Effect of initial concentration and input flux on equilibrium and non-equilibrium transport of Zn in soil columns

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Abstract

In order to accurately predict contaminant transport in soil, the processes and factors affecting on this phenomenon should be identified, measured and mathematically defined. The amount of initial concentration and input flux (release rate) of contaminant are among these factors. In this study, transport of the heavy metal Zn in saturated sandy soil columns was simulated and evaluated by the equilibrium and non-equilibrium models. Also, the effects of initial concentration and input flux on Zn transport were investigated by choosing three levels of initial concentration (10, 50 and 100 mg L⁻¹) and input flux of 0.5K_s, 1K_s and 1.5K_s. The results showed that for simulating the Zn transport in the columns containing the initial concentration of 50 and 100 mg L⁻¹, the equilibrium model and for the columns with the initial concentration of 10 mg L⁻¹, the physical non-equilibrium mobile-immobile model had a better performance. The initial concentration and the adsorption (retardation factor) were inversely and linearly related to each other; while the input flux was directly and linearly proportional to the adsorption. The increase in initial concentration of Zn from 10 to 50 and from 50 to 100 mg L⁻¹ and under the input flux of 1K_s decreased the amount of Zn adsorption by 13.38% and 57.71%, respectively. The increase in the input flux from 0.5 to 1K_s and from 1 to 1.5K_s and under an initial concentration of 100 mg L⁻¹ resulted in an increase of 34.79% and 17.88%, respectively, in the amount of Zn adsorption in the soil columns.

Keywords CXTFIT software · Peclet number · Retardation factor · Sandy soil · Zn

Introduction

Most of the heavy metals such as Zn are essential for the health of plants and animals. However, sometimes due to the abundance of contamination sources, the concentration of these metals in the environment exceeds the normal limit and results in toxicity. The contamination sources include mainly industrial waste water from factories and mines. In many cases, contamination of surface water and groundwater by heavy metals can affect human health (Sanfilippo et al. 2001; Santore et al. 2002). Zn along with Cu, after Cr, has the highest concentration in urban sewage (Dowdy and

Volk 1983). Studies have shown that among the heavy metals that added to the soil in different ways, the probability of Zn transfer to groundwater is higher than the rest (Alloway 1990). Therefore, the study of adsorption and retention of this heavy metal is of particular importance.

Accurate and reliable prediction of the solute movement in soil subsurface requires a proper understanding of how the solutes are adsorbed and dispersed based on the soil constituents in each region (Pang et al. 2002). Local equilibrium conditions are only valid when solute transport is in a homogenous porous medium and sorption is linear and reversible (Pang et al. 2002). However, the natural condition of an aquifer is different from the equilibrium condition, which is called non-equilibrium condition. In non-equilibrium condition, contaminant transport in soil can be subject to the physical conditions of the soil layers (due to the characteristics of the aquifer heterogeneity, preferential flow and kinetic diffusion) or their chemical conditions (due to the kinetic sorption/ion exchange or hysteretic sorption). Also, the effect of water velocity in the porous medium should

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not be neglected (although it is ignored in the equilibrium condition) (Pang et al. 2002).

