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Removal of zinc from contaminated groundwater by zero-valent iron permeable reactive barrier

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ABSTRACT

The possibility of using zero-valent iron (ZVI) as permeable reactive barrier (PRB) to remove zinc from a contaminated groundwater was investigated. Batch equilibrium tests were carried out. The effects of many parameters such as contact time between adsorbate and adsorbent (0–240 min), initial pH of the solution (4–8), sorbent dosage (1–12 g/100 ml), initial metal concentration (50–250 mg/l), and agitation speed (0–250 rpm) were studied. The best values of these parameters that achieve the maximum removal efficiency of Zn^{+2} (=91%) were 3 h, 5, 10 g/100 ml, 50 mg/l, and 200 rpm, respectively. Langmuir isotherm model gives better fit for the sorption data of Zn^{+2} ion by ZVI than Freundlich model under the studied conditions. Finite difference method and COMSOL Multiphysics 3.5a software, which is based on finite element method, were used to simulate the one-dimensional equilibrium transport of zinc through sandy aquifer with and without presence of PRB. The predicted and experimental results proved that the PRB plays a potential role in the restriction of the contaminant plume migration. A reasonable agreement between these results was recognized with root mean squared error not exceeded the 0.1487.

Keywords: Zero-valent iron; Zinc; Permeable reactive barrier; Groundwater; Transport

1. Introduction

Restoring the quality of contaminated groundwater is among the most difficult and expensive environmental problems. It is often the primary factor limiting closure of contaminated sites. The most common technology used for remediation of groundwater is ex situ pump-and-treat systems. These systems extract groundwater to the surface, treat it by different approaches such as adsorption onto granular activated carbon, and either re-introduce the treated water to the subsurface or discharge it to a storm drain. These approaches are difficult, costly, and ineffective most of the time in removing enough contamination to restore the groundwater to drinking water standards in acceptable time frames. Hence, there was a necessity to use other innovative methods to remediate groundwater contaminated with heavy metals. One of the most effective technologies is the *in situ* treatment of groundwater contaminants by means of permeable reactive or adsorbing barriers (PRBs). This technology combines subsurface fluid flow with contaminant

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treatment by combinations of physical, chemical, biological, or mixed processes [1–3].

The availability of fresh water with the proper quality is a prerequisite for human well-being and the consequential social/economic development of communities. In the past, human water requirements were considerably lower than the available natural resources. Additionally, the negative impact on water resources quality was limited due to the relatively low-level community social/economic activities. Presently, the global population overgrowth coupled with the accelerating technological advances and the concomitant environmental pollution/climate change, have all led to a significant reduction in water resource availability and appreciable deterioration of water quality. Iraq is currently facing severe water shortages across most parts of the country, with over 7.6 million Iraqis lacking access to safe drinking water, and an agriculture sector suffering from years of scarcity [4]. Accordingly, PRBs technology would have a significant positive impact on the quality of groundwater resources; making this resource a reliable complementary option to surface water.

Many theoretical and experimental studies concerning the migration of heavy metals through PRB were achieved [5–10]. The removal of organic and inorganic pollutants from groundwater by zero-valent iron (ZVI) and apatite was investigated. Reduction of organic or inorganic contaminants in the case of ZVI and immobilization of inorganic pollutants in the case of apatite were the predominant mechanisms of removal process [5]. The ZVI/pumice granular mixtures were proved to be a potentially suitable reactive medium for PRBs in remediation of groundwater contaminated with various concentrations of Ni and Cu [6]. The efficiency of PRBs containing organic material and limited quantities of ZVI, fly ash, or red mud to remove heavy metals from leachates was studied. Numerical modeling was developed for one-dimensional solute transport including chemical reaction to simulate the PRB column results, in which arsenite (As(III)) was removed using ZVI [7]. Mechanism of zinc removal by a packed column reactor with ZVI powder was studied. This mechanism was to be as follows: ZVI was firstly corroded and oxidized into ferric ion by dissolved oxygen. The ferric ion was precipitated as iron hydroxide onto the surface of the ZVI powder. Zinc ion was adsorbed on and/or co-precipitated with the iron hydroxide. The iron hydroxide was finally oxidized and transformed into iron oxides [8]. The treatment of the groundwater contaminated with metals by dumping sites located in the provinces of southern Poland was investigated. The simulated groundwater circulated through the column filled with ZVI in the laboratory tests. Chromium, copper, nickel, cobalt, lead, cadmium, and zinc, occurring in the water as cations and anions, have been removed in the iron bed. The rapid metal removal has likely occurred due to the reduction and precipitation/co-precipitation and/or due to adsorption onto the iron metal surface or/and onto the iron corrosion products [9]. A study for groundwater flow and zinc transport modeling to assess the performance of the continuous and funnel and gate PRBs with ZVI and activated sludge as reactive materials was conducted. Simulation results show that the 0.5 m thick PRBs are good for treating zinc-contaminated groundwater for operation time in the range of 2,170–2,248 and 1,675–1,803 d for continuous and funnel and gate PRBs, respectively [10].

