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Simulation of Ca^{2+} and Mg^{2+} removal process in fixed-bed column of natural zeolite

Babak Ebrazi, Mohammad Ebrahim Banihabib*

Department of Irrigation and Drainage Engineering, College of Abureyhan, University of Tehran, Abureyhan Campus, 20th km Imam Reza Road, P.O. Box: 11365/4117, Tehran 3391653755, Iran, Tel./Fax: +98 21 82116296; email: babakebrazi@ut.ac.ir (B. Ebrazi), Tel./Fax: +98 21 36040906; email: banihabib@ut.ac.ir (M.E. Banihabib)

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ABSTRACT

In this research, an explicit finite difference scheme is assessed for solving non-linear governing differential equation of contaminant transport to simulate the removal process of Ca^{2+} and Mg^{2+} within a fixed-bed zeolite column. Experiments were carried out in a continuous system at pH 7.5, with five samples at concentrations of 120, 50 ppm for Ca^{2+} and Mg^{2+}, respectively. The required parameters for Langmuir isotherms were obtained using batch experiments. The distribution coefficient of linear adsorption isotherm was evaluated through calibrating the proposed numerical model. In the calibration, the parameter adjusted to obtain the most suitable distribution coefficient by which outflow solution concentration best fits the experimental results. Furthermore, the dispersion coefficient was evaluated using an empirical relationship to calculate dispersivity. The comparison of the proposed numerical model and experimental results indicated that the proposed numerical model that uses linear adsorption isotherm and the utilized empirical relationship to determine dispersivity has considerable capability to simulate Ca^{2+} and Mg^{2+} removal processes in fixed-bed column.

Keywords: Numerical model; Natural zeolite; Water hardness; Removal process simulation; Adsorption

1. Introduction

Natural zeolites are minerals which have a three-dimensional framework and are considered as crystalline hydrated aluminosilicates. Their structure is formed by two types of tetrahedras called AlO_4^- and SiO_4^- which are joined by a shared oxygen atom. Natural zeolites' structure has a negative charge which is formed when an AlO_4^- tetrahedron is substituted for a SiO_4^- tetrahedron. This negative charge is balanced by the exchangeable cations like Na^+, K^+, Ca^{2+}, and Mg^{2+} [1]. Given the known traits of zeolites such as their chemical and thermal stabilities, some scientific studies have been carried out to determine their practical application [2].

Numerous batch and column studies have been conducted to examine heavy metal adsorption using zeolites [2–9], ammonium ion [10], dye contaminations [11] from industrial and municipal wastewaters, and ammonium components using different types of natural zeolites [10,12–14].

The other area in which some studies have been conducted is the simulation of a removal process

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*Corresponding author.

which happens in zeolite columns. Despite the conducted researches on the simulation of cations and the contaminants removal process within fixed-bed columns of zeolites, just a few of them have studied the use of mathematical models to explain and simulate the behavior of cations and contaminants removal in natural zeolite columns. Li et al. [15] used CXTFIT2 model, which employs a non-linear least-squares parameter optimization method to estimate solute transport parameters according to the observed concentration data using the advection dispersion equation to simulate the column results. Torgo et al. [2] used Bohart–Adams, Wolborska, Thomas and Yoon–Nelson empirical model to describe lead removal within a fixed-bed column of natural zeolite. But, in most of the researches conducted on removal process simulation in fixed-bed columns; empirical equations have been used. One of the challenges of the empirical models is their need for preliminary determination of parameters which requires additional experiments making them inconvenient for practical use. Therefore, the main purpose of this paper is to use an explicit finite difference (FD) numerical model, in which Langmuir and Linear adsorption isotherms are used for the simulation of cations adsorption phenomenon, in the simulation of Ca^{2+} and Mg^{2+} removal process by a fixed-bed column of a natural zeolite.

