbed in ferric dewatered sludge	-			mg HM day^{-1}	Calculated
DISHM	Dissolved amount of HM in ferric dewatered sludge	-			mg HM day^{-1}	Observed data
PLHM	Amount of HM found in plants	-			mg HM day^{-1}	Estimated
PLBHM	Amount of HM found in plants biomass	-			mg HM day^{-1}	Estimated
DETHM	Amount of HM found in detritus and used by bacteria	-			mg HM day^{-1}	Estimated
Processes						
Gr	HM requirement for growth	Eq.(4)			mg HM day^{-1}	-
Up	HM through plants	Eq.(5)			mg HM day^{-1}	-
Mp	Mortality of plant	Eq.(6)			mg HM day^{-1}	-
De	Decomposition of detritus	Eq.(7)			mg HM day^{-1}	-
Ad	HM adsorption	Eq.(2)			mg HM day^{-1}	-
Parameters		Pb	Cr	Cd		
HMmax	Maximum HM in plants	0.11	1	1.5	g (100g)$^{-1}$	Estímated
HMmin	Minimum HM in plants	0.001	0.195	0.016	g (100g)$^{-1}$	Estímated
Um	Maximum uptake of HM from plants	0.26	0.114	0.09	mg HM (L day)$^{-1}$	Calculated
Ku	Michaelis Menton for uptake	5.24	2.18	2	day^{-1}	Calculated
Mm	Maximum mineralization	0.2	0.2	0.2	day^{-1}	(Kumar et al., 2011)
Pe	HM equilibrium concentration				mgHM (L day)$^{-1}$	Calculated

Symbol	Description				Unit	Source
HMp	HM in plant	-	-	-	$mg\ mg^{-1}$	Calculated
		0.000024	0.00052	0.00002		Kumar et al.,
Mr	Mortality rate				$mg\ HM\ (L\ day)^{-1}$	2011)
		0.001	0.001	0.001		Calculated
Gm	Maximum growth of plant				$mg\ day^{-1}$	Calculated
Kr	Michaelis Menton plant growth rate	5.8	4.3	2	$mg\ HM\ (L\ day)^{-1}$	
		3.8	2.6	0.45		
Others						
INHM	Inflow of HM	TF			$mgHM\ day^{-1}$	Observed data
C_0	HM concentration of inflow	TF			$mgHM\ L^{-1}$	Observed data
T	Temperature requirement of plant growth	TF			$^\circ C$	Observed data
V	Volume of wastewater	12			L	Experiment
F	Flow rate of wastewater into the CW	12			$L\ day^{-1}$	Experiment
TA	Amount of adsorbent	2500			g	Calculated

214   TF is a Table function which is incorporated into the model.

215   3. Result and discussion

216   3.1. Simulation of heavy metals using STELLA software

217   Experiments were carried out for two periods using column A (215 days) for Period 1 and

218   columns A and B (185 days) for Period 2. A comparison of the measured and modelled data

219   was undertaken using Period 1 for calibration and Period 2 for validation. During the

220   calibration, the input parameters were obtained from experimental measurements,

221   theoretical calculations or existing literature (Table 1). The model was calibrated by trial and

222   error adjustment of the key parameters (within a reasonable range) until predictions under

223   similar conditions had good agreement with the observed data. The measured HM

224   concentrations ranged from 54 µg L^{-1}- 264 µg L^{-1}, 21 µg L^{-1}- 190 µg L^{-1} and 87 µg L^{-1}- 342 µg

225   L^{-1}, respectively, for Pb, Cr and Cd. Whereas the simulation ranged from 92 µg L^{-1}- 255 µg L^{-1}

226    $^{-1}$, 38 µg L^{-1}- 262 µg L^{-1} and 80 µg L^{-1}-324 µg L^{-1}, respectively, for Pb, Cr and Cd during the

227   calibration period. The maximum value of the measured effluent concentration (OBS) for all

228   of the HM was very close to the value simulated by the STELLA model. However, the

229   predicted data were slightly higher than the measured data for all of the HM, with the

230   exception of a few data points. In addition, the model did not simulate very low values for all

231   of the HM. Figure 4 shows the entire trend of model calibration and validation for column A.

232   The mean percent error (MPE = (OBS - OUT)/OBS × 100) equals 38%, 33% and 30%,

233   respectively, for Pb, Cr and Cd during the calibration period, and 15%, 20% and 10%,

234   respectively, for Pb, Cr and Cd during the validation period. It is worth noting that the

235   validated data for the HM was quite close to the observed data, despite the fact that the

236   simulation data was higher than the observation data for the period of 320- 400 days (during

237   validation between 105 and 185 days in period 2) in the case of Cr. This slight fluctuation in

238   the model simulation and the experimental data could be due to experimental error or

239   accumulation of biomass within the CWs (growth of microorganism). This could also be

240   attributed to the fact that the plants were not harvested during the experimental period. The

241   uptake of HM by plant is a step function during the growing season and zero after harvest

242   until the next growing season start (Jørgensen and Fath, 2011). However, the contribution of

243   plant harvesting is a small percent to the total HM removal in CWs, so that it is ignore in this

244   study (Cheng et al., 2002; Kosolapov et al., 2004; Marchand et al., 2010).

