Mathematical model for reactive transport of heavy metals in soil column: Based on PHREEQC and HP1 simulators

Fatemeh Izadi Tameh[1], Gholamreza Asadollahfardi[*2] and Ahmad Khodadadi Darban[3]

[1]Department of Civil and Environmental Engineering, Kharazmi University, Tehran, Iran
[2]Department of Civil Engineering, Kharazmi University, Tehran, Iran
[3]Department of Mining Engineering, Tarbiat Modares University, Tehran, Iran

Abstract. Mining activities play a significant role in environmental pollution by producing large amounts of tailings which comprise heavy metals. The impressive increase in mining activities in recent decades, due to their high influence on the industry of developing countries, duplicates the need for a substantial effort to develop and apply efficient measures of pollution control, mitigation, and abatement. In this study, our objective was to investigate the effect of simulation of the leachate, pH and inflow intensity of transport of Pb^{2+}, Zn^{2+}, and Cd^{2+} through Lakan lead and zinc plant tailings, in Iran, and to evaluate the modeling efficiency by comparing the modeling results and the results obtained from previous column studies. We used the HP1 model and the PHREEQC database to simulate metals transport through a saturated soil column during a 15 day time period. The simulations assumed local equilibrium. As expected, a lower pH and inflow intensity increased metal transport. The retardation of heavy metals followed the order $Zn^{2+}>Pb^{2+}>Cd^{2+}$ and the removal concentrations of Cd, Pb, and Zn at the inflow intensity critical scenario, and Cd and Pb at inflow acidity critical scenario exceeded the allowable EPA and Iranian's 1053 standard thresholds. However, although the simulation results generally agreed well with the results of the column study, improvements are expected by using multi-dimensional models and a kinetic modeling approach for the reactions involved. The results of such investigations will be highly useful for designing preventative strategies to control reactive transport of hazardous metals and minimize their environmental effects.

Keywords: lakan plant tailing; HP1; PHREEQC; heavy metals; Cd, Pb, and Zn; lakan lead and zinc plant

1. Introduction

Despite significant progress in science and technology, environmental problems are increasing at the national, regional, and international levels. Correlations between industrial activities and environmental contamination make it difficult to expect substantial industrial development without some impact on the environment. The production of inorganic wastes in mining operations has always been an important issue and a threat to the environment, especially the subsurface. The

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∗Corresponding author, Professor, E-mail: asadollahfardi@yahoo.com

mining wastes often contain high levels of heavy metals, which constitute a major threat to human populations, aquatic species, plants, ecosystems, and groundwater quality in general because of their biological non-degradability and stability in the environment. Large-scale mining can especially adversely, affect the environment. Iran, as a developing country, still needs to develop much of its mining activities. Unfortunately, a lack of necessary standards for proper processing and waste burial make environmental pollution more probable in Iran. Leaching of heavy metals from surface soils to deeper layers, and the risk of groundwater pollution depend on the retention, mobilization, and transport of heavy metals in soils. Specific adsorption, ion exchange, and precipitation of various solid phases are the main processes responsible for the retention of heavy metals. Previous studies indicate that the pH is one of the most important factors affecting the transport and sorption of heavy metals (Chotpantarat *et al.* 2001). Changes in the chemical composition or the pH of the soil solution may impact the sorption of elements on organic matter or iron oxides.