2. Materials and methods

2.1. Overview on solute transport

The governing equation of contaminant transport by fluid flow in the saturated porous media is used as follows [16]:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 {}_C}{\partial x^2} - V_x\frac{\partial c}{\partial x} - \frac{B_d}{\theta}\cdot\frac{\partial c^*}{\partial t} \tag{1}$$

where B_d is the soil bulk density [LT^{-3}], θ is the water content [L^3L^{-3}], V_x is the average of linear velocity [LT^{-1}], D is the diffusion dispersion coefficient [L^2T^{-1}], x is the spatial step [L], t is the time step [T], c is the solute concentration [ML^{-3}], and c^* is the amount of material adsorbed.

Contaminant transport in porous media is governed by three phenomena called advection, diffusion, and dispersion. Advection is the phenomenon in which the transport of material occurs by the net flow of the fluid. When a contaminant transport occurs in a porous media, all contaminants suspended in the flowing fluid, including both molecules and particles, are moved along with the fluid [17]. Convective transport can be expressed as:

$$J_m = q_s C \tag{2}$$

where J_m is the flux density for convective or mass transport [$ML^{-2}T^{-1}$], q_s is the volumetric fluid flux density with the dimension of velocity [LT^{-1}], and C is the average solute concentration [ML^{-3}].

The contaminants transport process which occurs by the random thermal motion of contaminant molecules is governed by a process called diffusion [18]. The rate of contaminant transport that occurs by diffusion can be expressed by Fick's law. This law for one-dimensional steady-state diffusive transport can be written as [19]:

$$J_D = -D_m\frac{\partial C}{\partial x} \tag{3}$$

where J_D is the solute flux density for diffusive transport of solute [$ML^{-2}T^{-1}$] and D_m is the diffusion coefficient in porous media [L^2T^{-1}].

Another phenomenon governing contaminant transport in porous media is called dispersion process. It is similar to the diffusion process macroscopically. However, contrary to diffusion, it occurs only during a water flow. It can be written as follows [19]:

$$J_h = \theta D_h\frac{\partial c}{\partial x} \tag{4}$$

where J_h is the solute flux density for dispersive transport of solute [$ML^{-2}T^{-1}$], D_h [L^2T^{-1}] is the mechanical dispersion coefficient and is assumed to be a function of fluid velocity, and θ is volumetric water content [L°]. The equation of mechanical dispersion coefficient can be written as follows [19]:

$$D_h = \lambda V^n \tag{5}$$

where λ is the dispersivity and exponent n is an empirical constant which is generally assumed equal to 1 [19]. Unlike dispersion which is a passive phenomenon, diffusion is an active process. Given this fact, these two processes can be described by one equation due to their similar behavior and can be expressed by the following equation:

$$D = D_h + D_m \tag{6}$$

where D_m is the diffusion coefficient in porous media [L^2T^{-1}] and D is the longitudinal hydrodynamic dispersion coefficient [19]. Thus, D can be written as:

$$D = \lambda V + D_0 \theta \xi \quad (7)$$

where D_0 is the diffusion coefficient of pure water [L^2T^{-1}] and ξ is tortuosity. Adsorption can be defined as the adherence of chemical materials on the surface of the porous medium. Physical and chemical characteristics of contaminants, as well as the surface of the solid phase in which contaminants' transport occurs, are the main factors which affect the adsorption of pollutants to or from the solid phase [20]. The amount of contaminants' adsorption is generally reliant on the contaminant traits and the composition of the medium.

2.2. Column study

In this research, the developed FD model was utilized to investigate Ca^{2+} and Mg^{2+} removal phenomenon in a column of natural zeolite with a diameter of 8 cm and five thicknesses of samples (including: 6, 9, 12, 15, and 18 cm). The zeolite sample used in this research was Semnan Clinoptilolite with a mean diameter of 0.5 mm gained through sieving the original samples. Furthermore, Ca^{2+} and Mg^{2+} were studied separately for each of the thickness of sample by making synthetic solutions. The concentrations of the synthetic solutions of Ca^{2+} and Mg^{2+} were, respectively, 120 and 50 ppm. The synthetic solutions were fed to the experimental column and they passed through the column containing zeolite sample. Ten water samples were taken from the output of column. Ca^{2+} and Mg^{2+} concentrations were measured using titration method based on which breakthrough curves were gained for each sample of Ca^{2+} and Mg^{2+}. Experimental setup has been illustrated in Fig. 1.