245   . Another possible reason may be that apart from the adsorption process, the HM in CW can

246   be removed by other processes, such as precipitation, oxidation, ion exchange and redux

247   reaction (Galletti et al., 2010). However, the system was operated to be fully saturated for

248   3:50 hours and unsaturated for 10 minute and due to a limitation of DO diffusion within HH

249   sludge (Wang et al., 2008), there is aerobic and anaerobic condition along the height of the

250   column as shown in figure (3). Therefore, the co-precipitation of HM with Fe oxide is very

251   dependent on DO variations so that the binding of metals with Fe oxide cannot be a long-

252   term removal mechanism, and then metals may be released back to the system. Moreover,

253   Fe oxide high affinity to metals that have similar size of Fe such as Cd, however the co-

254   precipitate is limited when there is sufficient amount of SO_4 which reducing the potential of

255   metal removal (Marchand et al., 2010). In addition, under anaerobic condition and because

256   of there is no sufficient carbon source required by sulphate- reducing bacteria to sulphides,

257   precipitation metals as metal sulphide cannot occur (Stefanakis et al., 2014).
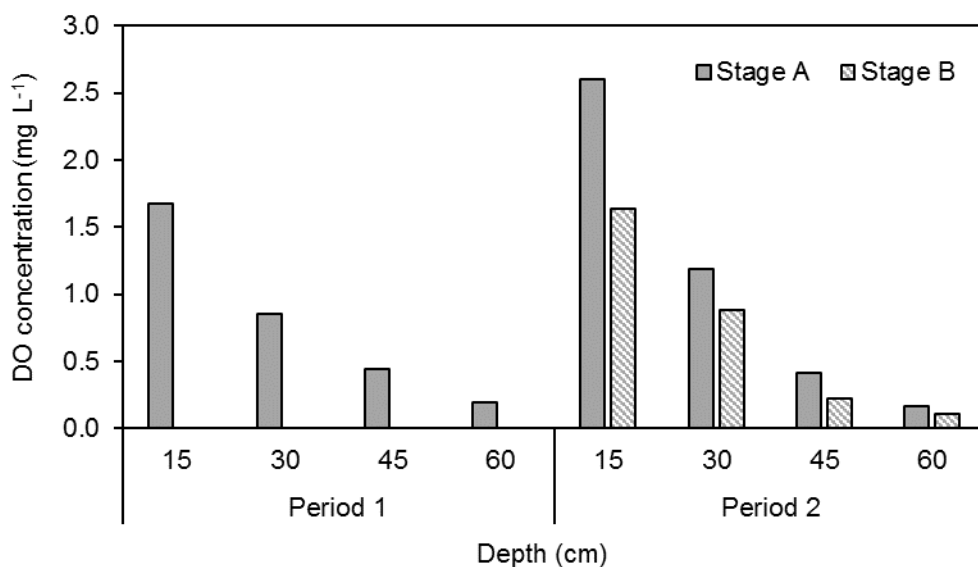
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259   Figure 3 Vertical initial DO distribution at different depth (from top layer to bottom) in four

260   stages of constructed wetland system.

261

262　A comparison of the observed and predicted Pb, Cr and Cd concentration values in the

263　effluent during the model calibration process obtained using linear regression is shown in

264　Figure 5. The R^2 values for Pb, Cr and Cd outlet concentration values were 0.75, 0.69 and

265　0.62, respectively. The R^2 values for comparisons of the observed and predicted Pb, Cr and

266　Cd outlet concentration values during the model validation process (Figure 6) were 0.78,

267　0.65 and 0.74, respectively for Pb, Cr and Cd concentration. These values represent good

268　correlations between the model predictions and the experimental measurements.

269　Based on these results, the mathematical model developed in this study could be used to

270　describe the HM removal process in the VFCW using ferric dewatered sludge as the primary

271　media. The model was run using STELLA software for a period of 185 days for column B.

272　Since the results of the validation data in column A displayed a good match between simu-

273　lated and experimental data, the calibration for column B was performed with the column A

274　data. The experimental effluent HM concentrations ranged from 25 µg L^{-1} to 76 µg L^{-1}, 8 µg

275　L^{-1} to 22 µg L^{-1} and 24 µg L^{-1} to 76 µg L^{-1}, respectively for Pb, Cr and Cd. On the other hand,

276　the simulation data for Pb, Cr and Cd ranged, respectively, from 23 µg L^{-1} to 63 µg L^{-1}, 11 µg

277　L^{-1} to 24 µg L^{-1} and 27 µg L^{-1} to 68 µg L^{-1}, as shown in Figure 7. This figure shows that the

278　mean concentration values of HM for the measured and simulated values were very close

279　and, therefore, the overall simulation is acceptable for column B. The MPEs for this column

280　were 17% for Pb, 17% for Cr and 17% for Cd.　A comparison between the observed and

281　predicted Pb, Cr and Cd concentrations in effluent during the model validation process for

282　column B showed good correlations between the model predictions and the experimental

283　measurements, with R^2 being 0.82, 0.71 and 0.76, respectively, for the Pb, Cr and Cd outlet

