Numerical and Analytical Simulation of Transport of Cd, Ni and Zn in Disturbed and Undisturbed Saturated Loamy Soil Columns

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ABSTRACT: *Contamination of soil, water, and air with heavy metals is an environmental issue and of particular importance due to its toxicity, persistence, and mobility in soil. For a better understanding of the environmental behavior and risks associated with heavy metals, modeling their fate and transport is prioritized as an efficient tool. In the present research, the transport of the heavy metals cadmium (Cd), nickel (Ni), and zinc (Zn) in two disturbed and undisturbed loamy soils with the initial concentrations of 50, 100, and 150 mg/L were simulated using CXTFIT and Hydrus-1D as analytical and numerical models, respectively. The results showed that both the models can simulate the transport of heavy metals and describe the BreakThrough Curves (BTCs) with a coefficient of determination (r^2) of higher than 0.9 and a root mean square error (RMSE) of less than 0.06. However, the analytical CXTFIT model showed a better fit to the BTCs compared to the numerical Hydrus model. Also, the models showed better efficiency in the disturbed soil than in the undisturbed soil. With the increase in the concentration of all three heavy metals, the retardation factor (R) decreased and indicated a trend as Zn>Ni>Cd. The hydrodynamic dispersion coefficient (D) in the undisturbed soil was estimated to be higher than in disturbed soil and followed the trend of Cd≥Zn≥Ni. The evaluation of the results showed that despite the better performance of the CXTFIT model, there is no major difference between the two models.*

KEYWORDS: *Heavy metal, Hydrodynamic dispersion, Retardation factor, CXTFIT, Hydrus.*

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INTRODUCTION

Nowadays, soil contamination due to heavy metals is an environmental issue worldwide and has attracted public attention owing to the growing concern about the safety of agricultural products [1]. Among the types of soil contaminants, heavy metals are of great importance in the environment due to their non-degradability in nature, toxicity, persistence, long lifespan, and mobility. They are easily transmitted through the food chain and endanger the health of living organisms [2-4]. The most important heavy metals in terms of environmental hazards in water and soil are cadmium, arsenic, mercury, zinc, vanadium, cobalt, iron, manganese, nickel, lead, chromium, and copper [5, 6]. Therefore, heavy metals such as cadmium, lead, copper, zinc, chromium and nickel were prioritized for control by the Environmental Protection Agency [7]. For example, zinc plays an important role in proper cell function, including cell differentiation and division, cell growth, cell migration, endocrine and immune systems, transcription, protein synthesis, RNA and DNA synthesis, and DNA replication [8]. This heavy metal is found in many body tissues such as testicles, muscles, liver, bones and brain [9]. Cadmium is very toxic to human kidneys and bones [10]. An excessive amount of nickel is harmful to the respiratory system and leads to cancer [11]. These heavy metals may eventually enter the food chain or find their way into the groundwater through leaching and pose a serious threat to the environment and public health [12]. Therefore, understanding the transport behavior of heavy metals is necessary to predict the level of contamination in the groundwater system, soil, and finally, to protect public health [13].

An important aspect in understanding the fate of a contaminant in porous media is to describe their transport behavior using appropriate models [14]. The Convection-Dispersion Equation (CDE) is the first model that has widely been used to characterize solute transport in porous media, providing satisfactory results in homogeneous soils and on a laboratory scale [15, 16]. The parabolic CDE for one-dimensional transport of a neutral and conservative solute under uniform and steady-state water flow is expressed as follows [17]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} \quad (1)$$

Where C is the solute concentration (M/L^3), D is the hydrodynamic dispersion coefficient (or in brief, dispersion coefficient) (L^2/T), V is the mean pore water velocity (L/T), x is the distance (L), and t is the time (T).

Nowadays, mathematical models are usually used as efficient tools in studying and managing transport of various contaminants in porous media. Several computer programs have been developed to model displacement of contaminants in porous media based on different analytical or numerical solutions, among which CXTFIT, Hydrus-1D and STANMOD are the most used models to estimate the transport parameters such as pore water velocity, retardation factor, adsorption coefficients, and degradation or production parameters [18]. In various studies, numerical models have been used to predict the transport behavior of ions in soil [18-20]. Also, owing to its versatility, the non-equilibrium CDE model has been used to simulate transport of heavy metals in soil columns in many research [21-25]. For instance, bromide movement in both disturbed and undisturbed soils was simulated with Hydrus-1D in equilibrium and non-equilibrium conditions by *Dousset et al*. [26]. It was concluded that the equilibrium and non-equilibrium models provided better estimates for the disturbed and undisturbed soils, respectively. The transport of heavy metals in soil was acceptably simulated using Hydrus-1D by *Dao et al.* [27]. *Abbasi et al*. [28] investigated the solute movement in homogeneous soils and estimated the dispersion and diffusion coefficients using the inverse solution method. The results of the two MIM and CDE models were not significantly different from each other, and both showed good ability in predicting the solute movement. The four models CDE, MIM, FADE and CTRW were evaluated in the transport of zinc, cadmium and nickel solutes in disturbed and undisturbed loamy soil columns by *Morsali et al*. [29]. The results showed that the CDE and MIM models were more suitable for simulating the transport of heavy metals than the FADE and CTRW models. *Pan et al*. [30] used the Hydrus software to investigate and quantify factors affecting nitrate transport. They concluded that Hydrus-1D was capable of simulating nitrate transport in soil columns under different temperature and hydraulic conditions. *Mahmood-ul-Hassan* [31] simulated the movement of boron and zinc using the CDE analytical solution of the CXTFIT code in the STANMOD model. The results demonstrated the effect of soil structure on solute transport and had implications for nutrient management in farm soils. To simulate the movement of cadmium in soil, *Qi et al*. [32] used the equilibrium and non-equilibrium models in the CXTFIT program to determine the parameters of the CDE and showed that both the models performed well. The transport of KCl in soil columns was investigated and validated using CXTFIT and Hydrus-1D, respectively. No significant difference was observed between the solute transport parameters estimated by CXTFIT and the numerical simulation of Hydrus-1D [33]. In investigating the bromide transport in soil columns, transport parameters based on BreakThrough Curves (BTCs) were estimated by the inverse modeling of the Convection-Dispersion Equation (CDE) and the Mobile-Immobile Model (MIM) using the CXTFIT software. The results showed that the CDE model is more efficient [34]. The research conducted on the BTCs of nickel, cadmium and lead ions in a single-phase system indicated that, in contrast to the tendency of soil to absorb metals, the heavy metal nickel (II) moved more quickly than the other two metals in the soil column. Due to the different adsorption characteristics of these metals in soil, cadmium and lead were in the next ranks. Also, the results of fitting with the Langmuir equation and non-equilibrium convection-dispersion showed that in the single-metal system, the adsorption capacity of metals in the soil was as Pb>>Cd>Ni.