In the second part of the research, a numerical method was used to discrete the contaminant transport equation for the simulation of Ca^{2+} and Mg^{2+} transport in a column of natural zeolite. To consider the adsorption phenomenon in Ca^{2+} and Mg^{2} transport, Langmuir and linear adsorption isotherms were employed. Details of experiments conducted in terms of adsorption isotherms are discussed in Section 2.3. Finally, the capability of the used numerical model in simulating Ca^{2+} and Mg^{2+} transport phenomenon was compared with the experimental results.

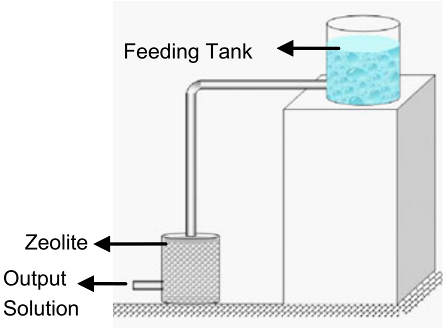

Fig. 1. The experimental setup.

2.3. Adsorption isotherms

The ion-exchange phenomenon is a stoichiometric process. In the ion-exchange process, one equivalent of an ion in the solid phase is replaced by the equivalent of an ion from the solution. The reaction may be written as [21].

$$Na^{+}{}_{(z)} + A^{2+}{}_{(s)} \Leftrightarrow Na^{+}{}_{(s)} + A^{2+}{}_{(z)} \quad (8)$$

The subscripts z and s refer to the zeolite and solution phases, respectively. And A^{2+} shows a divalent ion. The ion-exchange isotherms are the equations which show the equilibrium of an ion in a solid phase with the concentration of the ion in solution. For the effective utilization of a natural zeolite as an ion exchanger, it is essential to have chemical models and relationships that aid in describing Ca^{2+} and Mg^{2+} equilibrium accurately [21].

One of the isotherms used in this research was the Langmuir isotherm. This isotherm was used to simulate the adsorption process of Ca^{2+} and Mg^{2+} in the column of zeolite. It can be written as follows [16]:

$$C^* = \frac{\alpha \beta C}{1 + \alpha C} \quad (9)$$

where α and β are the empirical coefficients of this equation.

Langmuir isotherm was formulated by an experiment with 24 h contact time, 1 g zeolite, and 10–300 ppm concentrations of Ca^{2+} and Mg^{2+} at room temperature (20˚C). The total amount of adsorbed calcium and magnesium was divided by the dry weight of zeolite to find out the average amount of adsorbed cations. The capability of Langmuir adsorption isotherm for the removal process of the cations was assessed for 12 cm thickness. The comparison of simulated and observed values was done through the mean absolute relative error (MARE).

$$\text{MARE} = \text{Mean} \frac{|S_i - M_i|}{M_i} \quad (10)$$

where S_i and M_i are the simulated and measured (observed) values, respectively.

The other adsorption isotherm used in the research was the linear adsorption isotherm. This isotherm was used to simulate the removal of Ca^{2+} and Mg^{2+} in the column. It can be written as follows [16]:

$$C^* = K_d C \tag{11}$$

where C^* is the concentration of the solute in zeolite, C is the concentration of the solute in the flow [ML^{-3}], and K_d is the distribution coefficient [$L^{-3}M$].

The linear adsorption isotherm was calibrated by changing the distribution coefficient (K_d) for 12 cm thickness sample, based on minimization of MARE. That is to say, the distribution coefficient was used to minimize the MARE parameter. Then the appropriate K_d was considered for the rest of simulation using linear adsorption isotherm.