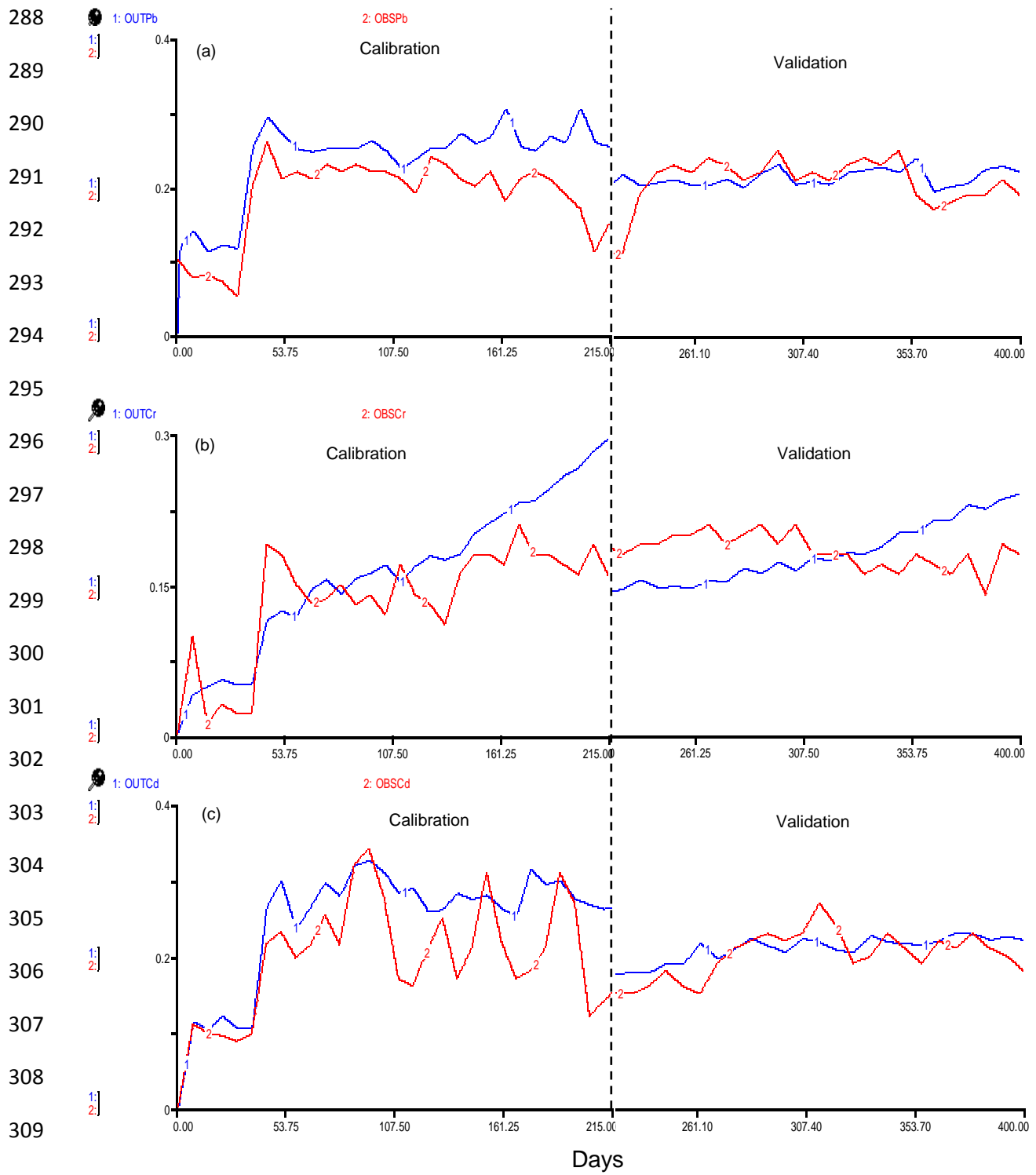284　concentrations (Figure 8).

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Figure 4. Model calibration and validation for (a) Pb, (b) Cr and (c) Cd removal in mg L^{-1} in VFCW for column A.

