A mathematical model for Ni phyto-extraction from contaminated soils

[1]Eslamian S. S., [1]Abedi-Koupai, J., [2]Hasheminejad, S. Y., and [3]E. Z. Hosseinipour

[1]*Associate Professors, Isfahan University of Technology, Isfahan, 8415683111, Iran*

saeid@cc.iut.ac.ir

[2]*Graduate Student, Water Department, Isfahan University of Technology, Iran*

[3]*Engineering Manager, Ventura County Water District, California, USA*

Corresponding Author: zia.hosseinipour@ventura.org

Abstract

Phyto-extraction is a technology that uses plants to remove heavy metals from contaminated soils. For effective planning, design and application of Phyto-extraction projects, mathematical models have emerged as a valuable tool. A mathematical model that predicts the time needed for remediation of soil Nickel (Ni) contaminations by plants is developed in this study. In the mathematical model sorption isotherm for Ni and the plant uptake rate of Ni were assumed to characterize the soil and plant responses, respectively, and results are then validated against published field data. *Tulsi* seeds were germinated in Polluted soils contained in a number of pots. A comparison of simulated and field results shows that adsorption of Ni from soil were better fitted to Freundlich and Linear isotherm models. The proposed model with linear sorption isotherm reasonably predicts the time needed for remediation of soil contaminated with Ni.

Introduction

Heavy metal contamination of soil due to industrial effluents used for agriculture poses a serious ecological concern and its remediation is needed to eliminate the risk to the environment. Conventional remediation methods such as physical, thermal and chemical treatments are very expensive and are often appropriate only for small areas where rapid and complete decontamination is required. Phyto-remediation is a novel technology which uses green plants to remove contaminants from the soil. This technology is an economic and effective remediation technique for contaminated sites [5, 16]. Phyto-extraction, which is an eco-friendly cleanup method, is a type of phyto-remediation that exploits the ability of plants to take up metals from soils and sequester them in their shoots [11]. For effective planning, design and application of Phyto-extraction program, models have emerged as a valuable tool [21]. A thorough literature search revealed that very few mathematical models have been developed for phyto-extraction during the last decade due to the complexity of the soil–plant–atmosphere continuum [13]. Modeling can be done using different approaches such as computer software, mathematical equation developed from data generated from field work and mechanistic model developed using mathematical principles. For example Alloway et al., (1990) used an empirical model to predict Cadmium (Cd) uptake and accumulation by vegetables (cabbage, lettuce and radish) from soil contaminated with Cd [1].

Christensen and Tjell (1984) presented a conceptual model to determine Cd uptake from sewage sludge amended soils. The model divided plant Cd concentration into three fractions based upon their source: topsoil, subsoil and atmosphere [6].

Trapp and McFarlane (1995) developed the PLANTX model to simulate uptake of xenobiotic contaminants into plants. The model describes the dynamic uptake from soil, solution, and atmosphere and metabolism and accumulation of anthropogenic chemicals in roots, stem, leaves, and fruits [19]. Jorgensen (1988) developed a model for lead and cadmium uptake based on lead and cadmium balance for average Danish agricultural lands. The model was calibrated using three years of experimental measurements, but the mathematical equations formulated were not based on partial differential equations governing solute transport in soil, it was just a conceptual model [10].

Boersma et al. (1988a,b and 1991) and Lindstrom et al. (1990) developed a one dimensional mathematical model for coupled transport of water, heat, and solutes in the soil–plant–atmosphere continuum (CTSPAC) in the vadose zone [2,3,4,12]. Although the current realistic or mechanistic simulation models almost exclusively discuss uptake of minerals or metals [15, 17], the mechanistic models are not well developed and the conceptual models are not reasonably efficient for the purpose of phyto-extraction [20]. In this study, a mathematical model is developed based on soil and plant responses to heavy metal pollution and simple models are proposed to predict the time needed for remediation of soil Ni contaminations.