Decision makers need predictions of the fate of heavy metals in soils to design management strategies that minimize adverse environmental impacts. In recent years, various multi-component reactive transport models have been developed to study the mobility of potentially toxic heavy metals in the subsurface, aiming at an extrapolation in time and space of experimental laboratory data or a prediction prior to the environmental catastrophes. In the case of reactive transport, providing accurate provisions for pollutant transport require 1-an accurate numerical code that integrates the physical processes of water flow and advective-dispersive solute transport with a range of biogeochemical processes, 2-a proper recognition of the major phenomena, and 3-the best set of parameters and data describing them. Many models have been developed to simulate and predict the fate and transport of pollutants in porous media (Šimůnek 2007, Šimůnek 2008b). Wu *et al.* (1998) indicated that at lower pH levels, Cd and Pb precipitation will cause a sharp decrease in their external concentrations. Lefebvre *et al.* (2001) described the coupled physical processes occurring in waste rock piles undergoing acid mine drainage production resulted from the oxidation of sulfides, main pyrite, presents in mine wastes. The oxidation process of pyrite initiated coupled processes of gas transfer by diffusion and convection as well as heat transfer. The physical transfer processes acting in waste rock piles are strongly described and a conceptual model is proposed. Seuntjens *et al.* (2002) studied how physical and chemical properties affected field-scale Cd transport in a heterogeneous soil profile; using Monte Carlo simulations, they demonstrated that variations in field- scale Cd flux were dominated by variations in deposition rate and the parameters of the Freundlich sorption isotherm. Pang *et al.* (2002) described that the breakthrough curves (BTCs) of Cd, Zn, and Pb in gravel columns with pore water velocities ranging from 3 to 60 m/day displayed long tailing, suggesting that non-equilibrium sorption conditions occurred in the gravel columns due to high pore-water velocities. Fala *et al.* (2003) viewed the internal structure and grain size distribution of typical waste rock piles with respect to their effect on internal water flow. HYDRUS 2D software was applied to simulate unsaturated flow within a waste pile, assuming two primary waste materials, different atmospheric conditions, and several geometric configurations. The results indicated water movement can be controlled by introducing fine-grained material layers within the coarser host material. Using geochemical analyses and investigations of samples from mine tailings and water resources adjacent to the Piscinas River in Sardinia, Italy, Concas *et al.* (2005) concluded that a decrease in the pH level increased metal dissolution and transport from mine tailings. Molsen *et al.* (2005) used HYDRUS and POLYMIN models for water flow and reactive transport simulation sulfide-bearing waste rock piles. They described that in the fine-grained layers, the high reactive surface area induces high

oxidation rates, even though capillary forces kept the local moisture content relatively high. Pot *et al.* (2005) used different physical and chemical equilibrium and non-equilibrium transport models to simulate the impact of various rainfall intensities on herbicide transport. Their study showed that physical/chemical, non-equilibrium conditions were dominant. Michel *et al.* (2007) used mathematical and empirical models to investigate nickel and cadmium transport in silty and sandy soils and concluded that a decrease in the pH increases the transport of heavy metals in acidic soils. Dolati Ardejani *et al.* (2008) investigated the pollutant problems associated with the waste produced by a coal washing plant using the Phoenics package to simulate pyrite oxidation and pollution generation from waste dump. Using HP1 model, Jacques *et al.* (2008) further presented that reducing the inflow intensity causes a decrease in the pH level, thereby promoting monovalent cations to adsorb on the cation exchange complex, and bivalent cations to adsorb into the soil solution. Simulating the effect of pH on Pb, Mn, Zn, and Ni transport using HYDRUS-1D, Chotpantarat *et al.* (2001) found that increasing the pH of the inflow solution increases the retardation of heavy metals. They also indicated that the use of a two-site model (TSM) for sorption produced a better match with measured heavy metal BTCs than linear or nonlinear Langmuir type equilibrium models. Grathwohl *et al.* (2013) introduced the featured catchments and describe a methodology of the Water and Earth System Science (WESS) by selecting samples. Maier *et al.* (2013) applied MIN3P to evaluate the water chemistry from the infiltration through soil into the unsaturated zone, transport through bedrocks and granular aquifers to a river to identify zones of steep concentration gradients and high dynamics under transient flow conditions. Their results indicated that subsurface water residence times range from approximately 2 to 2,000 years. Chen and Jiao (2014) applied the PHREEQC 2.0 to determine freshening time and hydro-chemical of coastal groundwater in two brackish aquifers in Shenzhen, china. Their sensitivity analysis indicated that the freshening time was most sensitive to the pore water velocity in the aquifer, while the groundwater chemical composition was more sensitive to the values of cation exchange capacity of the aquifer. Nair *et al.* (2014) used two Surfaces complexation models, electrostatic (ES) and non-electrostatic (NES) models were employed to simulate the sorption behavior of U (VI) on quartz in the absence of Mg, Ca, and Sr and ES model in the presence of alkaline earth metals. The surface reaction constants (log K) for ES and NES models were fitted to experimental data by coupling PEST with PHREEQC. In U (VI)-Mg-quartz, U (VI)-Ca-quartz, and U (VI)-Sr-quartz systems, only the ES model describes the general trend of the experimental data. Beni *et al.* (2014) conducted experiments and modeling of the possible effects of iron oxide coatings on the reactive surface area of calcite in the column. The losses and gains of calcite in the column compartments provided the data basis for modeling the entire experiment with the reactive transport code TOUGHREACT using a kinetic rate law. The simulated calcite changing patterns in the most compartments are consistent with the experiments. Wuana *et al*. (2016) tested some toxic heavy metals from municipal waste dump soil by the castor plant under natural and single or mixed chelant-assisted scenarios in pot microcosms. They suggested that the mixed chelants could be considered as alternative treatments for enhanced phytoextraction and revegetation of degraded waste dump soils.