Accordingly, the significance of the present study is to investigate the potential applicability of using ZVI, as an inexpensive material in PRBs, theoretically and experimentally for the removal of zinc from simulated contaminated groundwater.

2. Experimental work

2.1. Materials

Natural Iraqi soil was used as porous medium in the experiments conducted in the present study. Depended on particle size distribution (ASTM D 422), the percentage of sand, silt, and clay were 92.5, 7.5, and 0%, respectively. Accordingly, this soil can be classified as sandy soil. The permeability of this sand, measured with a constant head permeameter, was 2.2×10^{-4} cm/s. The measured values of the porosity and bulk density were 0.44 and 1.78 g/cm^3, respectively.

The ZVI was prepared from a scrap iron (iron filings of a work shop). It has a grain size ranged from 0.35 to 2.38 mm with average specific surface area of 0.555 m^2/g. The specific surface area was measured at the oil research and development center using the same method adopted by Rangsivek [11]. The typical Fe content of these filings is ~90% with porosity equal to 0.51. Fe^0 was pre-washed with acetone, dried, and kept in an oxygen free environment until used.

Zinc was selected as a representative of heavy metal contaminants. To simulate the water's zinc contamination, a solution of $Zn\ (NO_3)_2{\cdot}6H_2O$ (manufactured by E. MERCK, Denmark) was prepared and added to the specimen to obtain representative concentration.

2.2. Batch experiments

Batch equilibrium tests were carried out to specify the optimum adsorption conditions. The varied parameters used in these tests were contact time, initial pH of solution, initial concentration of metal, ZVI dosage, and agitation speed. Series of 250 ml flasks was employed and each flask was filled with 100 ml of zinc solution which has initial concentration of 50 mg/l. About 5 g of adsorbent was added into different flasks and the solution in the each flask was kept stirred in the high-speed orbital shaker at 200 rpm for 4 h. A fixed volume (20 ml) of the solution was withdrawn from each flask. This withdrawn solution was filtered to separate the adsorbent and a fixed volume (10 ml) of the clear solution was pipetted out for the determination of the concentration of metal ion still present in solution. The measurements were carried out using atomic absorption spectrophotometer (AAS) (Norwalk, Connecticut (USA)). However, the adsorbed concentration of metal ion on the resin was obtained by a mass balance.

Kinetic studies were investigated with different values of pH (4, 5, 6, and 8), initial Zn^{2+} concentration (50, 100, 150, 200, and 250 mg/l), ZVI dosage (1, 2, 3, 5, 10, and 12 g) per 100 ml, and shaking speed (0, 50, 100, 150, 200, and 250 rpm). However, the amount of metal ion retained in the ZVI phase, q_e in (mg/g), was calculated using [12]:

$$q_e = (C_o - C_e)\frac{V}{m} \tag{1}$$

where C_o is the initial concentration of metal in the solution before mixing with ZVI (mg/l), C_e is the equilibrium concentration of metal left in the solution (mg/l), V is the volume of solution (l), and m is the mass of ZVI (g). The adsorption isotherms were produced by plotting the q_e against the C_e at constant temperature. Langmuir (Eq. (2)) and Freundlich (Eq. (3)) models were used for the description of sorption data [13] as follows:

$$q_e = \frac{abC_e}{1 + bC_e} \tag{2}$$

$$q_e = K_F C_e^{1/n} \tag{3}$$

where a is empirical constant, b is the saturation coefficient (l/mg), K_F is the Freundlich sorption coefficient, and n is an empirical coefficient.

2.3. Continuous experiments

The experimental setup used in this study was constructed of Perspex cylinder having height and diameter equal to 70 and 5 cm, respectively, the column was equipped with seven sampling ports at the distance of 10 (port 1), 20 (port 2), 30 (port 3), 40 (port 4), 50 (port 5), 60 (port 6), and 65 cm (port 7) from the bottom. These ports were constructed of stainless steel fittings which blocked with Viton stoppers. Sampling was carried out at specified periods from sampling ports using needle. Sampling of the solution was done from the center axis of the column. Fig. 1 shows the schematic diagram of the reactor setup described above.

At the beginning of each test, the column was packed with 40 cm depth of soil specimen measured from the bottom. Then, ZVI with depth of 10 cm was placed at the top surface of the packed soil. Again, 15 cm of the soil was added above the ZVI. The column was then filled with distilled water that was fed slowly into the bottom of the column and forced upward through the medium, pushing up the air in front of it. As a result of this procedure, no difficulties with entrapped air were encountered. The up-flow column test was performed at constant temperature, 25˚C.

The contaminated solution with Zn^{+2} was introduced into the column from the storage tank. The flow rate from this tank, which is placed at the elevation higher than the level of column outlet, was controlled by valve A, valve B, and flow meter. Four values of flow rate (5, 10, 15, and 20 ml/min) were selected.