DERIVATION OF THE MODEL EQUATIONS

Heavy metals in the unsaturated media remain in two phases: in dissolved ionized form in the soil moisture and the adsorbed phase on the soil particles. Considering the total mass of a heavy metal in the unit volume of soil as M (M L^{-3}):

$$M = M_s + M_l \tag{1}$$

Where:

M_S: the mass of the heavy metal adsorbed in the soil (M L^{-3})
M_l: the concentration of heavy metal in liquid phase (M L^{-3})
Expanding M_s and M_l and rewriting Eq. (1) for a given volume of bulk soil V, gives:

$$M = S\rho_b + C\theta \tag{2}$$

Where:

M: the total mass of heavy metal in the soil volume V
S: the mass of heavy metal adsorbed per unit mass of soil solid phase (M M^{-1})
ρ_b: soil bulk density (M L^{-3})
C: the mass concentration of heavy metal in soil solution (M L^{-3})
θ: the volumetric soil water content (L^3 L^{-3})

Considering phyto-extraction rate as the remediated amount of heavy metal per unit volume of soil for a unit time:

$$r_0 = \frac{dM}{dt} = \frac{d(S\rho_b + C\theta)}{dt} \tag{3}$$

r_o: the Phyto-extraction rate (M L^{-3} T)

The adsorption of heavy metals in solution is governed by isotherm adsorption and is proportional to the heavy-metal concentration in soil, the adsorption isotherm model used in this study is the Langmuir, Freundlich and the linear equation described as [8,9]:

$$S_i = \frac{q_{max}K_L C_i}{1 + K_L C_i} \tag{4}$$

Where:
S_i: the amount adsorbed at equilibrium (M M^{-1})
C_i: the equilibrium concentration (M L^{-1})
q_{max}: maximum adsorption capacity (M M^{-1})

K_L: a constant related to the energy or net enthalpy of adsorption (L M^{-1})

$$S_i = K_F C_i^N \tag{5}$$

K_F and N are equilibrium constants indicative of adsorption capacity and adsorption intensity

$$S_i = K_d C_i \tag{6}$$

K_d: the soil distribution coefficient

Therefore, at equilibrium the soluble and adsorbed heavy metal are related by the soil distribution coefficient K

$$S \propto KC \tag{7}$$

Substituting Eq. (7) into Eq. (3) and rewriting Eq. (3), we have:

$$r_0 = \frac{d(K\rho_b C + C\theta)}{dt} \Rightarrow r_0 = (K\rho_b + \theta)\frac{dC}{dt}$$

$$\Rightarrow dC = \frac{r_0}{(K\rho_b + \theta)}dt \tag{8}$$

Hence the total amount of metal that accumulates in the plant is related to the metal concentration that is in the soil solution; assuming r$_0$ as a zero order ($r_0 = \frac{dC}{dt} = -k_0$), first

order ($r_0 = \dfrac{dC}{dt} = -K_1 C$), or a second-order ($r_0 = \dfrac{dC}{dt} = -\dfrac{K_2}{C}$) coefficient of C. Integrating Eq. (8) from $C = C_0$ to $C = C_f$ and $t = 0$ to $t = t_r$, the following equations will be derived for the time interval needed for remediation of soil contaminations:

$$r_0 = -\frac{dC}{dt} = K_0 \Rightarrow r_0 = -K_0$$

$$\Rightarrow \int_{C_0}^{C_f} dC = \frac{-K_0}{(K\rho_b + \theta)}\int_0^{t_r} dt \Rightarrow t_r = \frac{(K\rho_b + \theta)}{K_0}(C_0 - C_f) \quad , \tag{9}$$

$$r_0 = -\frac{dC}{dt} = K_1 C \Rightarrow r_0 = -K_1 C$$

$$\Rightarrow \int_{C_0}^{C_f} dC = \frac{-K_1 C}{(K\rho_b + \theta)}\int_0^{t_r} dt \Rightarrow \int_{C_0}^{C_f} \frac{dC}{C} = \frac{-K_1}{(K\rho_b + \theta)}\int_0^{t_r} dt \Rightarrow t_r = \frac{(K\rho_b + \theta)}{K_1}\ln\frac{C_0}{C_f} \tag{10}$$