We attempted to investigate the effect of aqueous pH conditions and inflow intensities on the sorption and transport of three heavy metal ions, Cd^{2+}, Pb^{2+}, and Zn^{2+}, using the HP1 numerical model, to evaluate the model's utility in simulating the transport of heavy metals and to investigate the sorption behavior of heavy metals in soil columns.

2. Materials and methods

2.1 General features of study area

The study was conducted on Lakan lead and zinc processing plant, located 46 km Southwest of Arak City in the Markazi Province, Iran. The geographical coordination of the study area is 33°42'5"N latitude and 49°43'26"E longitude. The Lakan plant is located in a temperate mountainous zone with hot summers and cold winters. Annual variations in temperatures are very high, ranging from -20℃ in the winter to +35℃ in the summer.

2.2 Soil physical and chemical properties

Khodadadi Darban *et al.* (2012) studied the deposited waste material characteristic of the Lakan plant using X-ray fluorescence (XRF) tests. Table 1 presents types and quantities of the elements, containing in a 100 g sample.

Using tailings from the same site, Khodadadi Darban *et al.* (2012) conducted 15 days leaching tests on 180 g samples in three 2.7-cm internal diameter columns in which the tailings occupied heights of 21 cm. The effluent from each column was analyzed after 3, 7, 10, and 15 days. Physical properties of the tailing dam soil as reported by Khodadadi Darban *et al.* (2012) are presented in Table 2. The same properties and times have been considered in our modeling simulations.

The dominant chemical reaction was cation exchange. Particle size (tailing size) as indicated in and Khodadadi Darban *et al.* (2012)'s study, which is the results of their experimental work, was approximately unified and the d80 of tailing assumed about 260 microns (50 mesh). Kinetic reactions were assumed to be in equilibrium status (based on the experimental data). PHREEQC database was then used for simulating relate chemical reactions.

Table 1 Quantities of elements in a 100 g sample

Compounds	Percentage	Compound/Element	Percentage
Na_2O	0.5	MnO	0.3
MgO	0.8	Ni	0.0146
AL_2O_3	3.5	Zn	1.15
SiO_2	66.6	Pb	1.5
SO_3	4.5	Cd	0.005
K_2O	0.7	P_2O_5	0.9
CaO	9.5	Fe_2O_3	2.9
BaO	0.4	LOI	6.73

Table 2 Physical properties of tailing dam soil

Soil Property	Unit	Value
Bulk Volume	(ml)	150
Weight	(g.)	221.77
Pore Volume	(ml)	40

Table 2 Continued

Specific Volume	(ml)	110
Bulk density	(g./ml)	1.48
Specific density	(g./ml)	2.02
Solid fraction	-	0.73
Porosity	-	0.27

2.3 Transport model

We applied HP1version2.2 developed by Jacques and Šimůnek (2010) in our study. The HP1 reactive transport simulator, obtained by weak coupling of HYDRUS-1D and PHREEQC-2, was developed and designed to address multicomponent geochemical transport processes in the vadose zone. The software integrates a broad range of physical and biogeochemical processes, as described in the original manuals of HYDRUS-1D (Šimůnek *et al.* 2008a), PHREEQC-2 (Parkhurst and Appelo 1999), and HP1 (Jacques and Šimůnek 2010). HYDRUS-1D was originally designed mostly for simulating water flow, solute transport, and heat transport in one-dimensional variably saturated media. The program can numerically solve the Richards equation for saturated-unsaturated water flow and the Fickian-based advection-dispersion equation for solute and heat transport. In this software, the solute transport module also considers equilibrium and non-equilibrium advection-dispersion in the liquid phase, and nonlinear equilibrium physical and chemical sorption. Both of the HYDRUS-1D and HP1 models account for soil heterogeneity at the macroscopic scale by using scaling factors (Vogel *et al.* 1988), and at the microscopic scale by using dual-porosity or mobile/immobile type flow models (Fala *et al.* 2003, Šimůnek *et al.* 2003). HP1 implements a weak coupling method in which the governing equations for water flow, heat transport, and solute transport are solved sequentially. The multicomponent reactive transport equations are solved using a non-iterative sequential approach, meaning that the physical part is solved first without any chemical interactions, while the chemical reactions that are uncoupled in space and coupled to the components are solved subsequently (Jacques *et al.* 2008). A flow chart of the operator-splitting approach used in HP1 was described in (Jacques *et al.* 2006). Although operator-splitting errors may occur with this approach. Jacques *et al.* 2006 and Jacques *et al.* 2008) indicated that very accurate results can be determined by carefully selecting the spatial and temporal discretization.