2.4. Numerical method used to solve the contaminant transport equation

The non-linear governing differential equations of contaminant transport were solved using backward explicit FD method. The discreted contaminant transport equation can be written as below:

$$R\frac{C_i^{n+1} - C_i^n}{\Delta t} + V\frac{C_i^n - C_{i-1}^n}{\Delta x} = D\frac{C_{i+1}^n + C_{i-1}^n - 2C_i^n}{\Delta x^2} \tag{12}$$

where i and n indicate the spatial step and the time step, respectively.

In order to determine the velocity of the solute transport in the column, the average observed velocity was used. On the basis of Eq. (5), the diffusion process in porous media includes two phenomena. To evaluate the diffusion coefficient, the equation presented by Vanderborght et al. [22] was used to estimate the dispersivity within the zeolite column as follows:

$$\lambda = 0.39\, q^{0.89} \tag{13}$$

where λ is the dispersivity [L] and q is the water flux [LT^{-1}]. To determine the retardation factor (R), the results of conducted adsorption isotherm experiments were used. In this study, as mentioned before, Langmuir and linear adsorption isotherms were utilized to simulate the Ca^{2+} and Mg^{2+} removal. Using the Langmuir adsorption isotherm, retardation factor can be written as [16]:

$$R = 1 + \frac{Bd}{\theta}\left(\frac{\alpha\beta}{(1+\alpha C)^2}\right) \tag{14}$$

where α and β are the empirical coefficients. These coefficients were evaluated using the results of conducted experiments. Also, using the linear adsorption isotherm, retardation factor can be written as [16]:

$$R = 1 + \frac{\rho_b K_d}{\theta} \tag{15}$$

where ρ_b is the zeolite bulk density [ML^{-3}] and K_d is the calibrated distribution coefficient [L^3M^{-1}].

Initial condition is used for this study based on the assumption that solute concentration decreases linearly from the top of the column to the bottom. The initial conditions only are utilized for the first time step of the calculations. Also the following boundary conditions were applied for the top and bottom of the column. The used boundary conditions are called reflexive boundary conditions.

$$C(0,t) = C_0 \tag{16}$$

$$C(L,t) = C(L - \Delta x, t) \tag{17}$$

where Δ_x represents the spatial steps.

3. Results

3.1. Langmuir adsorption isotherm

The interactions of Ca^{2+} and Mg^{2+} solutions with zeolite (Clinptilolite) are described with adsorption isotherms (empirical equations). These empirical equations are important for the interpretation and prediction of adsorption data. In this research, the Langmuir adsorption isotherm was tested as a part of the proposed model.

The constants of Langmuir adsorption isotherm have been shown in Table 1 for 20℃. The presented results of correlation coefficients (R^2) in Table 1 and Fig. 2 indicate that the Langmuir isotherm can be utilized to describe the equilibrium phenomenon in the interaction of a zeolite media and Ca^{2+} and Mg^{2+} cations. The gained relationship for Langmuir adsorption isotherm was employed in adsorption terms of the contaminant transport equation (Eq. (1)). Table 2 indicates the parameters of simulation of Ca^{2+} removal of a 12 cm thickness sample in the fixed-bed column. As the results depict in Table 2, the Reynolds number is in the laminar flow regime interval. Therefore, the

Table 1
Langmuir isotherm equation and constants for each cation

Cations	A	β	Equation	R^2
Ca^{2+}	0.025	11.8	$C^* = \frac{0.295C}{1+0.025C}$	0.99
Mg^{2+}	0.042	6.1	$C^* = \frac{0.2526C}{1+0.046C}$	0.98