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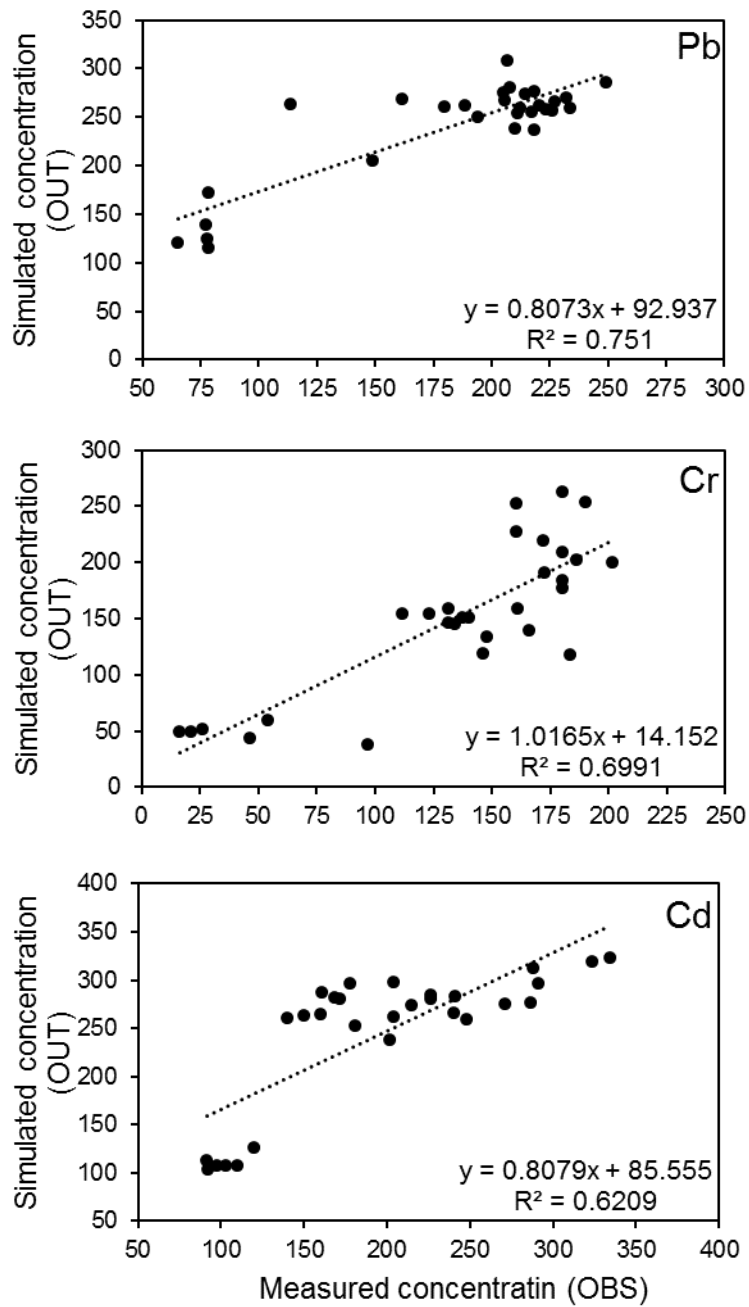
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335 Figure 5. Comparison of model predicted and field measured of Pb, Cr and Cd removal in µg L^{-1} in

336 VFCW for column A during model calibration.

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358   Figure 6. Comparison of model predicted and field measured of Pb, Cr and Cd removal in µg L^{-1} in