2.3.1 Soil hydraulic properties

Six analytical models are available in HP1 to describe the soil hydraulic properties, including the function of Brooks and Corey (1964), Van Genuchten (1980), and Vogel and Cislerova (1988). In our study, the van Genuchten-Mualem (1980) was used to describe the water retention and hydraulic conductivity ($K(h)$) functions

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{[1 + |\alpha h|^n]^m} & h < 0 \\ \theta_s & h \geq 0 \end{cases} \tag{1}$$

$$K(h) = K_s S_e^l [1 - (1 - S_e^{1/m})^m]^2 \tag{2}$$

$$S_e(h) = \frac{1}{[1+|\alpha h|^n]^m}$$ (3)

Where $\theta(h)$ is the soil water content [-] as a function of the pressure head; h[L], θ_s is the saturated water content [-]; θ_r is the residual water content [-]; K_s is the saturated hydraulic conductivity [LT^{-1}]. S_e is the effective water content [-]; α, m, and n are empirical parameters of the retention curve (m=1-1/n for n>1), and $K(h)$ is the unsaturated hydraulic conductivity [LT^{-1}]. The pore connectivity/tortuosity factor (l) used in the simulations was set to 0.5 for all simulation scenarios. This value was recommended by Mualem (1976) and is a default value used for soils in the HYDRUS software.

2.3.2 Water flow equation

A combination of the mass balance equation with the Darcy-Buckingham law results in the Richards equation describing water flow in variably saturated porous media. The one-dimensional form of the Richards equation can be written as

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

Where h is the water pressure head [L]; θ is the volumetric water content [-]; t is time [T]. z is the spatial coordinate [L] (positive upward). S is the sink term [L^{3}L^{-3}T^{-1}]; α is the angle between the flow direction and the vertical axis, and K is the unsaturated hydraulic conductivity [LT^{-1}].

2.3.3 Solute transport equation

Solute transport in porous media can be described with the one-dimensional convective-dispersive equation (CDE)

$$\frac{\partial \theta C}{\partial t} + \frac{\partial \rho_b S}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \frac{\partial q_w C}{\partial z}$$ (5)

Where C is the solute concentration in solution [ML^{-3}]; S is the sorbet solute concentration [MM^{-1}]. ρ_b is the soil bulk density; q_w is the volumetric water flux [LT^{-1}], and D is the effective dispersion coefficient [L^{2}T^{-1}]. The effective dispersion is given

$$D\theta = \lambda_L |q_w| + \theta \tau D_0$$ (6)

Where λ_L is the longitudinal dispersivity [L]; D_0 is the aqueous ionic or molecular diffusion coefficient of a solute in water [L^{2}T^{-1}], and τ is the tortuosity factor given by (Millington and Quirk 1961)

$$\tau = \frac{\theta^{7/3}}{\theta_s^2}$$ (7)

By manipulating Eq. (5), the modified convective-dispersive equation is obtained as follows

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z}$$ (8)

Where R is the retardation factor described by Eq. (9)

$$R = \frac{1 + \rho_b K_d}{\theta} \tag{9}$$

Where K_d is the partitioning coefficient of the solute [$L^3 M^{-1}$], and v is the average pore water velocity [LT^{-1}].

2.3.4 Numerical simulation

The water flow and solute transport equations were solved numerically using the HP1 code (Jacques *et al.* 2010). The upper and lower boundary conditions for water flow were assumed to be a constant pressure head, and for solute transport to be a concentration flux boundary condition (third type) and a zero concentration gradient (free drainage), respectively. In the HP1 model, the Galerkin finite element method with a space weighting scheme was selected, while the time derivatives of the solute transport solution were approximated using a Crank-Nicholson finite difference scheme. We conducted all simulations over a period of 15 days. The modeling procedure was divided into two separated parts (as the experimental scenarios). Part one was considered to cover the simulation of the flow rate effect (the inflow solution assumed to be neutral), in which the flow rates were 0.5,1, and 2 cc/min (cc stands for cubic centimeters), while in part two, the effect of inflow acidity is modeled by considering two different (0.12, and 0.29 g/L) inflow concentrations (for a 1 cc/min in flow rate). The boundary condition was specified as the experiment of Khodadadi Darban *et al.* (2012) which we selected the boundary conditions of our model the same as the experiments. Inflow rate was constant and the simulation column was in saturated flow condition. The rate of flow in outflow was zero. Acid concentration and pH of inflow were constant at the top of the column.