Zn^{2+} concentration along the length of the column in the effluent from sampling ports was measured for a period of 12 h from the beginning of the test. Water samples were taken regularly after 2, 4, 6, 8, 10, and 12 h. Four needles were connected to the four ends of Viton stoppers covered port 1, port 3, port 5, and port 7 in each test. In addition to specify four locations only for sampling, the column effluent line was closed and a small amount of water (1–1.5 ml) was withdrawn from these ports. In this way, the samples were taken at the flow rate of the column and this minimized disruption of flow within the column. The samples were immediately introduced in polyethylene vials and analyzed by AAS. The filling material in the column was assumed to be homogeneous and incompressible, and constant over time for water-filled porosity. All tubing and fitting for the influent and effluent lines were composed of an inert material.

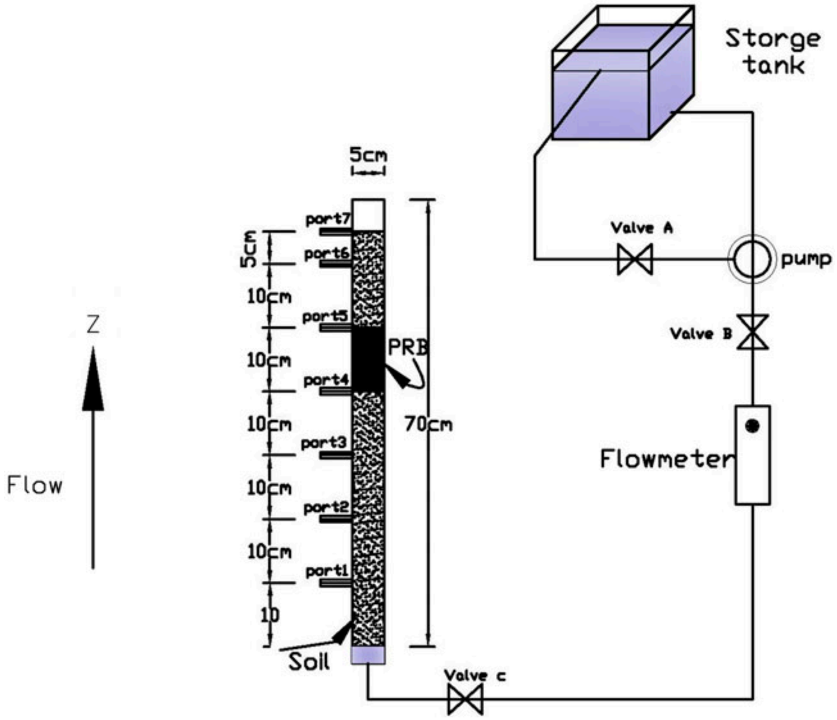

Fig. 1. Schematic diagram of the laboratory-scale column.

A tracer experiment was performed to determine the effective dispersion coefficient for the system. A sand soil was packed into the column in a dry condition for a depth of 45 cm. A solution of 1 g/l NaCl in distilled water as a tracer was continuously fed into the column, at a rate of 5, 10, 15, and 20 ml/min. Electrical conductivity was measured with time, as a representative of concentration, using conductivity meter at port 7 ($z_o = 65$ cm). In this case, the value of D_L is given by the following formula [14]:

$$D_L = \frac{1}{8}\left[\frac{(z_o - Vt_{0.16})}{(t_{0.16})^{0.5}} - \frac{(z_o - Vt_{0.84})}{(t_{0.84})^{0.5}}\right]^2 \tag{4}$$

where D_L is the longitudinal dispersion coefficient, V is the mean pore velocity of seepage (volume rate of flow per unit cross-sectional area of voids), and $t_{0.16}$ and $t_{0.84}$ are the arrival times of $C/C_o = 0.16$ and 0.84 relative concentration values, respectively.

3. Results and discussion

3.1. Effect of contact time and initial pH of the solution

Fig. 2 shows the effect of contact time on Zn^{+2} removal when 5 g of ZVI was added to 100 ml of metal solution for batch tests at 25°C. This figure demonstrates that Zn^{+2} removal efficiency is significantly increased with contact time. It is clear that the sorption rate is relatively high at the initial stage and gradually slowed down afterwards. The slower sorption rate is likely due to the decrease in sorption sites on the surface of the ZVI. It is obvious that Zn^{+2} ions removal mainly occurred within 3 h which is taken as equilibrium time for the next batch experiments.

The sorption of Zn^{+2} on the ZVI was examined at different pH values ranged from 4 to 8 with an initial metal concentration of 50 mg/l and different values of contact time (Fig. 2). The affinity of sorption is generally determined by pH at point of zero charge (pH_{PZC}). The pH_{PZC} is the pH at which a positive charge by protonation exists in approximately equal numbers with negative charges caused by the development of deprotonation on the iron surface. Under an acidic condition or pH value lower than pH_{PZC}, protons are sorbed on the functional group that causes the iron surface to have a net positive charge, thus, inhibit cation sorption. At pH value higher than pHpzc, the oxygen atom stays deprotonized and the surface prevails to have a net negative charge, thus, enhancing cation sorption [11]. However, the maximum removal efficiency of this metal was achieved at initial pH of 5.