359   VFCW for column A during model validation.

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Figure 7. Model validation for (a) Pb, (b) Cr and (c) Cd removal in mg L^{-1} in VFCW for column B.
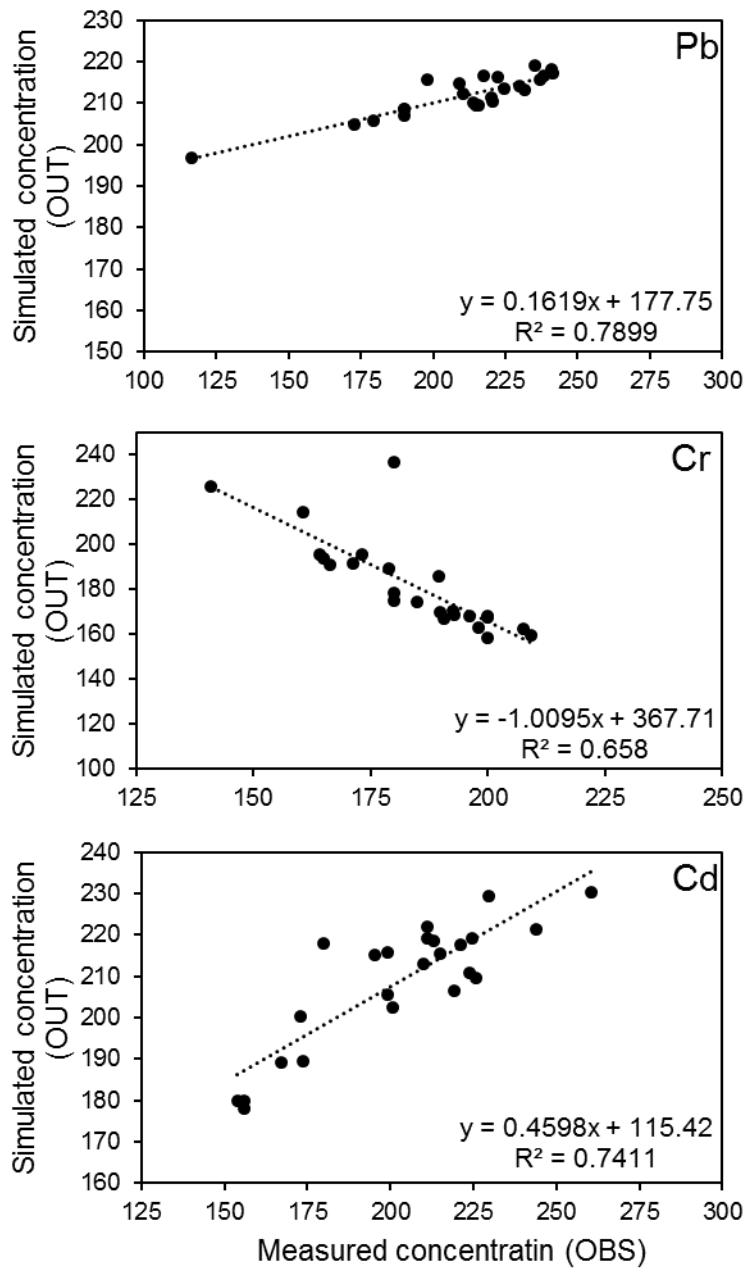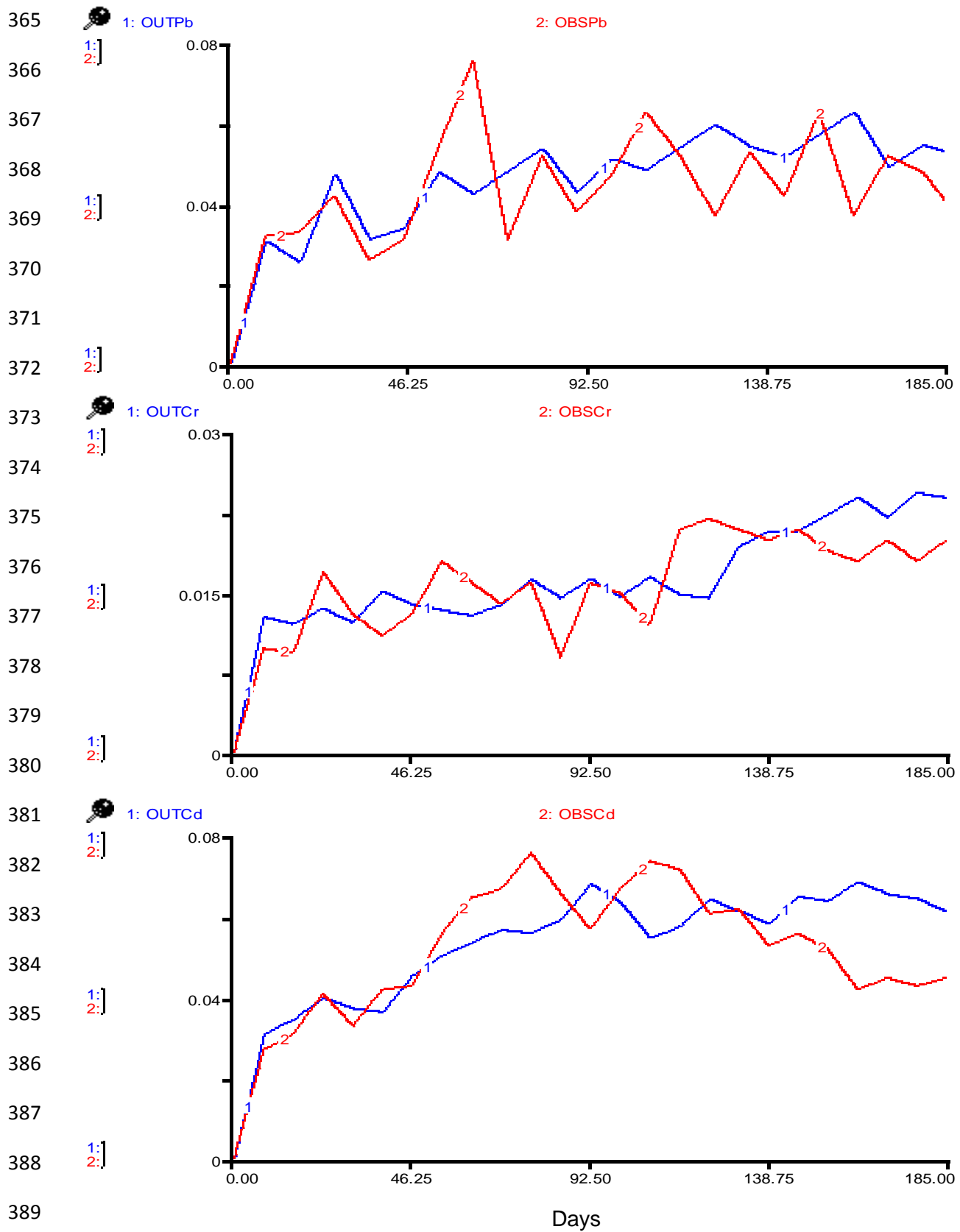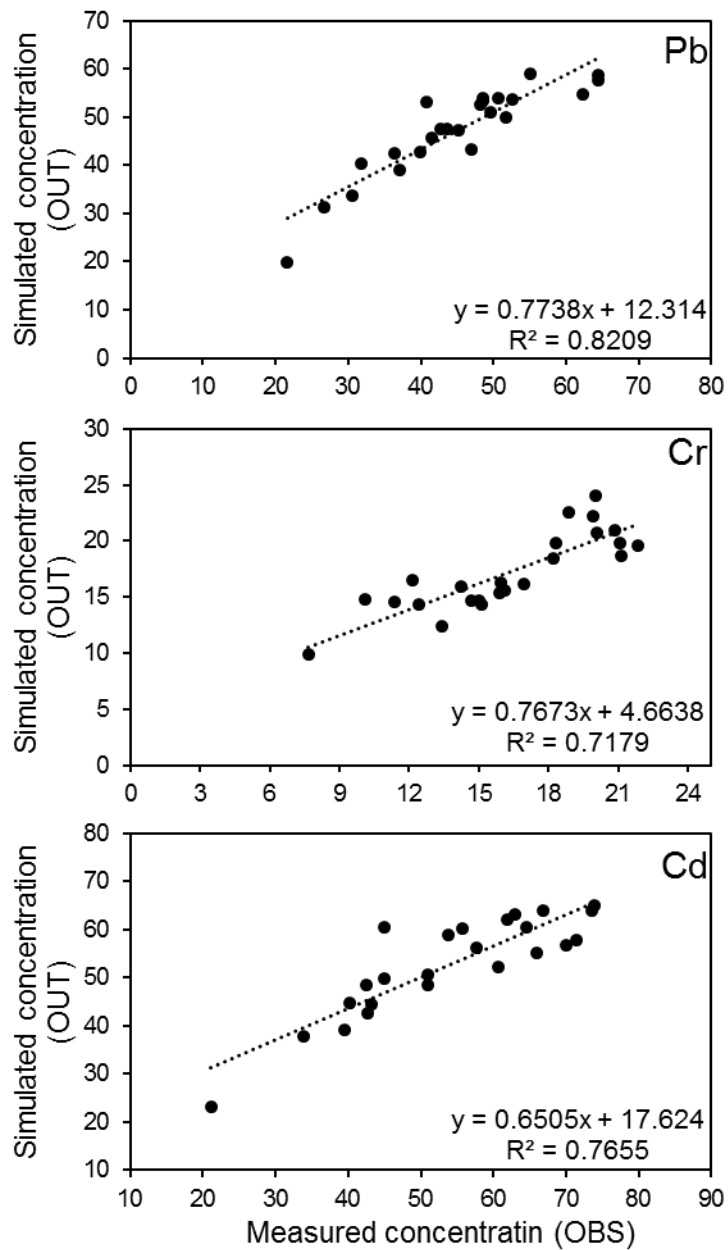
Figure 8. Comparison of model predicted and field measured of Pb, Cr and Cd removal in µgL^{-1} in VFCW for column B during model validation.