The concentration of contaminants in groundwater depends on the amount, concentration and nature of heavy metals as well as their release rate in the contamination source. To accurately predict the contaminant transport in the soil, it is necessary to identify and measure the impact of processes and important factors, and to define them mathematically and reliably. The initial concentration and the inlet flux (release rate) of contaminants are among these factors. However, little researches have been conducted about them. Singh et al. (2006) used Zn concentrations of 1–5 mg L⁻¹ (6–3 mg kg⁻¹ Zn) to experiment Zn adsorption isotherm in four soils. As expected, Zn adsorption increased with increasing concentrations in all the four soils, but the amount of this increase depended on the soil type. Also, the cumulative desorption content of Zn increased with increasing its concentrations, although the desorption amounts and patterns of natural and added Zn were different between the soils. They attributed the difference between the desorption amounts and patterns of Zn in these soils to the differences in (1) the total amount of Zn adsorbed on the soil particles, (2) soil properties such as pH and CEC (cation exchange capacity) and (3) the types, amounts and relationships of soil components on which Zn has been adsorbed. In a research by Tiwari et al. (2007), an increase in the initial concentration of Zn from 50 to 100, from 100 to 150, from 150 to 200 and from 200 to 250 mg L⁻¹, resulted in an increase of 83, 47, 28 and 21% in adsorption, respectively. In other words, the effect of increasing concentration on absorption gradually decreased and its trend was nonlinear and unpredictable. In addition to the initial concentration, the influence of pore-water velocity on contaminant transport has attracted a lot of attention which can be referred to Bajracharya and Barry (1997) and Pang and Close (1999a) research in conservative tracers, Jarvis (2007), Pang and Close (1999b) and Pang et al. (2002) research in the adsorption/desorption of reactive (non-conservative) contaminants and Lapworth et al. (2012) and Jarvis (2007) research in the transport of organic contaminants.

To our knowledge, there are little researches on the effect of initial concentration and pore-water velocity (or inlet flux) on the equilibrium and non-equilibrium transport of heavy metals especially Zn. The aim of this study is to evaluate the efficiency of equilibrium and non-equilibrium models for describing Zn transport in a saturated sandy soil column and to investigate the effect of initial concentration and input flux on its transport. For this purpose, three levels of initial concentration of 10, 50 and 100 mg L⁻¹ and three input flux of 0.5K_s, 1K_s and 1.5K_s were chosen. The CXTFIT2.1 software was used to estimate the transport parameters as well as simulate the equilibrium and non-equilibrium transport of Zn.

Materials and methods

Model theory

Equilibrium model or convection–dispersion equation

The convection–dispersion equation (CDE) for one-dimensional transport of a reactive solute under sorption process in a homogeneous porous medium is described as follows (Logan 2013):

$$R \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v \frac{\partial c_r}{\partial x} \quad (1)$$

where c_r is the resident concentration of the liquid phase (ML⁻³), D is the dispersion coefficient (L² T⁻¹), R is the retardation factor (–), v is the average pore-water velocity (L² T⁻¹), and x (L) and t (T) are distance and time, respectively.

Using the dimensionless parameters, Eq. 1 can be rewritten as follows:

$$R \frac{\partial C_r}{\partial T} = \frac{1}{P} \frac{\partial^2 C_r}{\partial Z^2} - \frac{\partial C_r}{\partial Z} \quad (2a)$$

where

$$T = \frac{vt}{L}, \quad Z = \frac{x}{L}, \quad P = \frac{vL}{D}, \quad R = 1 + \frac{\rho_b K_d}{\theta}, \quad C_r = \frac{c_r}{c_0} \quad (2b)$$

a C_r is the dimensionless concentration, T is the dimensionless time, L is the length of soil column (L), Z is the dimensionless distance (LL⁻¹), P is the Peclet number (–), ρ_b is soil bulk density (ML⁻³), K_d is the linear adsorption distribution coefficient (M⁻¹ L³), θ is the soil volumetric water content which is equal to the soil porosity in saturation condition (%), c_r is the resident concentration of the liquid phase (ML⁻³), and c_0 is the input concentration (ML⁻³).

Non-equilibrium or mobile–immobile model

The physical non-equilibrium model hypothesizes that soil consists of two mobile and immobile regions. In this model, it is assumed that the transport of solutes in soil occurs only in the mobile regions and the transport of solutes from the mobile region to the immobile region occurs through diffusion. Although the physical and chemical models of non-equilibrium transport equation are based on two different concepts, they can be defined in dimensionless form as the same equations (Torride et al. 2003). For transport of a reactive solute under sorption condition, the following equations are defined (Gao et al. 2010; Selim 2014):

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} - \omega(C_1 - C_2) \quad (3)$$