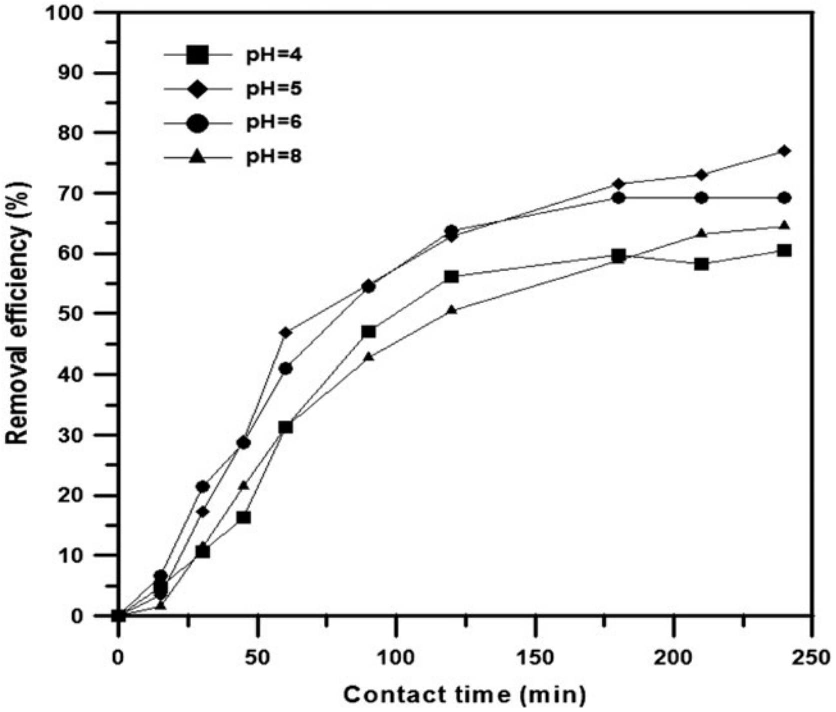

Fig. 2. Effect of contact time and initial pH on removal efficiency of zinc on ZVI ($C_o = 50$ mg/l; dose = 5 g; agitation speed = 200 rpm; $T = 25$°C).

3.2. Effect of ZVI dosage

The dependence of zinc sorption on sorbent dosage was studied by varying the amount of ZVI (from 1 to 12 g) added to 100 ml of metal solution (Fig. 3). It can be observed that removal efficiency was improved as sorbent dosage increased from 1 to 10 g at a fixed initial metal concentration. This can be attributed to the fact that the higher dose of sorbent in the solution, the greater availability of sorption sites. This means that the more ZVI particles are able to provide more iron surface-active sites for collision with metal molecules to accelerate the metal removal efficiency [15]. This also suggest that after a certain dose of sorbent, the maximum sorption sets in and hence, the amount of Zn^{+2} bound to the sorbent and the amount of this metal in solution remains constant even with further addition of the dose of sorbent.

3.3. Effect of initial zinc concentration

To investigate the effect of initial zinc concentration, batch experiments were conducted at various concentration of metal ranged from 50 to 250 mg/l. Fig. 4 explains that the removal efficiency had inverse proportion with the initial metal concentration. It is clear that the removal efficiency of Zn^{+2} decreased from 91 to 55% as the initial metal concentration increased. This plateau represents saturation of the active sites available on the ZVI samples for interaction with metal ions. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution [16].

3.4. Effect of agitation speed

The effect of agitation speed on removal efficiency of zinc ions was studied by varying the speed of agitation from 0 (without shaking) to 250 rpm and keeping other parameters equal to the best ones obtained in the previous steps. Fig. 5 shows that about 10% of the metal ion was removed before shaking and that Zn^{+2} uptake was increased with the increase of shaking rate. There was gradual increase in metal ions uptake when agitation speed was increased from zero to 200 rpm at which about 91% of zinc ion has been removed. The results also indicate that a shaking with 200 rpm is sufficient to ensure that all the surface binding sites were made readily available for metal uptake. Results proved that there was no significant change in ions removal after 200 rpm. These results