415 3.2. Sensitivity analysis

416 A sensitivity analysis provides a good overview of the most sensitive components in the

417 model. This type of analysis attempts to provide a measure of the sensitivity of the parame-

418 ters by forcing functions, initial values of the state variables of the sub models, to the state

419 variables of greatest interest in the model (Jørgensen and Fath, 2011). The sensitivity of the

420 model was tested using the 10 parameters which were most likely to be important: G_m, K_r,

421 U_m, K_u, M_m, M_r, HM_{max}, HM_{min}, n and K_f (Table 2). This was done by examining the rela-

422 tive change in the model output and dividing it by the relative change in the value of the test-

423 ed parameter. The magnitude of the changes in the parameter values may be proportional to

424 the value of the parameter; this also depended on the possible range of the parameter. Most

425 changes were made between -50% and +50% (van der Peiji and Verhoeven, 1999). In this

426 study, changes were made at ±40%. Table 2 shows that the increase and decrease of n

427 caused a significant change in the corresponding state variable of the model. Similarly, the

428 change in K_f also caused changes in the model output and the corresponding state varia-

429 bles. This is primarily because the adsorption process supposes that the main process for

430 the removal of HM by ferric dewatered sludge in the CWs. The rigid structure and fixed set of

431 parameters do not accurately reflect the changes in the output of VFCW.

432 Table 2. Sensitivity analysis for the selected parameters included in the model.

Change of	Parameter value			$S_{(+40\%)}$			$S_{(-40\%)}$		
	Pb	Cr	Cd	Pb	Cr	Cd	Pb	Cr	Cd
Gm	2.08	3	0.82	1.08×10^{-8}-1.33×10^{-7}	2.18×10^{-8}-1.43×10^{-7}	1.64×10^{-7}-3.22×10^{-7}	2.10×10^{-8}-1.32×10^{-7}	2.18×10^{-7}-6.23×10^{-7}	7.08×10^{-8}-2.47×10^{-7}
Kr	2.8	3	1.26	1.43×10^{-8}-2.1×10^{-8}	1.98×10^{-7}-2.13×10^{-6}	1.08×10^{-8}-2.33×10^{-8}	1.08×10^{-8}-1.33×10^{-7}	1.11×10^{-7}-5.01×10^{-6}	2.08×10^{-7}-4.91×10^{-7}
Um	0.26	0.114	0.09	1.48×10^{-5}-3.69×10^{-5}	0.41×10^{-5}-0.55×10^{-3}	6.63×10^{-6}-2.02×10^{-5}	1.56×10^{-5}-3.92×10^{-5}	0.41×10^{-3}-0.55×10^{-3}	6.63×10^{-6}-2.02×10^{-5}
Ku	5.24	2.18	2	3.91×10^{-6}-2.38×10^{-5}	0.19×10^{-3}-0.33×10^{-3}	2.14×10^{-6}-1.00×10^{-5}	1.41×10^{-5}-4.72×10^{-5}	0.31×10^{-3}-0.63×10^{-3}	2.71×10^{-6}-1.47×10^{-5}
HMmax	0.11	1	1.5	2.01×10^{-5}-8.75×10^{-5}	6.67×10^{-5}-8.93×10^{-5}	5.08×10^{-8}-1.55×10^{-7}	1.45×10^{-5}-6.33×10^{-5}	0.19×10^{-3}-0.26×10^{-3}	1.19×10^{-7}-3.65×10^{-7}
HMmin	0.001	0.195	0.016	2.32×10^{-5}-0.11×10^{-3}	0.11×10^{-3}-0.15×10^{-3}	7.17×10^{-8}-2.18×10^{-7}	8.83×10^{-9}-3.51×10^{-7}	0.15×10^{-5}-0.12×10^{-3}	7.12×10^{-8}-2.16×10^{-7}
Mr	0.001	0.001	0.001	2.48×10^{-6}-8.48×10^{-6}	7.73×10^{-5}-0.18×10^{-3}	1.32×10^{-6}-5.97×10^{-6}	2.67×10^{-6}-8.61×10^{-6}	8.03×10^{-5}-0.18×10^{-3}	1.41×10^{-6}-6.09×10^{-6}
Mm	0.2	0.2	0.2	1.16×10^{-5}-9.86×10^{-5}	1.82×10^{-6}-4.72×10^{-5}	5.84×10^{-8}-8.68×10^{-6}	1.09×10^{-7}-1.16×10^{-5}	5.05×10^{-6}-0.10×10^{-3}	1.41×10^{-6}-6.09×10^{-6}
n	0.53	1.52	0.5	0.60×10^{-1}-2.00×10^{-1}	2.72×10^{-3}-3.36×10^{-1}	1.32×10^{-1}-3.20×10^{-1}	3.10×10^{-1}-6.41×10^{-1}	4.70×10^{-3}-5.91×10^{-1}	2.03×10^{-1}-6.70×10^{-1}
Kf	43	1.7	0.43	0.12×10^{-1}-0.54×10^{-1}	1.4×10^{-3}-4.44×10^{-1}	0.3×10^{-1}-1.43×10^{-1}	0.23×10^{-1}-1.03×10^{-1}	7.50×10^{-3}-22.70×10^{-1}	5.00×10^{-1}-2.60×10^{-1}