,
$$\tag{11}$$
$$r_0 = -\frac{dC}{dt} = \frac{K_2}{C} \Rightarrow r_0 = -\frac{K_2}{C}$$

$$\Rightarrow \int_{C_0}^{C_f} dC = \frac{-K_2}{C(K\rho_b + \theta)}\int_0^{t_r} dt \Rightarrow \int_{C_0}^{C_f} C dC = \frac{-K_2}{(K\rho_b + \theta)}\int_0^{t_r} dt \Rightarrow t_r = \frac{(K\rho_b + \theta)}{2K_2}(C_0^2 - C_f^2)$$

where: k_0 (M L^{-3}T), k_1 (L/T), and k_2 (M^2 L^{-6}T) are zero, first and second-order rate coefficients, respectively, C_0 is the concentration of soil heavy metal in soil solution at the start of remediation process, C_f is the desired or acceptable concentration of heavy metal in soil solution and t_r is the time needed for remediation of soil contaminations from C_0 to C_f. Further, the time duration needed to achieve remediation at any given level of soil contamination can be obtained from:

$$t_r^m = \begin{cases} \dfrac{1}{365}\displaystyle\sum_{i=1}^{n}\dfrac{\left(C_S^{i+1} - C_S^i\right)\rho_b}{r_0^{i,i+1}} & \text{for } C_S^{i+1} > C_a \\[4mm] 0 & \text{for } C_S^{i+1} \le C_a \end{cases} \tag{12}$$

Where:

t_r^m: the calculated remediation time (years)
i: 1,2,…,n: the soil contamination level for Ni used in the study

C_s^i: the soil total metal concentration (mg kg^{-1}) at contamination level i
C_a: the acceptable concentration of metal in soil (in this study considered to be 50 mg kg^{-1} for

Ni)

$(C_S^{i+1}-C_S^i)\rho$: the total mass of contaminant (mg m^{-3}) which is subject to remediation, r_0^{i+1} is the average measured phyto-extraction rate (mg m^{-3}day) of Ni between two consecutive contamination levels i and $i+1$

MATERIALS AND METHODS

The experiment was conducted at the greenhouse of the college of Agriculture, Isfahan University of Technology, in a sandy clay loam soil. Some chemical and physical properties of the soil are given in Table 1. The soil was air-dried and passed through a 2mm sieve. The designated amounts of Ni (NO$_3$)$_2$ were calculated and added to a large quantity of soil to obtain soil Ni concentrations of 50, 70, 90, 110, and 130 mg kg^{-1}. The soil was then completely mixed to homogenize the applied Ni contaminations and was subsequently packed into PVC pots of 20 cm height and 22 cm diameter with three replicates. The packed soils were incubated for four weeks to achieve equilibrium between the Ni in soil solution and the soil particles surface. Each pot was planted with some tulsi (*Ocimum tenuiflorum*) seeds. To avoid leaching out the contaminations, no drainage pathway was allowed.

The moisture content in pots was kept between 80% and 100% of field capacity. Fertilizer was applied according to the crop nutrient requirement, with irrigation water to prevent any possible nutrient deficiency. The plants were harvested by cutting the stem above the soil surface in 4 time intervals after germination.

TABLE 1.some physical and chemical properties of the soil

Soil texture	%Sand	%Silt	%Clay	ρ_b (g cm^{-3})	θ_{FC}	EC$_e$ (Ds m^{-1})	pH$_e$	%OC
Sandy Clay Loam	64	16	20	1.42	0.22	1.4	7.2	0.286

Isotherm adsorption

Nickel solutions were prepared by diluting 1000 ppm of stock nickel solution which was obtained by dissolving weighed quantity of nickel nitrate (Merck) in double- distilled and de-ionized water. The range of concentrations of prepared Nickel solutions changed between 20 and 100 mg l^{-1}. The pH of each solution was adjusted to the required value with diluted or concentrated HNO$_3$ (Merck) solutions before mixing the soil. The experiments were conducted in 50 ml Erlenmeyer flasks containing 25 ml of Nickel solutions with different concentration. The flasks were agitated on a shaker at a 200 rpm constant shaking rate for 24h to ensure equilibrium was reached. Before analysis, the samples were centrifuged at 5000 rpm for 25 min [7, 18].

Analysis of Nickel Concentration in Plants and Soil

The water-soluble fraction of soil Ni was obtained by extracting with distilled water for 24 h at 1:2 soil-liquid ratios. The total metal concentration in the soil and plant samples was determined by HNO$_3$ digestion method. Nickel concentration was determined using a flame

atomic absorption spectrometer (AAS) [18]. After collecting the needed data, the accuracy of proposed models was evaluated using statistical parameters (ME, RMSE, CD, EF and CRM).