Although the mentioned numerical and analytical models have been evaluated in different laboratory and field conditions and types of porous media with different boundary conditions on conservative and non-reactive solutes, these models have neither been assessed together in terms of efficiency nor compared in better fitting in simulating the transport of heavy metals in disturbed and undisturbed soils so far. Considering that the analytical and numerical solution of the CDE (Eq.1) are developed in the form of codes and computer programs such as CXTFIT and Hydrus, respectively, therefore, in the present study, these codes were used for analytical and numerical investigation of the transport of the heavy metals Cd, Zn and Ni in disturbed and undisturbed soil columns.

EXPERIMENTAL SECTION

The analytical CXTFIT model

The CXTFIT software [35] is used to estimate transport parameters using several analytical models for solute transport during one-dimensional steady flow. This model enables the simulation in equilibrium and non-equilibrium conditions by fitting mathematical solutions of theoretical transport models based on the CDE and Richards' equation using observed data (column experiments) or field data through inverse modeling. The analytical solution of the CDE (Eq. (1)) using the boundary condition of the third type (constant mass flow at the inlet boundary) (Eq. (2)) in a semi-infinite system is obtained as Eq. (3)[36]:

$$C\,(x,t),\ x \to \infty \qquad \left(\frac{\partial C}{\partial x}\right)(\infty,t) = 0 \tag{2}$$

$$C\,(x,t) = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{x-Vt}{2\sqrt{Dt}}\right) + 2\sqrt{\frac{V^2t}{\pi D}}\exp\left(\frac{-(x-Vt)^2}{4Dt}\right) - \left(1+\frac{Vx}{D}+\frac{V^2t}{D}\right)\exp\left(\frac{Vx}{D}\right)\operatorname{erfc}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)\right] \tag{3}$$

Where, C_0 is the constant inlet concentration, and *erfc* is the complementary error function.

This model may also be used to simulate solute concentration as a function of time and/or leaching depth [18, 37]. The inverse solution is performed by minimizing the objective function (sum of the squared difference between the observed and fitted concentrations) [38].

The numerical Hydrus-1D model

In the Hydrus-1D model, the one-dimensional movement of water in soil is expressed using the numerical solution (linear finite element model) of the Richards' equation:

$$\frac{\partial \Theta}{\partial t}=\frac{\partial}{\partial x}\left[K(\Theta)\left(\frac{\partial h}{\partial x}+\cos\alpha\right)\right]-S \tag{4}$$

Where, Θ is the volumetric water content (L^3/L^3), $K(\Theta)$ is the unsaturated hydraulic conductivity (L/T), h is the matric suction (L), α is the angle between the flow direction and the vertical axis (with $\alpha=0^\circ$ for vertical flow, $\alpha=90^\circ$ for horizontal flow, and $0^\circ<\alpha<90^\circ$ for other flow directions), S is the root water uptake (L^3/L^3T), x is the distance (L), and t is the time (T).

In this model, several relations are defined to describe soil hydraulic characteristics, such as moisture characteristics curve and unsaturated hydraulic conductivity. The most common relations are [39]:

$$\Theta(h)=\Theta_r+\frac{\Theta_s-\Theta_r}{[1+(\alpha h)^n]^m} \qquad m=1-\frac{1}{n} \quad n>1 \tag{5}$$

$$K(h)= K_s Se^l\left[1-\left(1-Se^{\frac{1}{m}}\right)^m\right]^2 \tag{6}$$

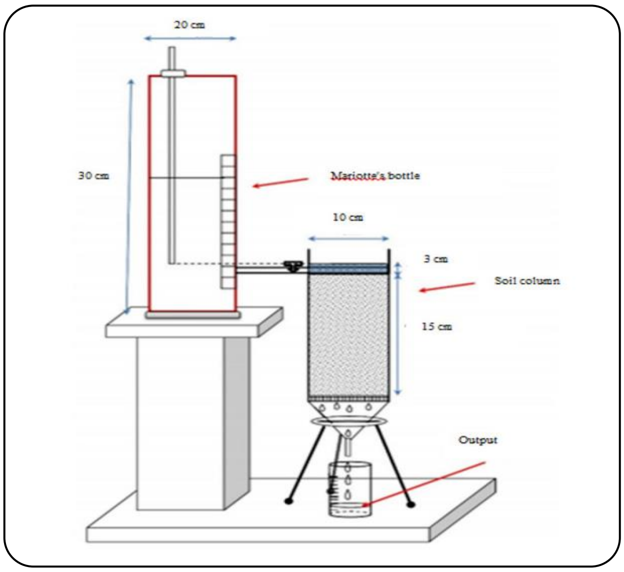

Fig. 1: The schematic of the soil column during the breakthrough the heavy metals