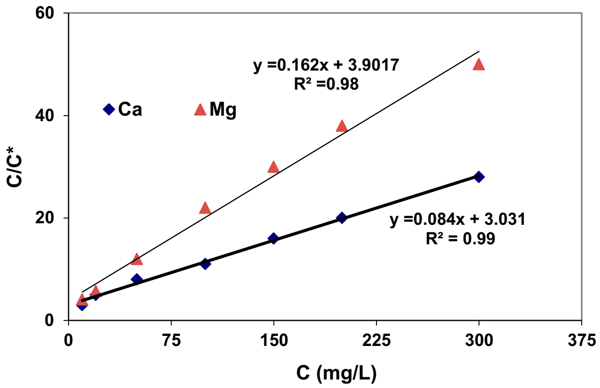

Fig. 2. Langmuir isotherm curves of Ca^{2+} and Mg^{2+} ($T = 20$).

Table 2
Model parameters used for calcium transport (12 cm thickness)

Parameter	Values
Saturated water content (θ)	0.6
Zeolite bulk density (ρ_b)	1.1 ($g\,cm^{-3}$)
Solute velocity (V)	0.0021 ($cm\,s^{-1}$)
Diffusion coefficient (D)	0.0000031 ($m^2\,s^{-1}$)
Reynolds number (Re)	1.04
Courant number (Cr)	0.48
Spatial step (Δx)	0.005 (m)
Time step (Δt)	2 (s)

Darcy equation can be used to simulate the removal process. In addition, the Courant number in Table 2 indicates the stability of the applied numerical model.

Comparison between the simulated (using Langmuir adsorption as isotherm) and experimental results is presented in Fig. 3. As Fig. 3 shows, there is a significant difference between the simulated and experimental results. The simulated concentration of solution increases faster than the experimental data.

Correspondingly, Table 3 indicates the parameters used to simulate Mg^{2+} removal of a 12 cm thickness sample in the fixed-bed column. According to the calculated Reynolds number, Darcy equation can be applied to simulate Mg^{2+} removal in the column and the Courant number value indicates that the proposed model is stable.

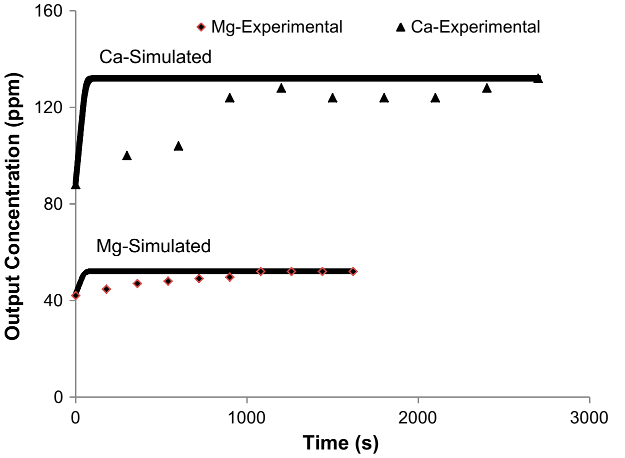

Fig. 3. Comparison between simulated and experimental (Langmuir adsorption isotherm) Ca^{2+} and Mg^{2+}.

Table 3
Model parameters used for magnesium transport (12 cm thickness)

Parameter	Values
Saturated water content (θ)	0.6
Zeolite bulk density (ρ_b)	1.1 ($g\,cm^{-3}$)
Solute velocity (V)	0.0024 ($cm\,s^{-1}$)
Diffusion coefficient (D)	0.0000043 ($m^2\,s^{-1}$)
Reynolds number (Re)	1.2
Courant number (Cr)	0.96
Spatial step (Δx)	0.005 (m)
Time step (Δt)	2 (s)

Fig. 3 demonstrates the comparison between the simulated (using Langmuir adsorption as isotherm) and experimental data for Mg^{2+}. In the same way, the figure shows that there is a considerable difference between the simulated and experimental data. The simulated concentration of Mg^{2+} in the discharged solution increases faster than the experimental data.