Fig. 1 indicates time of information and number of iterations.

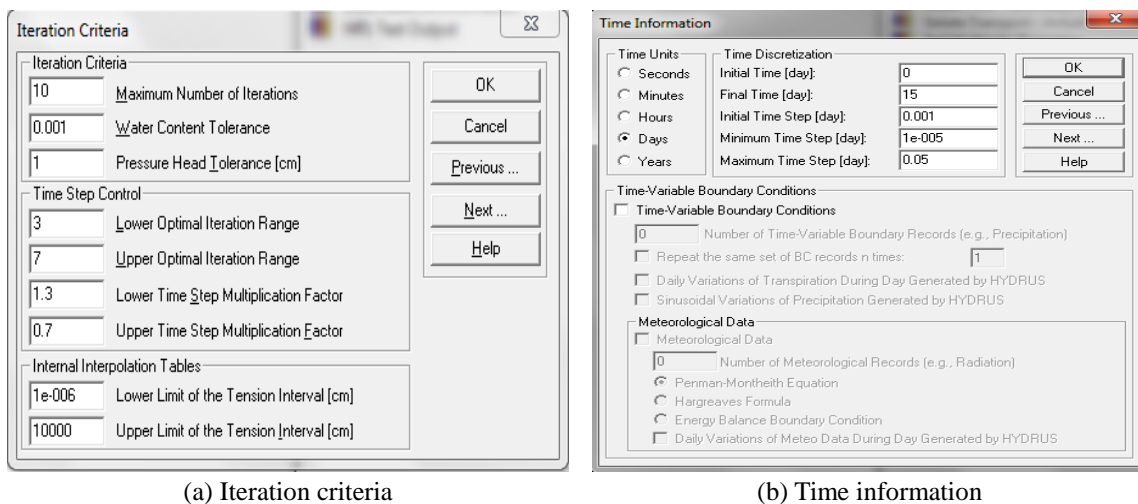| (a) Iteration criteria | (b) Time information |

Fig. 1 Detail of simulation procedure

Simulating the transport using HP1 model, the Van Genuchten-Mualem (1980) was used to describe the water retention and conductivity functions. The upper and lower boundary conditions

for water flow equation are assumed to be the constant pressure head, and the solute transport equation to be concentration flux BC (third type) and zero concentration gradient (free drainage), respectively. In HP1, the Galerkin finite element method for a space weighting scheme was selected, the time derivations for the solute transport equation are approximated by Crank-Nicholson finite difference scheme. Fig. 2 presents the simulated soil column.
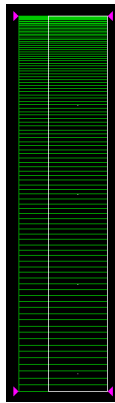

Fig. 2 The simulated column

Fig. 3 describes the water flow parameters.

Fig. 3 Water flow parameters

2.3.5 Model efficiency
The modeling efficiency (*EF*) was calculated from the measured and modeled data using (Marzban 2008)

$$EF = \frac{\sum_{i=1}^{n}(x_i - x_n)^2 - \sum_{i=1}^{n}(y_i - x_i)^2}{\sum_{i=1}^{n}(x_i - x_n)^2} \tag{10}$$

Where x_i, y_i, x_n and n are measured values, model predictions, arithmetic means of the measured values, and the number of measured and modeled values, respectively. When model predictions perfectly match the measured data, *EF* is equal to 1. A negative value indicates that the predictions describe the data less than the mean of the observations.

3. Results and discussions

3.1 Inflow intensity

The first investigated parameter in our study was the inflow intensity (the inflow solution assumed to be neutral). Fig. 4 presents the effects of flow rate on the removal of Cd, Zn, and Pb. To simulate which happens in nature, we selected three flow rates 0.5 cc/min, as the slow flow rate, 1 cc/min, as the medium flow rate, and 2 cc/min as faster flow rate, which was similar to the experiments were carried out by Marzban (2008) and Khodadadi Darban *et al.* (2012). We achieved maximum removal of Cd, Zn, and Pb after three days at a flow rate of 0.5 cc/min (Fig. 4).