Where, θ_r is the residual water content, θ_s is the saturated water content, α, n, m and l are empirical parameters, K_s is the saturated hydraulic conductivity, and S_e is the relative saturation.

In order to estimate the hydraulic parameters, inverse modeling, which is an optimization method, is usually used. In this research, due to the inverse modeling capability, CXTFIT 2.1 and Hydrus were used. In the inverse solution method, optimal parameters are estimated by minimizing the difference between the observed concentrations and those estimated by the model.

Evaluation criteria

Statistical criteria are used to assess models qualitatively. These criteria provide a purposeful method for evaluating the performance of models. In this research, the statistical indices coefficient of determination (r^2), Root Mean Square Error (RMSE), Mean Relative Error (MRE) and model efficiency (EF) were used to evaluate the accuracy of the models. These indices can be calculated using the following relations:

$$\frac{\left(\sum_{i=1}^{n}(P_i-\bar{P}_i)(O_i-\bar{O}_i)\right)^2}{\sum_{i=1}^{n}(P_i-\bar{P}_i)^2\sum_{i=1}^{n}(O_i-\bar{O}_i)^2} \qquad (8)$$

$$RMSE=\sqrt{\frac{1}{n}\sum_{i=1}^{n}(P_i-O_i)^2} \qquad (9)$$

$$MRE=\frac{1}{n}\sum_{i=1}^{n}\frac{|P_i-O_i|}{O_i}\times 100 \qquad (10)$$

$$EF=1-\frac{\sum_{i=1}^{n}(P_i-O_i)^2}{\sum_{i=1}^{n}(O_i-\bar{O}_i)^2} \qquad (11)$$

Where, P_i shows the estimated or simulated values, O_i indicates the observed (measured) values, $\bar{P}_i$ and $\bar{O}_i$ are respectively the average of the estimated and measured values, and n is the total number of the samples (observed or estimated).

Soil sampling

The loamy soil samples were collected in both disturbed and undisturbed forms from a farm in the Qaramalek area with suitable humidity located in the western Tabriz, Iran, at 38° 5' 59.89" north and 45° 12' 38.57" east.

Preparation of disturbed and undisturbed soil columns

In order to prepare the undisturbed soil columns, polyethylene (PVC) pipes with a diameter of 10 cm and height of 20 cm were used. After being filled with soil up to a height of 15 cm, the pipe was covered with a mesh at the top part to prevent the soil from falling. Then, the pipe along with the undisturbed soil inside it was dug up. The disturbed soil columns were prepared using the same soil (loamy). For this purpose, a sufficient amount of soil was removed from a depth of 0-15 cm with a trowel. After air-dried and lightly beaten, the soil was passed through a 2 mm sieve and filled in the PVC pipes in such a way that its bulk density was equal to that of the undisturbed soil. In order to prevent the direct flow of the tracer solution from the space between the wall of the soil column and the PVC pipe, before the pipes were filled with the soil, their inner walls were coated with melted paraffin. Three columns were prepared with each soil, disturbed and undisturbed, and the columns were used to perform miscible displacement experiments using $CdCl_2$, $ZnCl_2$ and $NiCl_2$ solutions. It is noteworthy that all the experiments were conducted with three repetitions (disturbed and undisturbed soils for each heavy metal and each concentration). In order to conduct the miscible displacement experiments, first the columns were gradually saturated from the bottom with a 0.01 M $CaCl_2$ as a background solution. After saturation, the soil was successively washed out with the background solution, so that the disturbed soil completed its possible natural settlement, and the $CaCl_2$ solution reached an equilibrium throughout both the disturbed and undisturbed soils. A Mariotte's bottle was used to wash out the soil columns with the background solution (0.01 M $CaCl_2$) (Fig.1). The Mariotte's bottle was also used to maintain the constant flow intensity of the solution on the soil column. The bottom of the columns was fixed inside a plastic funnel on a sponge and a wire mesh (Fig.1). The sponge and wire mesh were used to support the weight of the soil column and prevent the soil particles from being washed away from the bottom of the column. The holes of the sponge and wire mesh were large enough to allow water to flow through the soil columns without any restrictions.

By stopping the flow of the background solution in each treatment, a solution of each of the heavy metals ($CdCl_2$, $ZnCl_2$, or $NiCl_2$) with a concentration of 50, 100 and 150 mg/L (C_0) was applied to the column in each of the treatments using another Marionette's bottle (with a constant flow intensity equal to that of the background solution). The effluent was collected from each column immediately after the injection of the solution within 5-15 min and the concentration of the heavy metal (C) was measured. This process continued until the concentration of the heavy metal in the effluent reached a constant value. The measured concentrations were converted into relative concentrations (C/C_0), and the BTCs were obtained by plotting the C/C_0 values against the cumulative time (t). The concentration of the heavy metals Zn, Ni and Cd in the effluents was measured using an atomic absorption device.