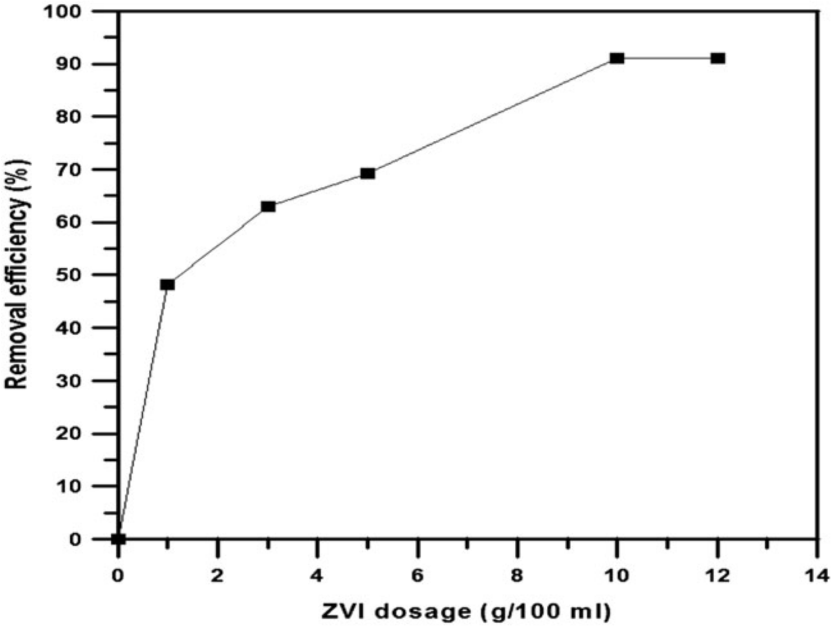

Fig. 3. Effect of ZVI dosage on removal efficiency of zinc ($C_o = 50$ mg/l; pH = 5; agitation speed = 200 rpm; contact time = 3 h; $T = 25$℃).

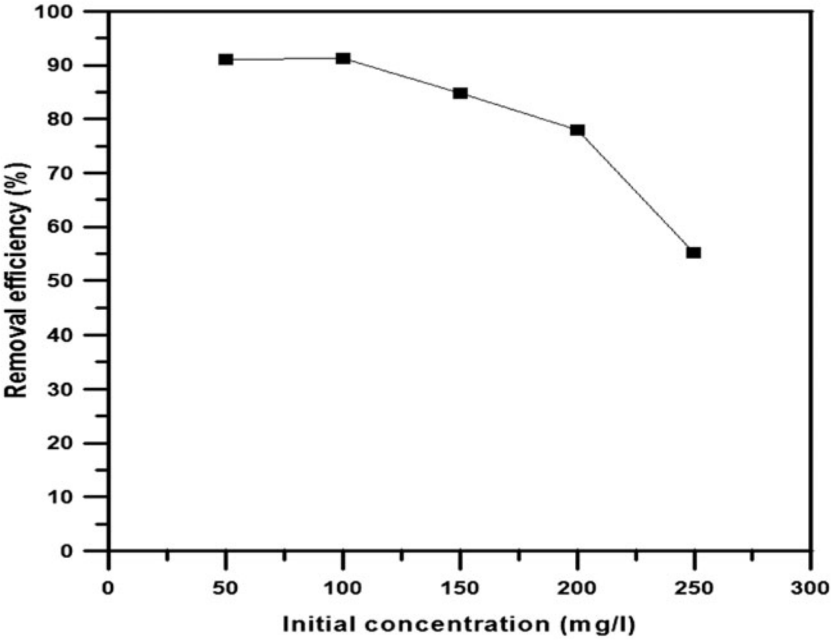

Fig. 4. Effect of initial concentration on removal efficiency of zinc on ZVI (pH = 5; dose = 10 g/100 ml; agitation speed = 200 rpm; contact time = 3 h; $T = 25$℃).

can be attributed to the fact that the increase in the agitation speed improves the diffusion of metal ions toward the surface of the reactive media. Thus, proper contact is developed between metal ions in solution and the binding sites, which promotes effective transfer of sorbate ions to the sorbent sites.