433

434 3.3. Fate of heavy metals in VFCW

435 To assess the performance of the VFCW for the removal of HM from landfill leachate, a sim-
436 ulation scenario investigated the HM dynamics for the anoxic condition using ferric de-
437 watered sludge as the primary media in the VFCW. The input data of the HMs were inserted
438 into the STELLA software during model calibration and integrated by using the second order
439 Runge-Kutta method with a time step of 0.02 day. Once the model finished its run (i.e., at the
440 end of 215 days), the amount of HM that accumulates into the state variables, and the pro-
441 cesses of the model show how much HM is removed by the individual pathways. Therefore,
442 it is possible to calculate the efficiency of the individual processes, such as Ad (Eq. 2), Up
443 (Eq. 5) and Mp (Eq. 6) and De (Eq. 7). A mass balance for all state variables, as simulated
444 by the model, revealed that approximately 89%, 91% and 91% for Ad; 6%, 5.1% and 5.2%
445 for Up; and 1%, 1.15% and 1% for Mp and De for respectively Pb, Cr and Cd. The results
446 from the mass balance show that the major HM transformation routes in this study were ad-
447 sorption, with a small amount of uptake by the plant. The effect of various parameters on
448 adsorption was studied via batch experiments (Mohammed et al., 2016). The adsorption
449 results of Pb, Cr and Cd ions by ferric dewatered sludge showed a slightly better fit with the
450 Freundlich compared to Langmuir. The Langmuir isotherms data found that ferric dewatered
451 sludge had 40 µg g^{-1}, 130 µg g^{-1} and 30 µg g$_{-1}$ adsorption capacity for Pb, Cr and Cd, re-
452 spectively. On the other hand, the Freundlich isotherm results showed that a precipitation
453 reaction may occur for Pb and Cd removal where n values > 1 (Mohammed et al., 2016).
454 Lead and cadmium could precipitate to form insoluble compounds with sulphide in anaerobic
455 zones of CWs (Kadlec and Wallace, 2008). Figure 9 indicates, as per the laboratory batch
456 experiment, a sharp rise in the Pb and Cr removal within the first hour, indicating the instant
457 at which the removal of these HM takes place. This can be adduced to the excess of binding
458 sites on highly accessible surfaces, like particles and macropores. Over time, the curve
459 starts to plateau because the rate of removal is much slower. This is due to the accumulation

460   of metal ions on the binding sites until it reaches equilibrium; and thereafter, sorption would

461   be via intraparticle diffusion in meso- and micropores and/or sorption by the organic matter

462   (Zhou and Haynes, 2011).

463   The adsorption process in STELLA was described in such a way to calculate the P_e concen-

464   tration using the Freundlich isotherm. From the model simulation, approximately 526 μg, 518

465   μg and 640 μg of Pb, Cr and Cd, respectively, adsorbed during the calibration stage of the

466   model run and the corresponding inflow of these heavy metals amounts were 591 μg, 570

467   μg and 712 μg for Pb, Cr and Cd, respectively. The high amount of HM adsorbed by the me-

468   dia was a result of using ferric dewatered sludge as the main substance and an anoxic con-

469   dition to elongate the contact time between the media and HM. The overall simulation of Ad

470   is reasonably good in the STELLA model, especially for the adsorption process.