RESULTS AND DISCUSSION

The BTCs simulated by Hydrus-1D and CXTFIT

The observed BTCs of the heavy metals Cd, Ni, and Zn with the three initial concentrations of 50, 100 and 150 mg/L in the disturbed and undisturbed loamy soils as well as those simulated by Hydrus-1D and CXTFIT are shown in Figs. 2-4. These graphs showed the capability of the Hydrus and CXTIFIT models to fit the breakthrough curves of cadmium, nickel, and zinc. Examining the BTCs of cadmium in the disturbed and undisturbed soils (Fig. 1) showed that the fitted curves using the Hydrus and CXTIFIT models and the measured curve almost coincided with each other, which was more obvious in the disturbed soils. The BTCs of nickel and zinc were similar to the cadmium curves in the models (Figs. 3 and 4). Also, the evaluation of Figs 2- 4 and comparison of the behavior of the metals showed that the adaptation of the resulting curves in cadmium in both the disturbed and undisturbed soils was more than in the other two metals. The difference between the curves in the undisturbed soil in cadmium was less than the other two metals. The statistical results also confirmed these results (Table 2). According to these Figs., the comparison of the observed and simulated BTCs indicated a high agreement between the Hydrus-1D and CXTFIT models. Similar results have been reported by *Simunek* [40] and *Kanzari et al.* [33].

According to Figs. 2-4, it appears that CXTFIT was more efficient and accurate than Hydrus. However, due to the fact that it is difficult to determine the superiority of CXTFIT over Hydrus only by examining the fitted BTCs, the statistical results were also considered. Accordingly, the statistical results presented in Table 2 also confirm the results of the BTCs. According to this table, it can be concluded that both the models with r^2=0.9 and RMSE=0.06 were highly accurate in simulating the transport of the metals. As it is clear in Figs. 2-4, the models fitted better in the disturbed soil than in the undisturbed soil. This could be due to the disruption of the structure and the increase in the contact surface of the particles in the disturbed soil and the presence of heterogeneity in the undisturbed soil column. Similar results were obtained by *Ersahin et al.* [43] and *Morsali et al.* [29]. According to Figs. 2-4, it was concluded that the BTCs resulting from fitting the CXTFIT and Hydrus-1D models were slightly lower than the those of the measured values, which indicated that the prediction of cadmium, nickel and zinc concentration in the fitting models was lower than the measured concentration of these metals. This condition was especially evident in the undisturbed soil due to the heterogeneity in the particles. Considering that the BTCs related to the initial concentrations of 50, 100, and 150 mg/L were very similar and indistinguishable, it could be concluded that the changes in concentration did not have a significant effect on the simulation of the transport of the heavy metals. In fact, as the concentration changed and increased, only the transport time slightly decreased. Examining the time in the cadmium, nickel and zinc graphs in both types of the soil columns (disturbed and undisturbed) at different initial concentrations showed

Table 1 : The efficiency of some methods of the heavy metals transport studies

Subject	Results	Ref.
Determining the parameters of the convection dispersion equation (CDE) for cadmium transport, estimating the CDE parameters using equilibrium and non-equilibrium models in the CXTFIT program	High efficiency of both equilibrium and non-equilibrium models in cadmium transport modeling	*Zhi-Ming et al.*, [41]
Using Hydrus-1D model to simulate copper, lead and zinc breakthrough in paddy soils	The Hydrus 1D model is a suitable tool for simulating the transfer of heavy metals in paddy soil	*Dao et a*l., [27]
Studying the hydraulic movements of phenol and investigating the movement of solutes using bromide as a tracer, determining the hydrodynamic dispersion coefficient (D) in the vertical and horizontal directions in the soil using the nonlinear least-squares parameter optimization method in the CXTFIT model, using the equilibrium convection dispersion model in HYDRUS 1D to simulate the fate and transport of phenol in vertical and horizontal directions using Freundlich isotherm constants and estimated hydrodynamic parameters	High efficiency of both models in simulation, better simulation of CDE model rather than HYDRUS 1D in transport of phenol in saturated soil in vertical direction	*Pal et al.*, [42]
Modeling of solute transfer process using KCl by CXTFIT and Hydrus-1D models	Estimation of solute transport parameters, lack of significant difference between estimation of solute transport parameters and numerical simulation	*Kanzari et al.*, [33]
Investigation of four models CDE, MIM, FADE and CTRW in the transport of zinc, cadmium and nickel solutes in disturbed and undisturbed loam soil columns using CXTFIT model	More appropriate simulation of heavy metal transport by CDE and MIM models	*Morsali et al.*, [29]
A review of available software for modeling the migration of organic pollutants in groundwater	Choosing the appropriate model depending on the conditions based on applications, usefulness, advantages and limitations	Pietrzak [18]
Investigating the migration of lead (II), nickel (II) and cadmium (II) in single and multi-metallic systems by Langmuir equation and non-equilibrium convection-dispersion	Presenting the process of absorption coefficient Pb>>Cd>Ni in single-phase system and reduction of durability of metals in multi-metal system due to competition effect	*Liu et al.*, [13]

that when the initial concentration increased, the time shortened. In other words, the time to reach equilibrium depended on the initial concentration of the heavy metal. *Simunek* [40] and *Morsali et al*. [29] reached similar results. The results given in Table 2 confirmed this.