RESULTS AND DISCUSSION

The experimental equilibrium data obtained were fitted with Linear and Freundlich isotherm models (Fig 1). Correlation coefficient (R^2) of the adsorption isotherm data showed that adsorption of Ni to soil particles were best fitted to Freundlich isotherm model but were close enough to the linear model (Table 2). Therefore, the simpler linear model was used in this study. The isotherm constants are given in Table 3. The K values of linear model obtained from the experiments can be used in the proposed phyto-extraction model to determine soil response to different levels of soil Ni contaminants.

TABLE 2. The calculated statistics parameters for quantitative evaluation of isotherm models

Model	R^2	ME	RMSE	CD	EF	CRM
Linear	0.912	435.437	16.55	0.652	0.879	0.075
Freundlich	0.93	335.699	14.86	0.833	0.903	0.0339
Langmuir	0.276	1016.51	47.88	$7.9E10^7$	0.00016	1.4E-6

TABLE.3. Coefficient values of isotherm models

Model	K	n	b
Linear	K_d=297.81	__	__
Freundlich	K_F=504.5	0.716	__
Langmuier	K_L=1410.995	__	35639.17

TABLE.4. Calculated statistics for quantitative evaluation of accuracy of models (Eqs. 9, 10, 11)

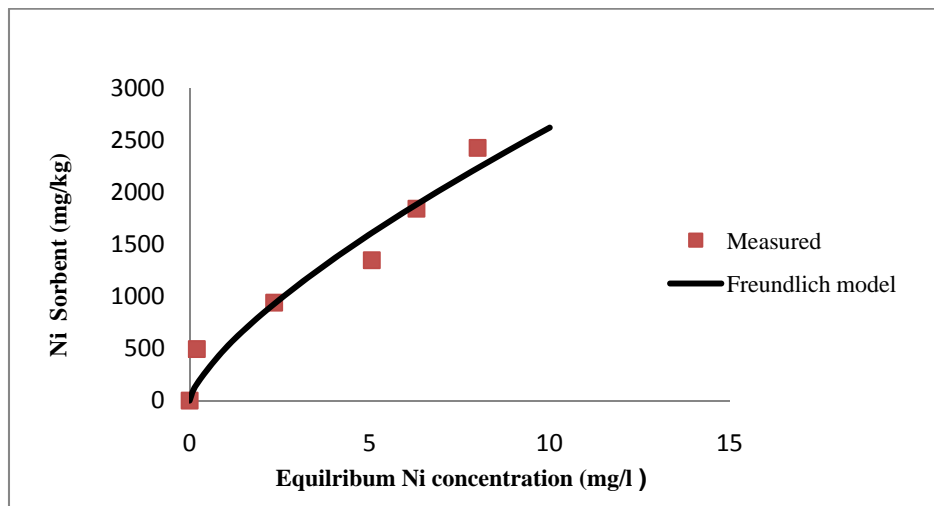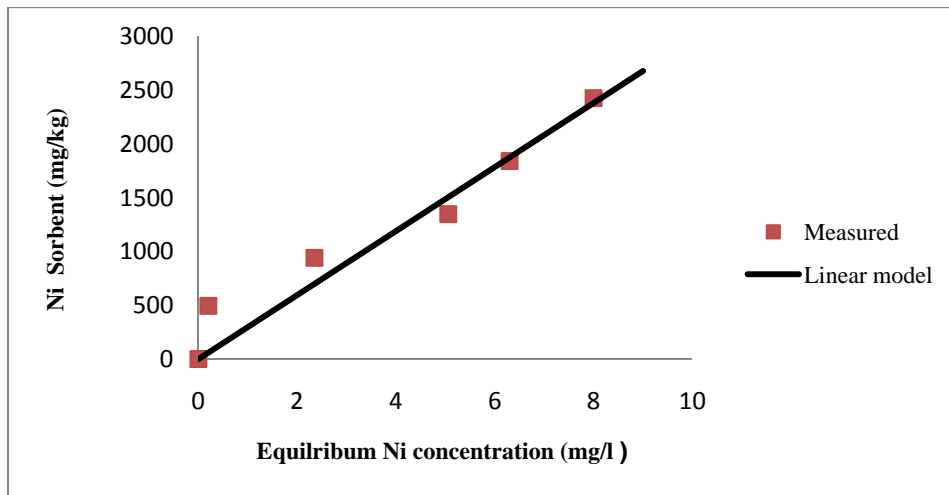| Order	R^2	ME	RMSE	CD	EF	CRM
Zero	0.76	320.934	18.04	1.487	0.853	-0.0269
First	0.96	166.34	8.28	1.14	0.969	-0.0136
Second	-0.16	508.086	40.173	1.629	0.27	0.05
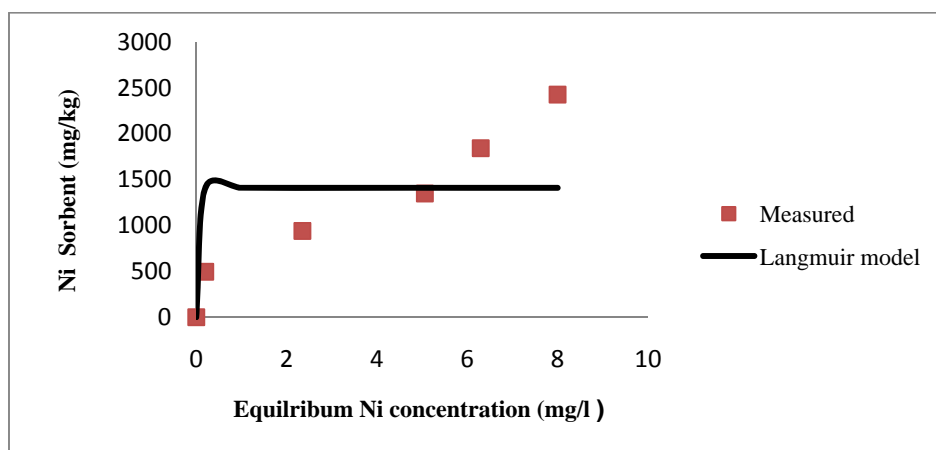
Fig.1. Measured and predicted sorption isotherms for Nickel with Linear, Freundlich and Langmuir models