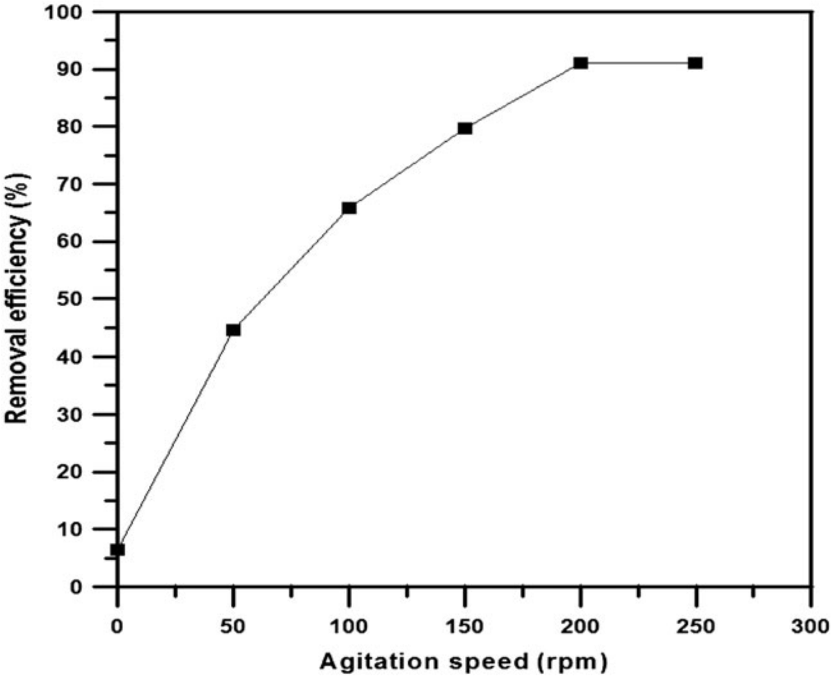

Fig. 5. Effect of agitation speed on removal efficiency of zinc ($C_o = 50$ mg/l; pH = 5; ZVI dose = 10 g/100 ml; contact time = 3 h; $T = 25$°C).

3.5. Sorption isotherms

The adsorption isotherms were produced by plotting the amount of zinc removed from the solution (q_e in mg/g) against the equilibrium metal concentration in the solution (C_e in mg/l) at constant temperature [17,18]. The data of the batch tests were fitted with linearized form of Langmuir and Freundlich models. Accordingly, the equations of these models will be:

$$q_e = \frac{0.302C_e}{1 + 0.203C_e} \quad R^2 = 0.9887 \tag{5}$$

$$q_e = 0.365C_e^{0.335} \quad R^2 = 0.7468 \tag{6}$$

Depending on the coefficient of determination (R^2), the Langmuir isotherm model was used to describe the sorption of zinc on ZVI in the partial differential equation governed the transport of a solute undergoing equilibrium sorption through PRB in the continuous mode.

3.6. Longitudinal dispersion coefficient

Results of the experimental runs concerned the measurement of longitudinal dispersion coefficient (D_L) at different values of velocity (V) for soil and ZVI could be described by the following linear relationships:

$$\text{For soil,} \quad D_L = 3.3391V + 0.0819 \quad R^2 = 0.998 \tag{7}$$

$$\text{For ZVI,} \quad D_L = 14.453V + 0.168 \quad R^2 = 0.9537 \tag{8}$$

These equations are in consistence with the general expression form of longitudinal hydrodynamic dispersion coefficient as follows:

$$D_L = D_{mech} + D^* \tag{9}$$

where D_{mech} and D^* are the mechanical dispersion coefficient and effective molecular diffusion coefficient, respectively.

3.7. Theoretical modeling

The one-dimensional transport of solute in the soil saturated zone is described by the well-known advection–dispersion equation as follows:

$$D_z \frac{\partial^2 C_{Zn}}{\partial z^2} - V_z \frac{\partial C_{Zn}}{\partial z} = R \frac{\partial C_{Zn}}{\partial t} \tag{10}$$

where D_z is the dispersion coefficient in the direction z, V_z is the velocity of flow, C_{Zn} is the concentration of zinc, and R is known as the retardation factor since it has the effect of retarding the transport of adsorbed species relative to the advection front. It is reasonable to assume that the value of R equal to 1 for pollutants transport in sandy soil. On the other hand, the sorption of solute on ZVI barrier is governed by Langmuir sorption isotherm and the retardation factor is expressed as follows:

$$R = 1 + \frac{\rho_d}{n_B}\left(\frac{0.302}{(1 + 0.203\ C_{ZnB})^2}\right) \tag{11}$$

where n_B is the porosity of the barrier. To present theoretical verification for column test described previously, Eq. (10) was applied for sandy soil aquifer in the regions where $0 \le z \le 40$ cm and $50\ \text{cm} \le z \le 65$ cm. The same equation was applied for ZVI barrier in the region where $40\ \text{cm} \le z \le 50$ cm. However, parameters and constants related to the sand soil and ZVI as well as initial and boundary conditions adopted for this verification are reported in Table 1.

An explicit method among finite difference methods (FDMs) was applied to the PDE describing the transport of contaminant through saturated zone of the sand soil and ZVI barrier. The equation was formulated with the following producer: for time, forward difference was used; for space, backward difference was used for simple partial difference; and center difference was used for quadratic partial difference. A computer program written in MATLAB R2009b (version 7.9) was developed to implement the model described above. Also, the same model was solved using the COMSOL Multiphysics 3.5a software which is based on finite element method.

Fig. 6 reports the concentration lines of zinc in the aquifer without presence of PRB at different values of contaminated groundwater flow rate after many time intervals. These concentrations were calculated from numerical methods described above and they were compared with those calculated by analytical solution given by [19]:

$$C(z,t) = \frac{C_o}{2}\left\{\operatorname{erfc}\left(\frac{z - V_z t}{\sqrt{4D_z t}}\right) + \exp\left(\frac{zV_z}{D_z}\right)\operatorname{erfc}\left(\frac{z + V_z t}{\sqrt{4D_z t}}\right)\right\} \tag{12}$$

where erfc(-) is a complimentary error function. It is clear that there is a good agreement between analytical and numerical solutions. This demonstrates that the numerical solution procedure is representative of contaminant distribution through saturated soil. This figure shows that the propagation of contaminated plume is very fast and the time required for the normalized concentration (ClCo) at the column outlet to be equal to 1 do not exceed 3 h. Also, it seems that an increase in flow rate, consequently an increase in interstitial velocity, resulted in a higher contaminant plume propagation velocity.