Table 1 shows the efficiency of the methods used in the studies of heavy metal transport. Comparing our obtained results with the results presented in Table 1, confirmed that both the models (CXTFIT and Hydrus-1D) had high efficiency and were able to predict the transport of the heavy metals in the soil column reliably.

The transport parameters estimated by Hydrus-1D and CXTFIT

Table 3 gives the transport parameters of the heavy metals Cd, Ni and Zn in the disturbed and undisturbed saturated loamy soil columns estimated by the Hydrus and CXTFIT models. The hydrodynamic dispersion coefficient (D) can be estimated by using soil physical properties and regression relation or by fitting BTCs. Table 3 indicates that the D values estimated by CXTFIT were higher in the undisturbed soil than in the disturbed soil, while those estimated by Hydrus suggested no special trend in the disturbed and undisturbed soils. The higher dispersion coefficients in the undisturbed soil compared to the disturbed soil implied the existence of non-Fickian behavior in the former due to greater heterogeneity. *Huang et al.* [44], *Xiong et al*. [45], *Moradi* and *Mehdinejadiani* [46], and *Morsali et al.* [29] have reported similar results. The comparison of the D values in the undisturbed and disturbed soils in different concentrations showed that, numerically, there was a greater difference in the undisturbed soil, which could be due to different hydrodynamic characteristics in the undisturbed soil. Moreover, soils usually show different hydrodynamic characteristics even with the same components due to the different arrangement of sand, silt and clay particles. This was more visible in the undisturbed soil due to the preservation of the particles arrangement. This result was reported by Palacio *Filho et al.* [47]. The Hydrus model estimated the D values considerably higher than the CXTFIT model. According to Table 2, the estimated D

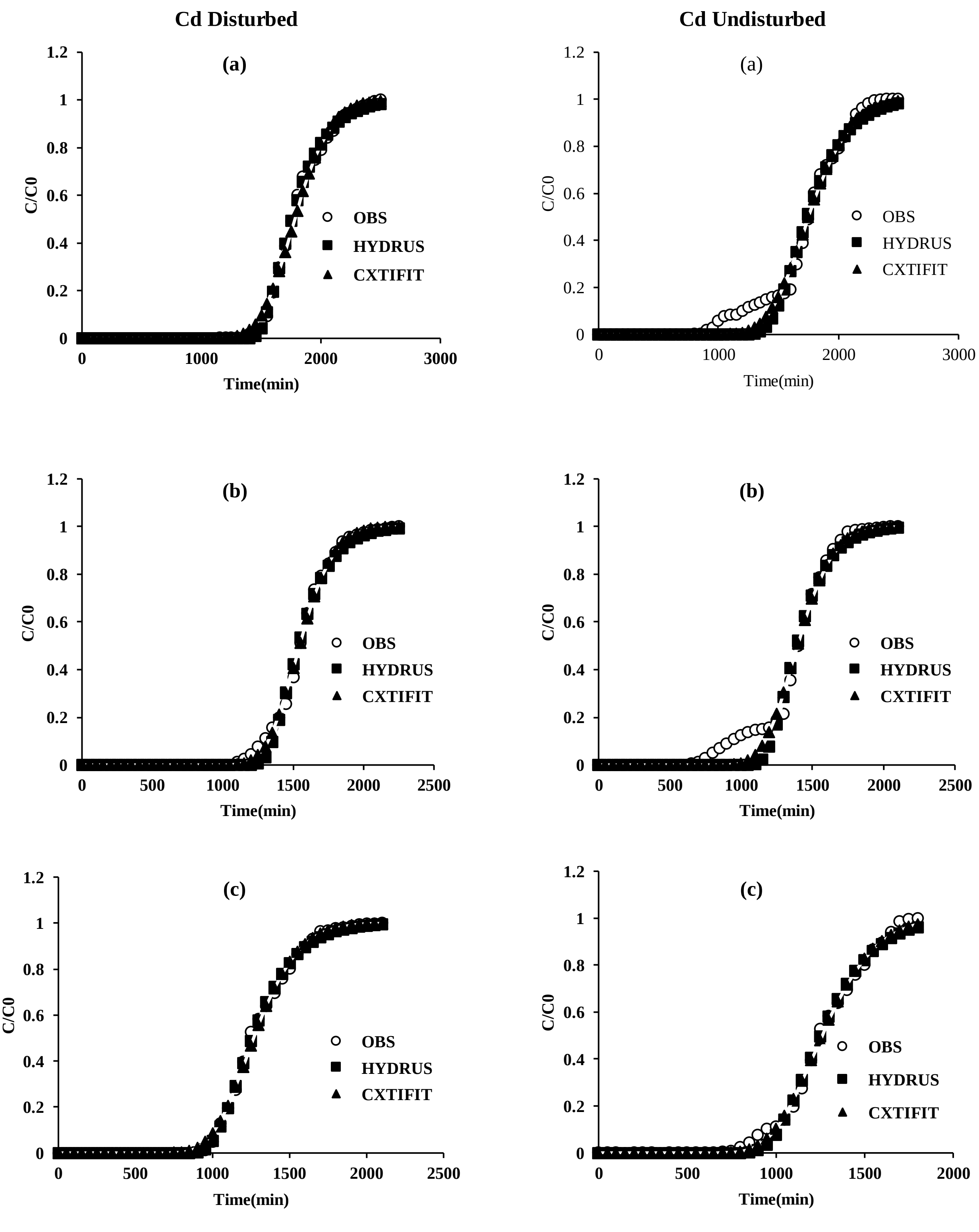

***Fig. 2:** The comparison of Hydrus and CXTFIT with the observed values in different concentrations of Cd in the disturbed and undisturbed soil columns*
(a) C_0=50 mg/L, (b) C_0=100 mg/L, (c) C_0=150 mg/L