The values of k_0, k_1, and k_2 were optimized by fitting Eqs (9), (10), and (11) to the measured time needed for remediation of soil contaminations, using least square optimization

procedure. The parameter values of k_0, k_1, and k_2 for Ni remediation by tulsi (*Ocimum tenuiflorum*) are 0.0686 (mg l^{-1} yr^{-1}), 0.238 (yr^{-1}) and 0.0244 (mg2 l^{-6} yr^{-1}) respectively. These parameter values can be used in Eqs (9), (10), and (11) to predict the time needed for phyto-remediation of Ni contaminated soil. Figure 2 plots the calculated time needed for remediation of Ni-contaminated soils by *Tulsi*. Figure 2 shows a good agreement between the calculated times and those predicted with Eq. (10).

Table 4 gives the values of statistical parameters for the calculated and predicted time needed for remediation of soil Ni contaminations based on Eqs (9), (10), and (11). These results indicate a reasonable performance for Eq. (10) for Ni remediation by *tulsi*. In other words, assuming the ability of *tulsi* in Ni uptake to be increased with increasing Ni concentration in soil is more reliable in the range of Ni contamination of soil. These results also reveals that one can approximate the time needed for remediation of soil Ni contamination by *tulsi* , assuming the phyto-extraction rate to be constant up to the Ni contamination of soil. Conversely, there was no practical prediction with Eq. (12) for phyto-extraction of soil Ni contaminations. This result showed the existence of any second-order relation between phyto-extraction rate and soil Ni contaminations.
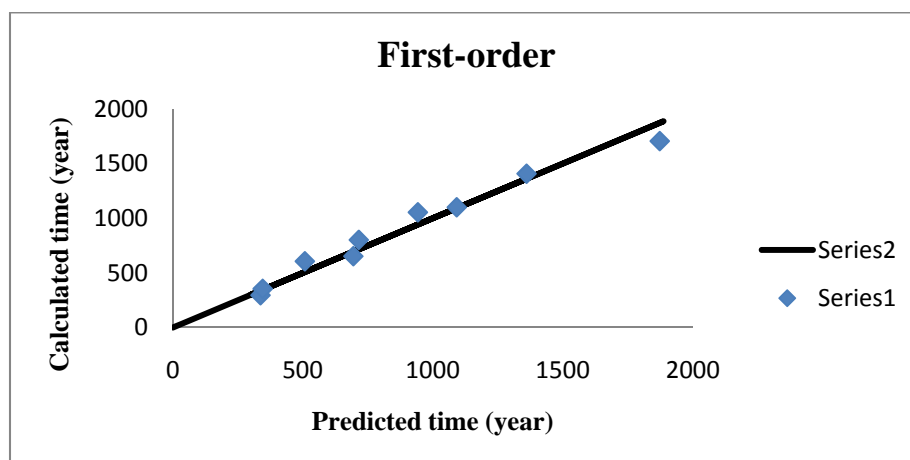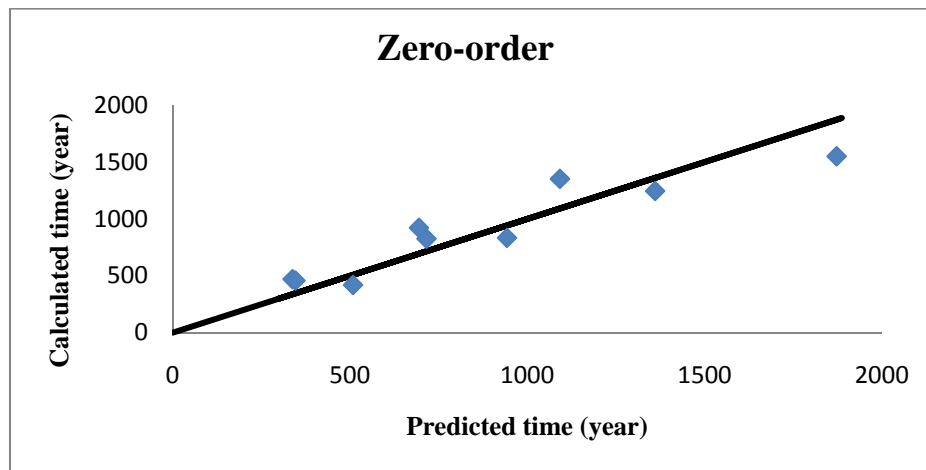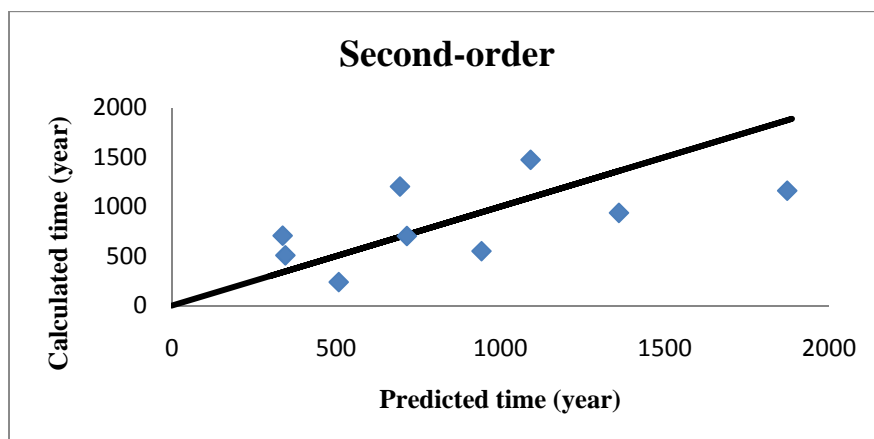
Fig.2. Comparison of predicted and calculated time needed for the phyto-extraction of Ni from contaminated

soils with Eq. (12) as measured time by *tulsi* with those predicted with Eqs. (9), (10) and (11)

CONCLUSIONS

Testing and validating the proposed model showed that the assumptions made to derive this model concerning soil and plant responses to heavy metal stress are reasonable for Ni contamination with the linear adsorption isotherm. The proposed model can be used to test the phyto-extraction management scenarios and to predict the optimal harvestings for phyto-extraction purposes. Further investigations are needed to confirm the finding of this research for different soil and plants.