In order to assess the performance of the Langmuir isotherm and have a quantitative comparison, MARE was calculated for each cation. The calculated MAREs for Ca^{2+} and Mg^{2+} are 0.091 and 0.047, respectively. These numbers show that the Langmuir isotherm has low potential to simulate both the Ca^{2+} and Mg^{2+} removal in the fixed-bed zeolite column. Although the MARE parameter for the Mg^{2+} is fairly lower than the MARE parameter of Ca^{2+}, the application of Langmuir isotherm does not give proper results.

3.2. Simulation of the removal phenomenon using linear adsorption isotherm

Considering the lower potential of the Langmuir isotherm, the capability of linear isotherm to simulate Ca^{2+} and Mg^{2+} removal in the column of zeolite was studied. As mentioned before in Section 2.3, the capability of the linear adsorption isotherm was determined using calibrated distribution coefficient (K_d) by the experiment (12 cm thickness). Then the calibrated K_d was considered for the other four samples of simulation.

Figs. 4 and 5 illustrate the MARE parameter vs. the distribution coefficient variation for Ca^{2+} and Mg^{2+}. As it has been presented in the Figs. 4 and 5, the calibrated distribution coefficients of 12 cm thickness sample for Ca^{2+} and Mg^{2+} are 0.011 and 0.01, respectively.

The linear isotherm (using calibrated distribution coefficients) was applied for the simulation of 6, 9, 15, and 18 cm thickness samples of each cation. The results are presented in Fig. 6 for Ca^{2+} and Fig. 7 for Mg^{2+}. The figures indicate that the proposed linear isotherm model had a significant potential to simulate cations removal in the zeolite column. For quantitative assessment, MARE*s* were calculated and presented in Table 4. The MARE*s* in the samples of 6 and 9 cm for Ca^{2+} removal are 0.022 and 0.019, respectively. These numbers indicate that linear adsorption isotherm for 6 and 9 cm thickness samples of zeolite has appropriate potential to simulate the removal process of Ca^{2+}. The MAREs for Ca^{2+} removal for 15 and 18 cm thickness samples of zeolite are 0.03 and 0.044, respectively. This result shows that the accuracy of the model slightly decreases with the increase of sample thickness in the column.

Additionally, in Table 4, the MARE parameter for Mg^{2+} removal simulation has been presented. The MAREs for Mg^{2+} removal, in 6 and 9 cm thickness, are 0.022 and 0.019, respectively. These numbers indicate that the linear adsorption isotherm for 6 and 9 cm thickness samples of zeolite generates appropriate results. The MAREs for Mg^{2+} removal by 15 and 18 cm thickness samples of zeolite are 0.026 and 0.086, respectively. Similar to Ca^{2+} results, the results show that the accuracy of the model slightly decreases with the increase of zeolite sample thickness in column.

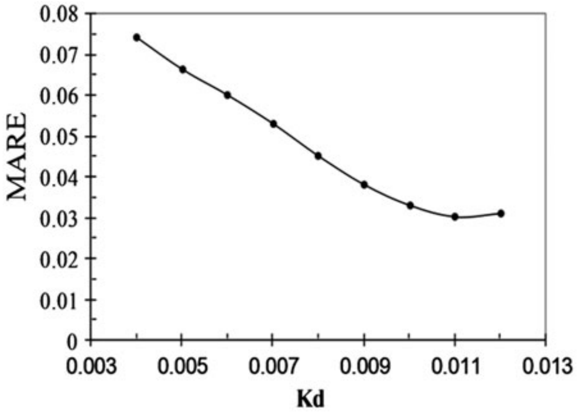

Fig. 4. MARE changes of Ca^{2+} vs. K_d changes.