The predicted concentrations of Zn^{+2} ions by the numerical solutions for different values of flow rate after the introduction of the PRB show that the contaminant plume is hindered by the ZVI barrier and the zinc concentration level reaching the outlet of

Table 1
Measured parameters, related constants and conditions used in the modeling of zinc transport in 1D column

Item	Parameter	Value
Aquifer characteristics	Aquifer bed depth before barrier (cm)	40
	Aquifer bed depth after barrier (cm)	15
	Porosity of aquifer (n_A)	0.44
	Longitudinal dispersivity (α_L, cm)	3.339
	Bulk density (g/cm^3)	1.78
	Particle density (g/cm^3)	2.66
ZVI characteristics	Barrier bed depth (cm)	10
	Porosity of barrier (n_B)	0.51
	Longitudinal dispersivity (α_L, cm)	14.353
	Bulk density (g/cm^3)	6.5
Initial condition	Concentration of Zn^{+2} (mg/l)	0
Boundary conditions	Concentration of Zn^{+2}@ $z = 0$ (mg/l)	50
	Advective flux ($\frac{\partial C}{\partial Z}$) @ $z = 65$ cm	0

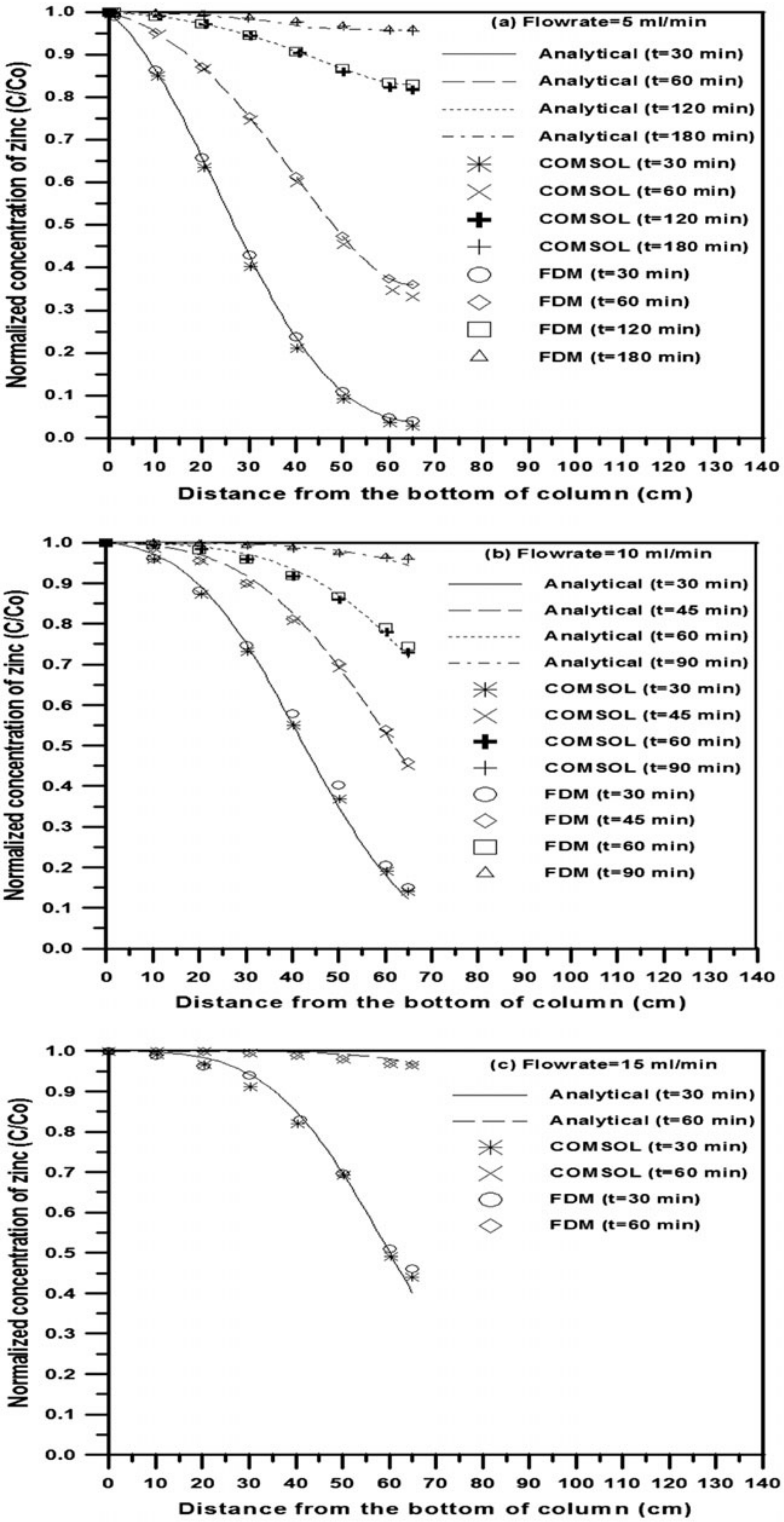

Fig. 6. Comparison between analytical and numerical solutions of conservative solute transport along the length of the soil column without using PRB at different values of travel time and flow rate.