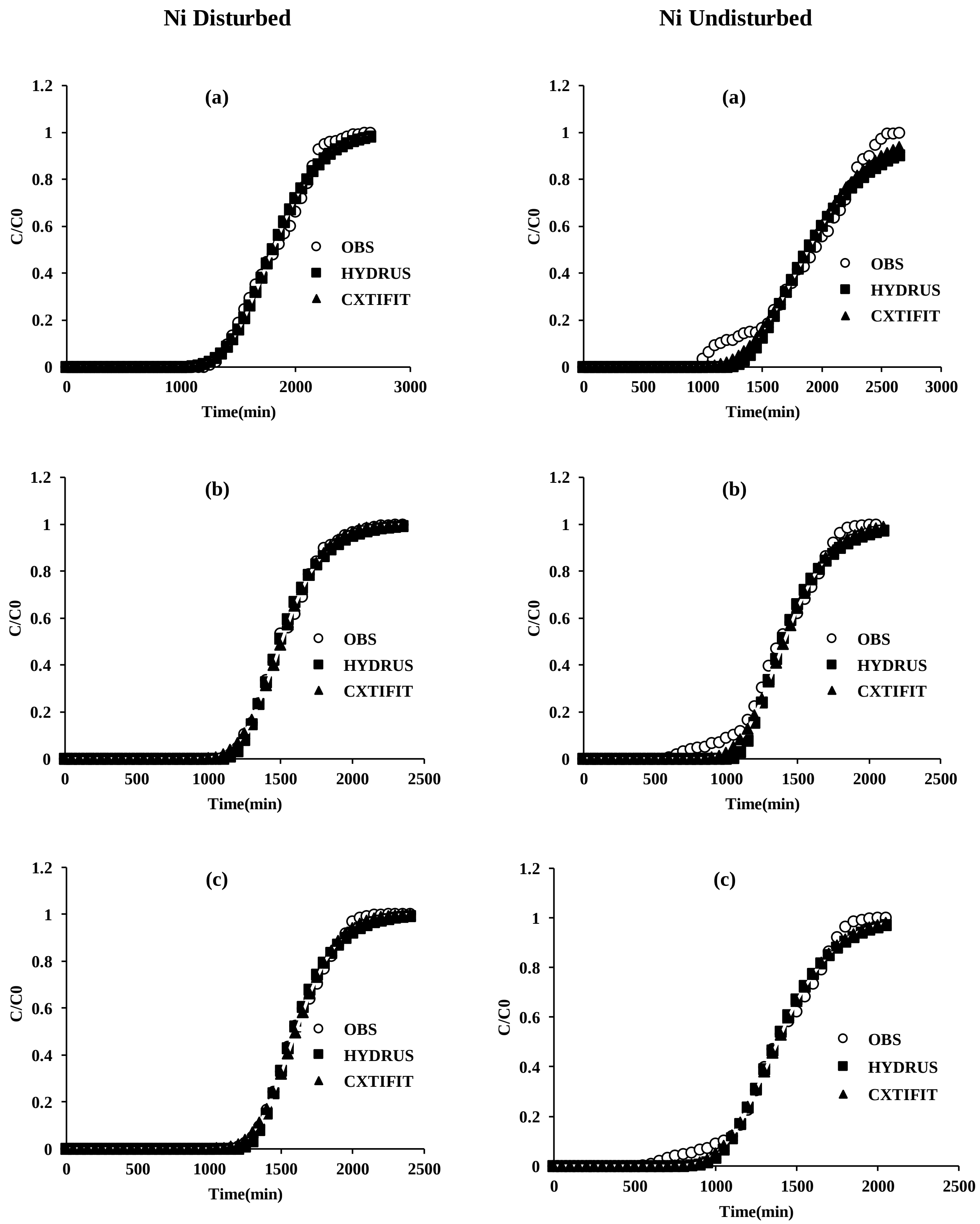

Fig. 3: The comparison of Hydrus and CXTFIT with the observed values in different concentrations of Ni in the disturbed and undisturbed soil columns
(a) C_0=50 mg/L, (b) C_0=100 mg/L, (c) C_0=150 mg/L