REFERENCES

[1] Alloway, B.J., Jackson, A.P. and Morgan, H. 1990. The accumulation of cadmium by vegetables grown on soils contaminated from a variety of sources. The Science of the Total Environment, 91: 223 – 236.

[2] Boersma, L., Lindstrom, F.T., Childs, S.W., 1991. Model for steady state coupled transport in xylem and phloem. Agronomy Journal 83, 401–415.

[3] Boersma, L., McFarlane, C., McCoy, E.L., 1988a. Uptake of organic chemicals by plants: a theoretical model. Soil Science 146, 403–417.

[4] Boersma, L., McFarlane, C., McCoy, E.L., 1988. Model of coupled transport of water and solutes in plants, Spec. Report 818. Agric. Exp. Sta., Oregon State University, Corvallis, Oregon, USA, p. 109.

[5] Chappell, J. 1997. "Phyto-remediation of TCE using Populus." Status Rep. Prepared for the U.S. EPA Technology Innovation Office under a National Network of Environmental Management Studies Fellowship, Washington, D.C.

[6] Christensen, T. and Tjell, J. 1984. Interpretation of experimental results on cadmium crop uptake from sewage sludge amended soil, p. 358-369. In P.D. L'Hermite and H. Ott (ed.), Processing and use of sewage sludge. Reidel, Dordrecht, the Netherlands.

[7] E.D. Van Hullebusch, A. Peerbolte, M.H. Zandvoort, P.N.L. Lens, Sorption of cobalt and nickel on anaerobic granular sludge: isotherms and sequential extraction, Chemosphere 58 (2005) 493–505.

[8] H.M.F. Freundlich, U ber die adsorption in lo¨sungen, Z. Phys. Chem. 57 (1906) 385–470.

[9] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[10] Jorgensen, S. E. (1988). "Modeling the contamination of agricultural products by lead and cadmium", Advances in environmental modeling, A. Marani, ed., 343–350.

[11] Lasat, M. M. 2002. "Phyto-extraction of toxic metals: A review of biological mechanisms." J. Environ. Qual., 31, 109–120.

[12] Lindstrom, F.T., Boersma, L., Yingjajaval, S., 1990. CTSPAC: mathematical model for coupled transport of water, solutes, and heat in the soil–plant–atmosphere continuum. Mathematical theory and transport concepts, Agric. Exp. Sta., Oregon State University, Corvallis, Oregon, USA, Bulletin 676.

[13] Mathur, S. 2004. "Modeling phyto-remediation of soils." Pract. Period. Hazard. Toxic Radioact. Waste Manage. 84, 286–297.

[14] Nash J. E., Sutcl i f fe J. V.: J. Hydrol., 10, 282, 1970.

[15] Rengel, Z. (1993). Mechanistic simulation models of nutrient uptake: a review. Plant Soil 152:161–173.

[16] Salt, D. E., Blaylock, M., Kumar, P. B. A. N., Dushenkov, V., Ensley, B. D., Chet, I., and Raskin, I. 1995. "Phyto-remediation: A novel strategy for the removal of toxic metals from the environment using plants." Biotechnology, 13, 468–475.

[17] Silberbush M.: Simulation of ion uptake from the soil. In: Plant Roots, the Hidden Half, (Eds. Waisel Y., A. Eshel, and U. Kafkafi), 643. Marcel Dekker, 1996.

[18] Soon Y. R., Abboud S.: Cadmium, chromium, lead, and nickel. In: Soil Sampling and Methods of Soil Analysis (Ed. Carter M. R.), 101, Lewis Publishers, 1993.

[19] Trapp, S., McFarlane, J.C., 1995. Plant Contamination: Modeling and Simulation of Organic Chemical Processes, Lewis Publishers, Boca Raton.

[20] Tudoreanu, L. and C.J.C. Phillips. (2004). Modeling Cadmium Uptake and Accumulation in Plants. Adv. Agron. 84: 121-157.

[21] Verma, P., George, K. V., Singh, H. V., Singh, S. K., Juwarkar, A., and Singh, R. N. 2006. "Modeling rhizofiltration: Heavy-metal uptake by plant roots." Environ. Model. Assess. 11, 387–394.