Table 1 Dimensionless parameters of the two-region model (TRM) (Van Genuchten and Wagenet 1989)

Dimensionless parameters	Equations	Dimensionless parameters	Equations
Z	$\frac{z}{L}$	β	$\frac{\theta_m + f\rho_b K_d}{\theta + \rho_b K_d}$
P	$\frac{VL}{D}$	ω	$\frac{\alpha L}{\theta V}$
R	$1 + \frac{\rho_b K_d}{\theta}$	C_1	$\frac{C_m}{C_0}$
C_r	$\frac{C}{C_0}$	C_2	$\frac{C_{im}}{C_0}$

$$(1 - \beta)R \frac{\partial C_2}{\partial T} = \omega(C_1 - C_2). \quad (4)$$

where β is the dimensionless non-equilibrium partitioning coefficient, ω is the dimensionless transfer coefficient, and the subscripts 1 and 2 refer to equilibrium and non-equilibrium sites, respectively. The dimensionless parameters for the physical non-equilibrium condition are presented in Table 1.

In Table 1, the subscripts *im* and *m* represent the immobile and mobile conditions in the soil liquid phase, respectively. *f* shows the fraction of the equilibrium sorption sites which are defined by the mobile region of the liquid phase for the two-region physical (TRM) condition. α is the first-order coefficient of solute transport in the TRM condition which controls the amount of solute exchange between the two mobile and immobile regions.

Soil columns preparation

The soils samples were collected from the research station of the Faculty of Agriculture and Natural Resources, Islamic Azad University of Tabriz, with a longitude of 38°02'77.88' N and a latitude of 46°43'97.07''E from the depths of 0–15 cm. Soil was air-dried and passed through a 2-mm sieve in the laboratory. 18 PVC columns with a height of 40 cm and a diameter of 6.16 cm were used to conduct the experiment. At the bottom of each column, a plastic funnel was embedded to collect the outflow. At the top of each funnel, a wired plate was placed to hold the weight of the top soil and a porous plate was placed to prevent washing away of soil. To overflow the solution, an outlet was installed at the 10 cm above the columns to keep the water head constant on each column. The outlet height was adjustable according to the required flow rate. Some physical and chemical properties of the used soil are given in Table 2. The hydrometer method was used to determine the soil texture. Soil reaction (pH) was determined in 1.0:2.5 soil–water suspension (Kacar and Inal 1972; Durak et al. 2010). Cation exchange capacity (CEC) was determined by saturating the samples

Table 2 The physical and chemical properties of the soil

Soil property	Value
Sand (%)	80.5
Silt (%)	14
Clay (%)	5.5
Bulk density (g cm ⁻³)	1.31
Saturated water content (%)	44.2
pH of soil saturation extract	8.2
EC of soil saturation extract (μS cm ⁻¹)	1013
Cation exchange capacity (cmol kg ⁻¹)	7
Calcium carbonate equivalent (%)	2.92
Organic carbon (%)	0.078

with sodium acetate; electrical conductivity (EC) in 1.0:2.5 soil–water saturation and organic carbon (OC) using Walkley–Black method (Durak et al. 2007, 2010).

Filling and saturation the soil columns

The PVC columns were filled with 780 g of air-dried, 2-mm sieved soil. Then, the soil columns were saturated from the bottom with a Ca(NO₃)₂ solution of 0.01 molar (as the background solution). The saturation of soil columns was carried out without making any hydrostatic pressure in the wetting front to prevent the air entrapment. This was performed by putting the bottom of the soil columns at an equivalent height to the surface of the background solution. The background solution rose due to capillarity and saturated the column from the bottom. By stopping the capillary rise, the solution level was raised 1 cm to complete the saturation process and reach the level of the background solution to the soil surface. To ensure full saturation, at the end, a 1 cm height of solution was allowed to be on the soil surface. After saturation process using successive washings with the background solution, the soil was allowed to complete its natural compaction. The soil bulk density in all the columns after soil compaction was 1.31 g cm⁻³.