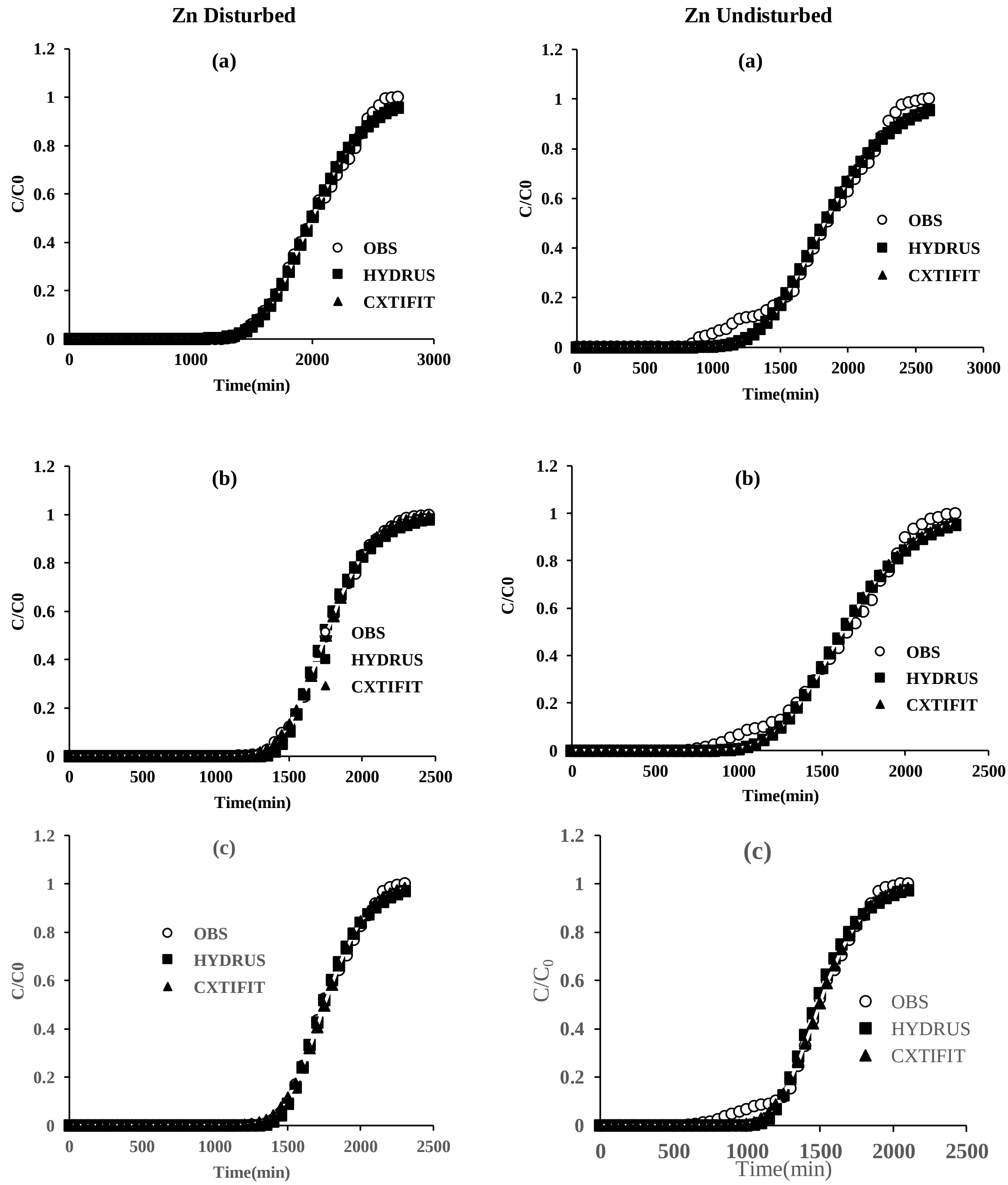

Fig. 4. The comparison of Hydrus and CXTFIT with the observed values in different concentrations of Zn in the disturbed and undisturbed soil columns
(a) C_0=50 mg/L, (b) C_0=100 mg/L, (c) C_0=150 mg/L

values for the heavy metals followed the trend of Cd≥Zn≥Ni, which is consistent with the results obtained by Morsali et al. [29]. The trend of D could be due to the ionic radius of Cd, Zn and Ni. [48, 13]. The results of Table 3 showed that in both the disturbed and undisturbed soil columns, the retardation factor followed the trend

Table 2: The values of r^2, RMSE, MRE and EF obtained from the simulation by Hydrus-1D and CXTFIT

Heavy metal	Soil column	Concentration	r^2		RMSE		MRE		EF	
			Hydrus	CXTFIT	Hydrus	CXTFIT	Hydrus	CXTFIT	Hydrus	CXTFIT
Cd	Disturbed	50	0.99940765	0.997329	0.00974116	0.02026	59.4814893	74.91508	0.99938016	0.997319
		100	0.99680579	0.998804	0.02444555	0.014426	60.1289065	52.56766	0.99642642	0.998755
		150	0.9992588	0.998661	0.01187875	0.015782	47.6706082	270.2265	0.99921656	0.998617
	Undisturbed	50	0.98689201	0.990031	0.04969731	0.042066	60.3356186	57.676	0.98308527	0.987881
		100	0.98749792	0.990396	0.05301623	0.044689	58.6299580	55.74216	0.98302465	0.987938
		150	0.99569506	0.997262	0.02593964	0.02003	55.2532551	50.76318	0.99515218	0.997109
Ni	Disturbed	50	0.99431860	0.996033	0.03124210	0.025506	52.4522583	103.485	0.99358465	0.995724
		100	0.99879231	0.999192	0.01550685	0.011952	51.4237695	82.24072	0.99862641	0.999184
		150	0.99848120	0.999084	0.01831233	0.01283	54.7425324	69.4558	0.99803524	0.999035
	Undisturbed	50	0.97764513	0.985207	0.05786813	0.044356	56.8642414	51.18944	0.97188844	0.983484
		100	0.99049100	0.994327	0.04398072	0.033015	55.7332703	51.62866	0.98716301	0.992766
		150	0.99406499	0.995563	0.0326039	0.027838	51.2684073	49.10427	0.99271295	0.994688
Zn	Disturbed	50	0.99706322	0.996947	0.01883874	0.019	70.4984727	67.31667	0.99693952	0.996887
		100	0.99880645	0.999692	0.01460626	0.006875	58.9520300	48.08805	0.99856937	0.999683
		150	0.99872783	0.998664	0.01360664	0.013323	55.9426830	76.72494	0.99856278	0.998622
	Undisturbed	50	0.98970669	0.98962	0.03953742	0.039525	52.4460651	52.79487	0.98767075	0.987678
		100	0.99086139	0.991287	0.03725210	0.036094	53.0561143	52.95422	0.98925187	0.98991
		150	0.99235778	0.996078	0.03425578	0.026016	58.389243	55.25006	0.99157600	0.995141