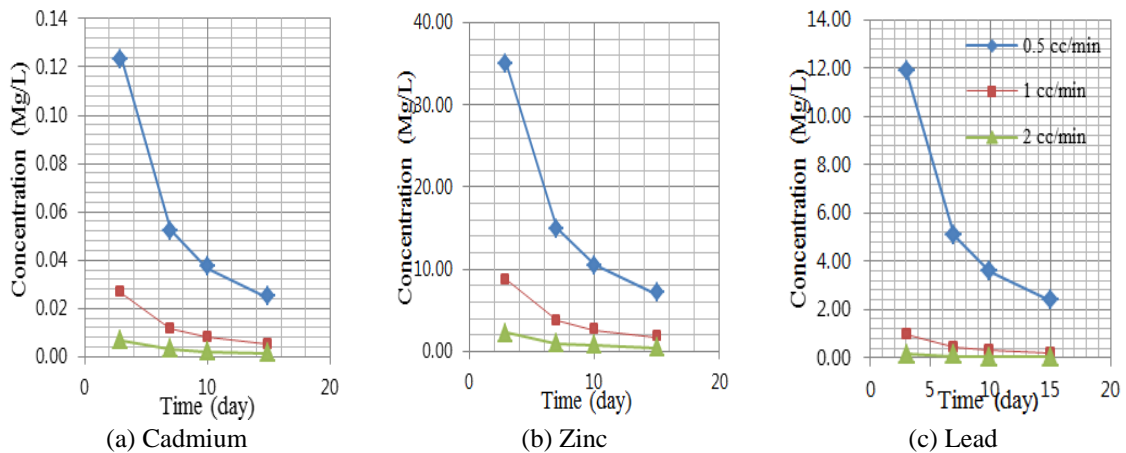| (a) Cadmium | (b) Zinc | (c) Lead |

Fig. 4 the effluent concentration of Cd, Zn, and Pb from simulation columns for different flow intensities in different days

Table 3 the effluent concentration of Cd, Zn, and Pb from simulation columns for different flow intensities on day 15

Element/inflow intensity (cc/min)	0.5	1	2
Cd (mg/l)	0.02	0.005	0.001
Zn (mg/l)	6.97	1.73	0.45
Pb (mg/l)	2.37	0.19	0.03

The total removal concentrations of these metals were 0.12, 34.85, and 11mg/l, respectively (Fig. 4). The higher leach ability in lower flow rates could be justified by having sufficient time for the reactions between the soil solid phase and the soil solution. The removal concentrations of

three metals after 15 days are indicated in Table 3.

Fig. 5 indicates the experimental and simulated removal concentrations of Cd, Zn, and Pb after 15 days, and Table 4 presents the simulation efficiencies for different inflow intensity.

Comparing the simulated and experimental results, we achieved the highest efficiency for Zn removal concentration followed by Pb and Cd (Table 4).
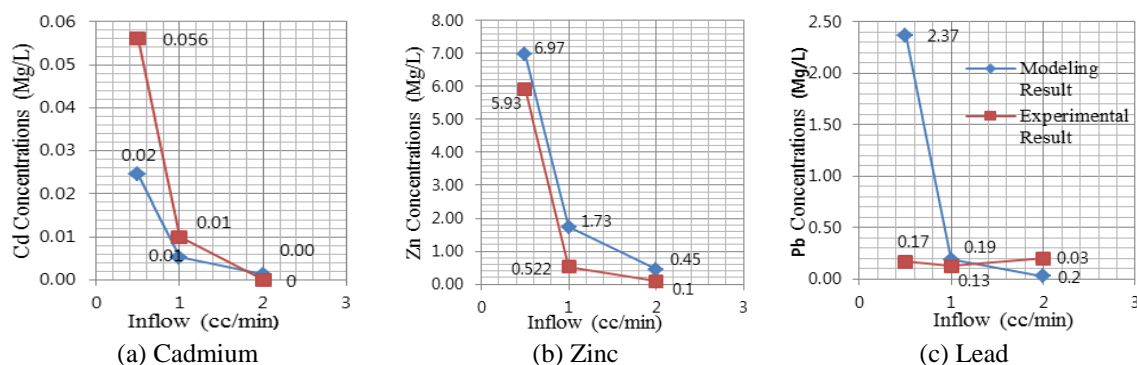

(a) Cadmium   (b) Zinc   (c) Lead

Fig. 5 Cd, Zn, and Pb removal simulated and experimental Concentrations after 15 days

Table 4 Modeling efficiencies for the heavy metals removal concentrations at different inflow intensities