In order to extract the exchangeable Zn with calcium, the columns were washed with the background solution (0.01 molar of Ca(NO₃)₂ solution). For this purpose, a steady flow was established for 24 h in the columns. Then, the flow was stopped and the soil was kept saturated for 24 h. Again, the flow of background solution was established and washing was continued until the Zn concentration reached the detection limit of the atomic absorption device. After the saturation process and soil compaction, the saturated hydraulic conductivity of each column was measured by Darcy method (Klute 1992; Klute and Dirksen 1986). The reason for choosing salt of nitrate instead of chloride salt as the background solution is that the nitrate is less complex with Zn²⁺ compared to chloride. In addition, compared to

chloride, nitrate is less interfering with Zn measuring using the atomic absorption spectroscopy (AAS) (Boekhold et al. 1993a, b).

Concentration pulses and flux regulation

In order to obtain the breakthrough curves, Zn with concentrations of 10, 50 and 100 mg L⁻¹ (prepared in 0.01 molar of Ca(NO₃)₂) was used as input solution (tracer) with pulse-injection technic. In all the experiments, the columns were placed vertically and a steady flow was established through stabilizing a constant water pressure at the inlet (upper surface of the columns) and outlet (lower surface). At certain times, the output solution was sampled and its Zn concentration was measured using the atomic absorption spectroscopy (AAS). To adjust the flux of 0.5K_s, 1K_s and 1.5K_s, the outlet was embedded at 20, 10 and 0.2 cm above the bottom of the column, respectively.

Results and discussion

Transport parameters and Zn breakthrough curves simulated by the equilibrium and non-equilibrium models

The estimated parameters from simulation of Zn transport in saturated sandy soil columns by equilibrium and non-equilibrium models are presented in Table 3. The parameters ω and β can be considered as indices of identifying the equilibrium and non-equilibrium transport conditions, so that $\omega \geq 100$ and $\beta = 1$ represent the equilibrium transport and $\omega \ll 100$ and $\beta \ll 1$ indicate non-equilibrium transport in the porous medium (Pang et al. 2002). $\beta \approx 1$ for a neutral and inactive solute indicates a lack of stagnant water and therefore is a reason for the existence of physical equilibrium, while for a sorbent solute, it implies that all the sorption sites are instantaneously occupied by the solutes, resulting in local equilibrium. $\beta < 1$ indicates that there is a fraction of stagnant water or rate-limited sorption sites and therefore non-equilibrium conditions. Higher values of ω represent rapid adsorption, and its lower values indicate adsorption with limitation and delay. For $\omega > 100$, the solute transport is equilibrium (Torridge et al. 2003). However, for $\beta = 1$, the transport is equilibrium and the value of ω is not determinative and can have any value (Hillel 2012). The values of ω and β parameters in this study (Table 3) indicate equilibrium transport of Zn in columns with the initial concentrations of 50 and 100 mg L⁻¹, and physical non-equilibrium transport in columns with the initial concentration of 10 mg L⁻¹. In general, the equilibrium model (CDE) is valid when the solute transport in soil follows the Fick's law. According to Fick's law, solute dispersion in soil is linearly proportional

Table 3 The estimated parameters from simulation of Zn transport in sandy soil columns by equilibrium and non-equilibrium models under different initial concentrations and input flux