Table 3. The transport parameters estimated by Hydrus-1D and CXTFIT

Heavy metal	Soil column	Concentration	Hydrus-1D		CXTFIT	
			D	R	D	R
Cd	Disturbed	50	0.51697	19.4391	0.0125	11.8
		100	0.34904	7.9069	0.0111	10.3
		150	0.53166	4.51582	0.0235	8.41
	Undisturbed	50	0.39962	13.6328	0.0182	11.7
		100	0.37193	7.24281	0.0146	9.3
		150	0.50669	8.2556	0.0307	8.36
Ni	Disturbed	50	0.27055	8.43384	0.0252	12
		100	0.45474	7.32511	0.0175	10
		150	0.40226	5.74188	0.0151	10.7
	Undisturbed	50	0.11078	19.1315	0.0383	12.5
		100	0.76251	5.91898	0.0225	9.15
		150	0.46152	3.54602	0.0172	9.92
Zn	Disturbed	50	0.24113	9.18545	0.0241	13.2
		100	0.36825	7.97818	0.0144	11.7
		150	0.30044	5.4	0.0128	11.7
	Undisturbed	50	0.34864	21.5115	0.0334	11.6
		100	0.35909	4.61772	0.033	10.7
		150	0.42922	9.8	0.0203	10.7

Of Zn>Ni>Cd, indicating the greater mobility of Cd than the other two heavy metals. According to the research conducted by *Tyler* and *McBride* [49] on the mobility of heavy metals in organic and mineral soils, the result of the present study (Zn>Ni>Cd) is confirmed. The findings of the investigation made by *Morsali et al*. [29] also signifies the same trend as the results obtained in the present research.

As the parameter R indicates the amount of adsorption, taking into account the capacity of each of these heavy metals for hydrolysis, a similar trend for their adsorption (Cu>Zn>Ni>Cd) was reported by *Brumme*r [48]. As the concentration increased, the retardation factors of Zn, Cd and Ni decreased, expressing a decrease in the adsorption. *Tiwari et al*. [50] concluded that the relation between initial concentration and changes in adsorption is inverse and unpredictable. This is probably due to the competition between the heavy metals for the vacant adsorption sites. At low initial concentrations, the ratio of the vacant adsorption sites to the heavy metals is high. As a result, adsorption occurs at a significantly higher rate. As the initial concentration increases, the adsorption rate decreases due to the accumulation of the ions in the vacant adsorption sites. *Morsali et al*. [29] reported similar results.

Statistical analysis

The results of the quantitative evaluation of Hydrus-1D and CXTFIT in simulating the transport of Cd, Ni and Zn in the disturbed and undisturbed soil columns are presented in Table 2. According to the results (table 2), in all three metals (cadmium, nickel and zinc), r^2 >0.99, RMSE > 0.06, EF value >0.98, which indicated the high efficiency of the models in describing the behavior of heavy metals. The values of r^2 and RMSE in Hydrus-1D and CXTFIT were acceptable, and for the two models were close together. The values of r^2 and EF higher than 0.99 in both the models indicated their ability to simulate the transport of Cd, Ni and Zn in the disturbed and undisturbed soils. Nonetheless, the higher values of r^2 and EF and lower values of RMSE and MRE in CXTFIT than in Hydrus implied a relatively greater accuracy and efficiency of the former model. However, no major difference was observed between the accuracy of the two models.

CONCLUSIONS

Transport behavior of contaminants, especially heavy metals, in soil and water is important to describe. Mathematical models are usually used as efficient tools in studies and management of solute transport in porous media. In this study, the efficiency of the numerical Hydrus-1D and analytical CXTFIT models in simulating the transport of the heavy metals cadmium, nickel and zinc in two disturbed and undisturbed loamy soils were investigated graphically and statistically. The results showed a high agreement between the Hydrus-1D and CXTFIT models, and no major difference was observed between them. However, compared to Hydrus-1D, the CXTFIT model had higher values of the statistical indices r^2 and EF and lower values of RMSE and MRE, and therefore showed a better fit. Also, the results indicated a better fit of the models in the disturbed soil than in the undisturbed soil due to the disturbance in the structure of the disturbed soil. The dispersion coefficient of Cd was higher compared to the other two heavy metals. This could be due to the difference in the ionic radius of Cd, Ni and Zn. Owing to the greater mobility of Cd, its retardation factor was smaller than those of the other two heavy metals. Considering the fact that the present results were obtained in laboratory conditions, in order to make a more reliable judgment on the accuracy of the models, further studies are needed to be conducted on other contaminants in field conditions and cultivated lands.

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