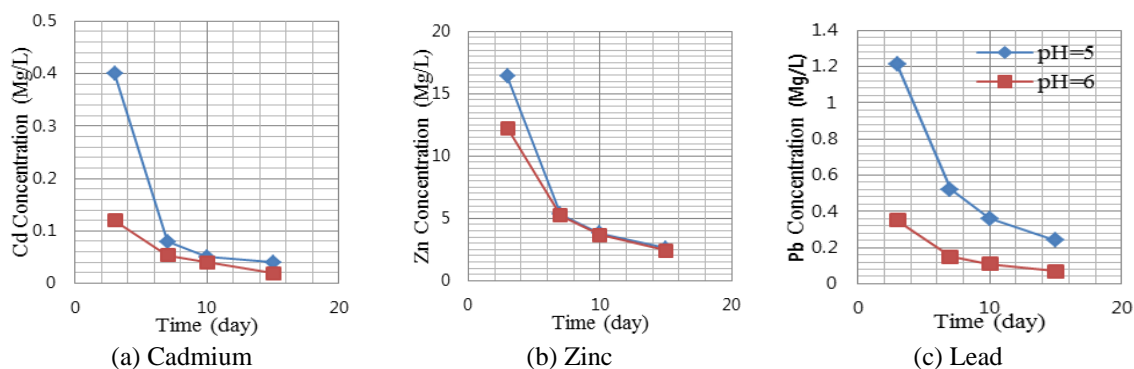| Element/Inflow (cc/min)	0.5	1	2	Average
Cd	0.30	0.32	0.35	0.32
Zn	0.88	0.85	0.48	0.74
Pb	0.80	0.89	0.43	0.71

(a) Cadmium   (b) Zinc   (c) Lead

Fig. 6 The effluent concentration of Cd, Zn, and Pb in different pH and days

3.2 Leachate pH

Fig. 6 describes the effects of pH on the transport of Cd, Zn, and Pb. Considering the pH of rain in the Arak City which was 5.5, we selected three input solutions with pH values of 5, and 6 for the simulation and the K_s equaled to 0.105 cm/s which were similar to the experiments was conducted by Khodadadi Darban *et al.* (2012) (The maximum removal of Cd, Zn, and Pb was

achieved after three days using the input solution with a pH of 5. The removal concentrations of these three metals were 0.4, 16.38, and 1.21 mg/L, respectively. Zn and Cd are considered mobile mainly in dissolved forms (Weber *et al.* 1991), whereas Pb considered as low or non-mobile in soils. The lower removal concentrations of Cd and Pb, compared to Zn in both inflow intensity and acidity scenarios, is likely due to precipitation of Cd and Pb species, especially at lower pH levels. The higher removal of metals with decreasing pH is reasonable because higher pH indicates lower quantities of H^+ ions and an increase in the retardation factor of heavy metals as indicated by Chotpantarat *et al.* (2001), among many others. Table 5 presents the removal concentrations of the three metals after 15 days.

For the two difference pH, the simulation of the outflow concentrations after 15 days reached approximately zero. Table 6 describes the experimental and simulated concentrations of Cd, Zn, and Pb after 7 days. Table 7 indicates the simulation efficiencies for different pH levels. Comparing the simulated model with the experimental results, we achieved the highest efficiency for Cd removal concentrations, followed by Zn and Pb.

Table 5 the effluent concentration of Cd, Zn, and Pb from simulation columns for pH5 and pH6 on day 15

Element/pH	pH=5	pH=6
Cd (mg/l)	0.04	0.02
Zn (mg/l)	2.62	2.44
Pb (mg/l)	0.24	0.07

Table 6 the experimental and simulated removal concentrations of heavy metals

Element	pH=6 (Experiment) mg/l	pH=6 (Simulation) mg/l	pH=5 (Experiment) mg/l	pH=5 (Simulation) mg/l
Cd	0.041	0.054	0.053	0.08
Zn	4.47	5.24	5.46	5.32
Pb	0.039	0.15	0.078	0.052

Table 7 the Model efficiencies for the heavy metals removal concentrations at two pH values

Element/pH	pH=6	pH=5	Average
Cd	0.80	0.69	0.75
Zn	0.77	0.5	0.63
Pb	0.79	0.29	0.54

Permissible limits for concentrations of zinc, lead, and cadmium in groundwater, according to the U.S. Environmental Protection Agency US EPA (Weber *et al.* 1991) are 5, 0.005, and 0.01 ppm, respectively. The results in Table 4 (for inflow intensity scenarios) indicate that the concentrations of Cd, Zn, and Pb in solution exceeded the EPA limits. The results in Table 6 (for inflow acidity) indicate that the concentration of Cd and Pb exceeded the allowable limits. They also exceeded the Iranian standard for drinking water (Standard1053). Similar findings were reported by Khodadadi Darban *et al.* (2012). Heavy metal retardation followed the order $Zn^2+>Pb^2+>Cd^2$. The same results for similar conditions were reported by Wu *et al.* (1998), except

for Pb. This difference can be attributed to the lower simulation efficiency for Pb in our study. As reported also by Wu *et al.* (1998), Khodadadi Darban *et al.* (2012) and Nguyen *et al.* (2010), the removal concentrations were lower for neutral solutions, as compared to more acidic solutions, because of precipitation of metals under neutral aquatic conditions.