471   Unfortunately, no data from the use of ferric dewatered sludge as a substrate in CWs for HM

472   removal were found in the literature. Therefore, there is no comparison data. However, sev-

473   eral authors used the STELLA program to describe the adsorption process in CWSs and

474   used different kinds of substrate and pollutants. Pimpan and Jindal (2009) show that the

475   maximum cadmium removal simulated by the STELLA software occurred through the accu-

476   mulation in the soil with mass fraction values of 33.6–76.6% at different hydraulic retention

477   times. Kumar et al. (2011) revealed that 72% of phosphorus removed through the adsorption

478   process simulated by the STELLA software using alum sludge and vertical flow constructed

479   wetland. Accordingly, adsorption seems to be the main process to remove Cd and phospho-

480   rous in CWS.

481   The uptake of HM by plants in this study was low. This primarily because the CWs plants

482   can be contribute to HM removal through substrate stabilization, rhizosphere oxidation, the

483   supply of organic matter for microorganism and the transportation of water to wetland soil,

484   rather than through the direct uptake of metals (Kosolapov et al., 2004).

485

486
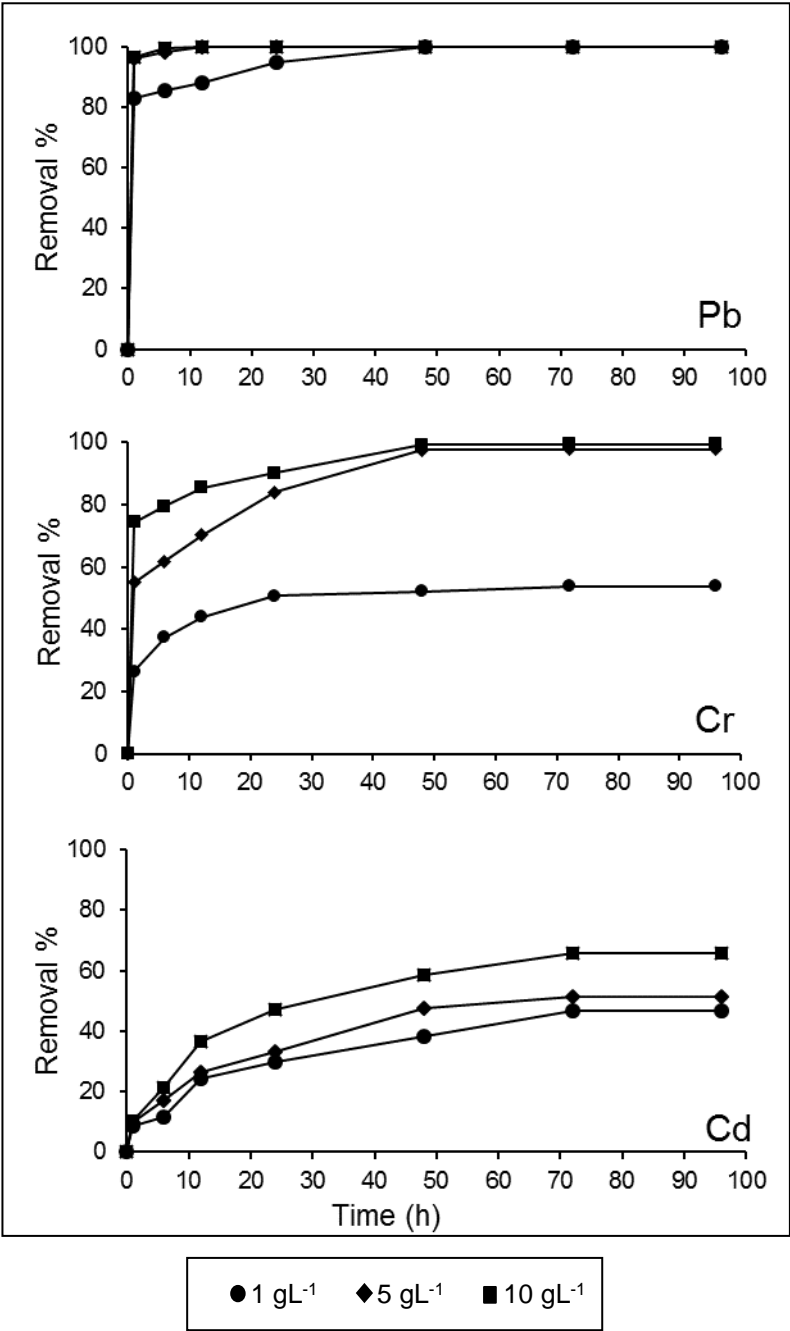
Figure 9. Removal efficiency of heavy metals by ferric dewatered sludge at different sludge dosage and contact time.

4. Conclusion

In this study, a dynamic model for HM transformation in a vertical flow constructed wetland and using ferric dewatered sludge as main substance was developed using STELLA. The mechanisms used in this modelling process included adsorption, uptake by the plant and

511 plant growth. The most significant pathway of heavy HM retention was adsorption. In terms

512 of the model's sensitivity, the adsorption parameter was the most important factor. The mod-

513 el was calibrated in order to achieve predictions that were close to the experimental data. A

514 reasonable agreement was obtained between the measured and predicted results. A mass

515 balance showed that up to 89%, 91% and 91% of the removal of HM was through adsorp-

516 tion, which is highly significant, whereas removal through the plants is about 6%, 5.1% and

517 5.2% for Pb, Cr and Cd, respectively. This study demonstrates that the developed mathe-

518 matical model could be used to describe the Pb, Cr and Cd removal process from landfill

519 leachate in the VFCW using ferric sludge.

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