Initial concentra- tion (mg L ⁻¹)	Input flux (cm h ⁻¹)	Equilibrium model					Non-equilibrium model								
		V (cm h ⁻¹)	D (cm ² h ⁻¹)	R (-)	Pe (-)	r ²	MSE	V (cm h ⁻¹)	D (cm ² h ⁻¹)	R (-)	Pe (-)	β (-)	ω (h ⁻¹)	r ²	MSE
10	0.5Ks	7.03	9.68	223.0	14.5	0.980	0.0012	7.06	4.00	246.2	35.3	0.35	0.85	0.985	0.0009
	1Ks	12.26	16.88	389.0	14.5	0.980	0.0012	12.09	6.91	421.2	35.0	0.35	0.85	0.985	0.0009
	1.5Ks	24.83	34.20	788.2	14.5	0.980	0.0012	17.70	10.09	616.7	35.1	0.35	0.85	0.985	0.0009
	0.5Ks	11.33	4.85	207.8	46.7	0.973	0.0009	7.80	8.33	144.9	18.7	0.99	100	0.935	0.0024
50	1Ks	16.13	6.91	296.0	46.7	0.973	0.0009	14.07	15.12	260.6	18.6	0.99	100	0.935	0.0024
	1.5Ks	22.06	9.45	404.7	46.7	0.973	0.0009	20.47	22.56	367.3	18.1	0.99	100	0.935	0.0024
	0.5Ks	12.5	22.06	73.1	11.3	0.945	0.0024	12.45	22.62	71.86	11.0	0.99	100	0.945	0.0025
	1Ks	19.53	34.47	114.2	11.3	0.945	0.0024	19.09	34.73	110.2	11.0	0.99	100	0.945	0.0025
100	1.5Ks	29.18	51.76	171.5	11.3	0.945	0.0024	23.25	42.31	134.2	11.0	0.99	100	0.945	0.0025

to concentration gradient. It seems that in sandy soils this condition is true and the equilibrium model is more applicable. According to Table 3, it is expected that the CDE (which is based on the equilibrium transport of solute) to be more effective in simulating Zn transport in columns with the initial concentrations of 50 and 100 mg L⁻¹ and the non-equilibrium physical mobile–immobile model (MIM) to be more effective in the case of columns with the initial concentration of 10 mg L⁻¹. The breakthrough curves in Fig. 1 and the statistics in Table 3 (mean squared error (MSE) and coefficient of determination (r^2)) confirm this.

Fig. 1 Comparison of Zn breakthrough curves obtained from the equilibrium and non-equilibrium models in the saturated sandy columns with the initial concentration of **a** 10, **b** 50 and **c** 100 mg L⁻¹

Peclet number (Pe) is defined as the ratio of advective transport rate to diffusive transport rate (Table 1). This number is one of the factors affecting the breakthrough curve and shows asymmetry and skewness or kurtosis of the breakthrough curve. The low value of Peclet number indicates more diffusive and hence more asymmetry (Hillel 2012). The low values of this number in Table 3 and the kurtosis of breakthrough curve in Fig. 1c confirmed this in the present study. Also, according to Table 3, the values of Peclet number are identical for the columns with the same input concentration and different input flux, indicating the matching and overlapping of the breakthrough curves obtained from these columns. For example, in Fig. 2, the breakthrough curves of the columns with an input concentration of 100 mg L⁻¹ match each other.

The effect of initial concentration

In order to investigate the effect of initial concentration of Zn on its transport, the effect of concentration on the transport parameters, namely the Peclet number (in terms of the dispersion coefficient and flow velocity) and the retardation factor (for the expression of adsorption), was investigated. As shown in Fig. 3 and Table 3, the initial concentration is inversely proportional to the Peclet number, and their relationship is as a power function independent of the inlet flux. Increasing the initial concentration has led to reduction in miscibility, and, as a result, the displacement throughout the columns has slowed down. The dominant process in moving Zn throughout the column, with the convection mechanism at a lower initial concentration, has tended to the dispersion and diffusion mechanism at higher concentrations. In other words, in lower concentrations of Zn, the convection mechanism has an important role in transport and, with increasing initial concentrations, the role of dispersion and diffusion mechanism becomes more pronounced.