Brown *et al.* (1998) attributed the differences in their observed and simulated results to the local equilibrium assumption. They indicated that due to the slow reaction kinetics and limited interactions of solid phase surfaces with solutes, the dominant process could not be effectively described using the assumption of local equilibrium in their simulation. Pot *et al.* (2005) concluded that the physical/chemical, non-equilibrium models were also more effective in simulating herbicide transport. Michel *et al.* (2007) investigated the removal of Ni and Cd from acidic sandy and silty soils using empirical and mathematical modeling. They determined the simulation efficiencies between 0.35 and 0.85 for different scenarios. The effects of different chemicals or other transport and reaction parameters were not considered.

Jacques *et al.* (2008) obtained that decreasing the pH level increases the bivalent cation removal concentrations. A comparison of our results with results reported by Motalebi *et al.* (2012) describes that the PHREEQC and HP1 models had approximately the same efficiency in Cd reactive transport, perhaps because of the saturated flow conditions in both studies. In these two studies, the modeling efficiencies in acidity scenarios where higher, compared with the inflow intensity rate scenarios.

We achieved a relatively good agreement between our model predictions and experimental results. Some small differences between the experimental and our simulated results were observed only during the first few days of the simulations. The presence of dissolved organic matter (DOM) may have influenced the mobility and retention of heavy metals in soils. The formation of complexes with DOM can be especially important for Pb (Weng *et al.* 2002, Tipping *et al.* 2003). The lower simulated removal concentrations of metals may be attributed to the formation of complexes during the first few days of simulation. Higher measured concentrations at the beginning of the solute breakthrough or tailing have also been observed in previous researchers (Snow *et al.* 1994, Jacques *et al.* 1998) in structured or macroporous soils. In these circumstances, an alternative is the use of the non-equilibrium convection-dispersion models to describe solute transport Jacobsen *et al.* 1992, Mallants *et al.* 1996, Vanderbroght *et al.* 2000). The absence of equilibrium between the soil and solution can also be caused by rate-limited sorption (chemical kinetic aspects) or by incomplete mixing of percolating solution with resident water (physical aspect). Another possible reason for the differences may be the fact that the soil hydraulic conductivity was assumed to be constant during the simulations. In reality, the hydraulic conductivity changes with changes in pH, this can affect the heavy metal precipitation rate. In general, disagreement between the model and the data (lower modeling efficiencies) of some of the scenarios can be attributed also to uncertainty in the value of some parameters, simplification of the transport process to a one dimension, ignoring the effects of macropores and other transport processes in natural soil (such as bioturbation), and/or local physical or chemical non-equilibrium processes.

4. Conclusions

The results and discussion of using the HP1 model to predict the removal of Cd, Zn and Pb in Lakan mine tailing in Iran can be summarized to the following conclusion:

• The retardation of heavy metals followed the order $Zn^{2+} > Pb^{2+} > Cd^{2+}$.

• Decreasing pH values and inflow intensities produced higher metal removal concentrations.

• The removal concentrations of Cd, Pb, and Zn at the inflow intensity critical scenario, and Cd and Pb at inflow acidity critical scenario exceeded the allowable EPA and Iranian's 1053 standard thresholds.

• Predicted early removal concentrations did not successfully match the observed data, likely due to the presence of sharp solute fronts, failure to establish local equilibrium, insufficient time for complete soil solid phase and soil solution reactions (the presence of macropores), or temporal variations in the physical properties. Some of the differences could be attributed also to the formation of complexes at the beginning of simulations.

• Differences between modeling and experimental results for some scenarios could also be attributed also to uncertainty in the values of some parameters, simplification of the transport process to one dimension, ignoring the effects of macropores and other transport mechanisms occurring in soils (such as bioturbation), or uncertainty in the dominant chemical processes and their parameters. In this study, lack of detailed data was the main barricade for improving the results.

• PHREEQC and HP1 models have approximately the same modeling efficiency for the Cd reactive transport simulations.

More research is needed to explore the various physical-chemical and biological processes that control the potential solubility of toxic metals from mine tailings. The use of two- and three-dimensional models, as well as kinetic modeling, is recommended to more accurately simulate reactive transport in actual field conditions.

Acknowledgments

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