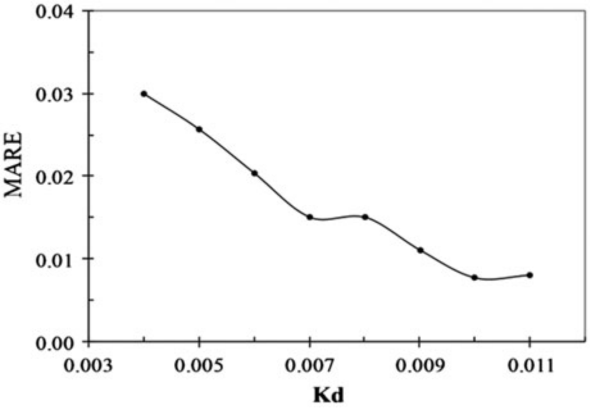

Fig. 5. MARE changes of Mg^{2+} vs. K_d changes.

4. Discussion

In this paper, an explicit numerical model was proposed which uses Langmuir and linear adsorption isotherms to simulate Ca^{2+} and Mg^{2+} removal process in fixed-bed column of zeolite. In addition, the usage of Langmuir and linear adsorption isotherms in the proposed model was examined by comparing the simulated results with the experiments. According to the results, the application of Langmuir adsorption isotherm by the proposed numerical model, in comparison to the application of linear adsorption isotherm, has a lower capability to simulate the Ca^{2+} and Mg^{2+} removal, whereas the application of linear adsorption isotherm denotes more appropriate agreement between the simulated and experimental results. To investigate the capability of an explicit FD scheme in which linear adsorption was used to simulate adsorption phenomenon, quantitative comparison was made between the simulated and experimental data. According to the findings, the proposed numerical model along with linear adsorption isotherm generates much more appropriate results for Ca^{2+} than Mg^{2+}. Based on the simulation results, the maximum amount of MARE for Ca^{2+} is about 4%, while MARE parameter for Mg^{2+} is about 8%.

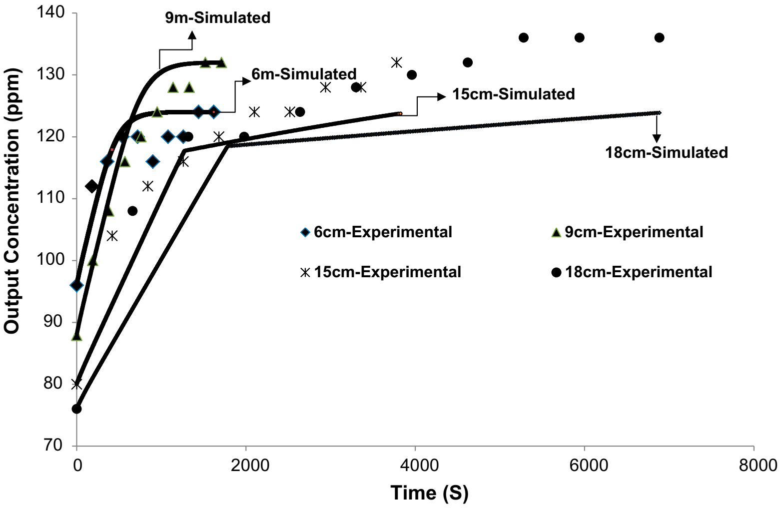

Fig. 6. Comparison of the observed and simulated results for 6, 9, 15, and 18 cm (Ca^{2+}).