Similar to the Peclet number, the initial concentration is also inversely proportional to the retardation factor, but

Fig. 2 The Zn breakthrough curves obtained from the equilibrium model in the sandy columns with an initial concentration of 100 mg L⁻¹ under different inlet flux

Fig. 3 The effect of changes in the initial concentration and the input flux on Zn transport parameters in saturated sandy columns

this relationship is linear and is a function of the input flux. In fact, with increasing the initial concentration of Zn, the amount of adsorption has decreased in the columns. This can be explained by the fact that at low concentrations, the ratio of adsorbable solute to the number of adsorption sites is low, and hence, a large amount of adsorption occurs. As the concentration increases, the number of adsorption sites decreases compared to the amount of adsorbable solute, and therefore, the adsorption percentage decreases from low concentrations to high concentrations. Also, the slope of these changes is more in the high input flux than the low input flux (Fig. 3). For example, an increase in the initial concentration of Zn from 10 to 50 and from 50 to 100 mg L⁻¹ under the input flux of 0.5K_s has resulted in a decrease of 41.14% and 50.45%, respectively, in the adsorption amount (retardation factor), while the decrease of adsorption under the input flux of 1K_s is 38.13% and 57.71% and under the input flux of 1.5K_s is 40.44 and 63.46, respectively. Similarly, Tiwari et al. (2007) have reported the effect of increasing concentrations on adsorption reduction.

The effect of input flux (release rate)

The effect of the input flux (release rate) on the Zn transport is shown in Table 3 and Fig. 3. According to Table 3, although the pore-water velocity and dispersion coefficient

are influenced by the inlet flux and there is a linear relationship between them, but since the rate of changes in these parameters with the flux is constant, in general, their ratio (in term of the Peclet number) is independent of the input flux and is constant for various input flux. This can be seen in Fig. 3. Unlike the Peclet number, the retardation factor has a direct and linear relationship with the input flux. In other words, with increasing the input flux, the amount of Zn adsorption increases throughout the columns. This can be attributed to the increase in dispersivity by increasing the input flux. By increasing the input flux, not only the amount of convection increases considerably, but even the dispersion into the aggregates that mainly controlled by molecular diffusion, becomes a function of convection and results in artificial adsorption. Artificial adsorption is not only due to the input flux, but also the inflow concentration has an effect on it. The slope of these changes in low concentrations is more than the high concentrations (see Fig. 3). For example, an increase in the input flux from 0.5 to 1K_s and from 1 to 1.5K_s at an initial concentration of 10 mg L⁻¹ has resulted in an increase of 41.55% and 31.70%, respectively, in the adsorption amount (retardation factor), while the adsorption amount has increased by 34.79% and 17.88%, respectively, under the same input flux and at the initial concentration of 100 mg L⁻¹. The effect of input flux (pore-water velocity)

on retardation factor has been reported by other researchers such as Pang et al. (2002), Shimojima and Sharma (1995) and Ptacek and Gillham (1992).

Conclusion

The concentration of contaminants in groundwater depends on the amount and nature of heavy metals in the source of contamination and their rate of release (input flux). In this study, in order to investigate the effect of initial concentration and input flux on Zn transport, the Zn concentrations of 10, 50 and 100 mg L⁻¹ (prepared in the 0.01 molar calcium nitrate solution) under the input flux of 0.5K_s, 1K_s and 1.5K_s as an input solution (tracer) were pulse-injected into sandy columns for derivation of breakthrough curves. The effect of initial concentration and the input flux on the transport parameters, namely the Peclet number (in terms of the dispersion coefficient and flow velocity) and the retardation factor (for the expression of adsorption), were investigated. The results showed that the initial concentration is inversely related to the Peclet number, and this relationship is as a power function and independent of the input flux. Similar to the Peclet number, the initial concentration is also inversely related to the retardation factor, but their relationship is linear and is a function of the input flux. Also, the slope of these changes was found to be more in the low concentrations than the higher concentrations. The fitting of the measured data to the equilibrium and non-equilibrium models showed that for simulating the Zn transport in the columns with the initial concentrations of 50 and 100 mg L⁻¹, the equilibrium model is more appropriate, while in the case of the columns with an initial concentration of 10 mg L⁻¹, the physical non-equilibrium mobile–immobile model has a better performance.

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