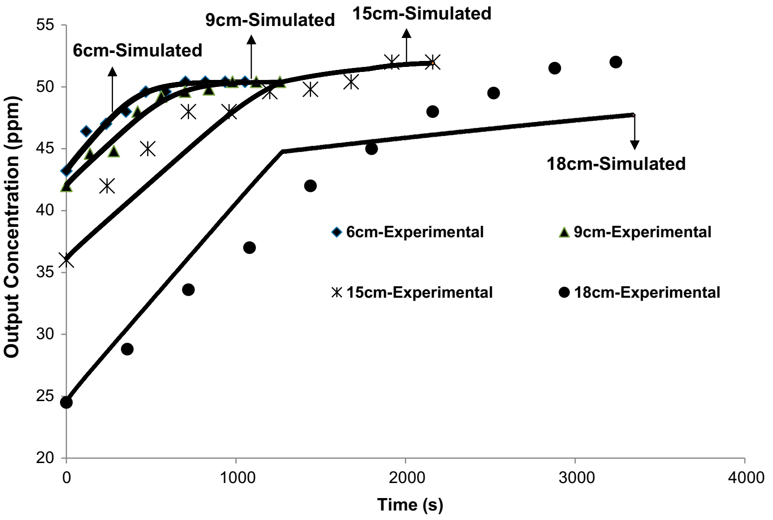

Fig. 7. Comparison of the observed and simulated results for 6, 9, 15, and 18 cm (Mg^{2+}).

Table 4
Calculated MAREs for 6, 9, 15, and 18 cm of Ca^{2+} and Mg^{2+}

Cations thickness	MARE	
	Ca^{2+}	Mg^{2+}
6	0.022	0.057
9	0.019	0.045
15	0.003	0.076
18	0.044	0.086

Furthermore, comparing MARE parameter for each cation shows that there is a relationship between the MARE parameter and the zeolite sample thickness within a zeolite column; the more the zeolite sample thickness is away from the 12 cm (the sample thickness used to calibrate proposed numerical model) the more the MARE parameter increases. While the increase in Mg^{2+} is more than Ca^{2+}, and it confirms that if the proposed numerical model is used to simulate the removal process of Mg^{2+} in a zeolite column, it is necessary to re-calibrate the utilized parameters. Finally, according to the obtained results, the empirical relationship for dispersivity (Eq. (13)) gives proper outcomes. Thus, the relationship can be used to estimate dispersion coefficient which is determined by the experiments.

5. Conclusion

In this study, the application of explicit FD method, which uses Langmuir and linear adsorption isotherms for the simulation of adsorption process, was utilized to simulate Ca^{2+} and Mg^{2+} removal process in the column of natural zeolite. According to the results, the application of Langmuir adsorption isotherm in the numerical method, in comparison to linear adsorption isotherm, has a lower capability to simulate the Ca^{2+} and Mg^{2+} removal, whereas the application of linear adsorption isotherm resulted in more appropriate agreement between the simulated and experimental results. To investigate the potential of the proposed numerical model in which linear adsorption was used to simulate the adsorption phenomenon, quantitative comparison was made between the simulated and the experimental data. The comparison of MARE parameter for two cations shows that the proposed model generates better results for Ca^{2+} removal process in the zeolite column than Mg^{2+} removal.

Nomenclature

J_m — flux density for convective [$ML^{-2}T^{-1}$]
q_s — volumetric fluid flux density [LT^{-1}]
C — volume-averaged solute concentration [ML^{-3}]
J_D — solute flux density for diffusive transport of solute [$ML^{-2}T^{-1}$]
D_m — diffusion coefficient in porous media [L^2T^{-1}]
J_h — solute flux density for dispersive transport of solute [$ML^{-2}T^{-1}$]
D_h — mechanical dispersion coefficient [L^2T^{-1}]
D_0 — the diffusion coefficient of pure water [L^2T^{-1}]
λ — dispersivity
ξ — tortuosity
n — empirical constant
B_d — soil bulk density [LT^{-3}]
θ — volumetric water content [L^3L^{-3}]
V_x — average of linear velocity [LT^{-1}]
D — diffusion dispersion coefficient [L^2T^{-1}]
x — spatial step [L]
t — time [T]
C — solute concentration [ML^{-3}]
C^* — amount of adsorbed material
α & β — empirical coefficients
MARE — mean absolute relative error
S_i — simulated data
M_i — measured data
K_d — distribution coefficient [$L^{-3}M$]
i — spatial step [L]
n — time step [T]
Q — water flux [LT^{-1}]
R — retardation factor
ρ_b — zeolite bulk density[ML^{-3}]
R^2 — correlation coefficients
Re — reynolds number
Cr — courant number

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