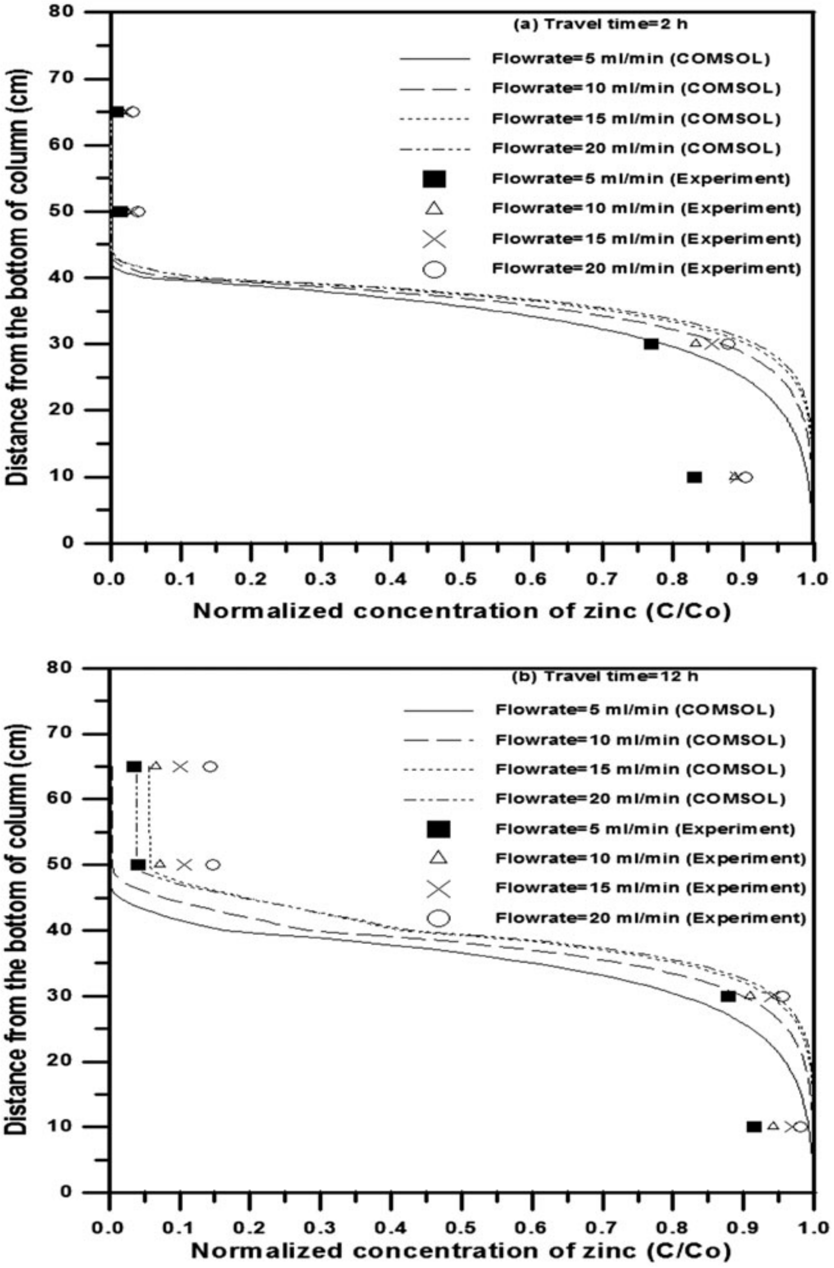

Fig. 7. Comparison between COMSOL solution and experimental results of Zn^{+2} concentrations in groundwater for two values of travel time.

the column is around zero (Figs. 7 and 8). In comparison with Fig. 6, these figures reveal the important role of barrier in restriction the propagation of contaminant plume. It seems that the barrier functionality is decreased with time because the decreasing of retardation factor. This may be due to formation of iron hydroxide and intermediate rust particles because the precipitation is the controlling mechanism in the zinc removal. These particles in turn may affect the longevity of an iron PRB by deposition and filling of the pores. This could eventually reduce the porosity of the reactive zone, and thereby block the flow path and reduce the efficiency of a PRB. However, there is a reasonable agreement between the predicted COMSOL (Fig. 7), FDM (Fig. 8), and experimental results for Zn^{+2} concentrations with root mean squared error [20] did not exceed 0.1487.

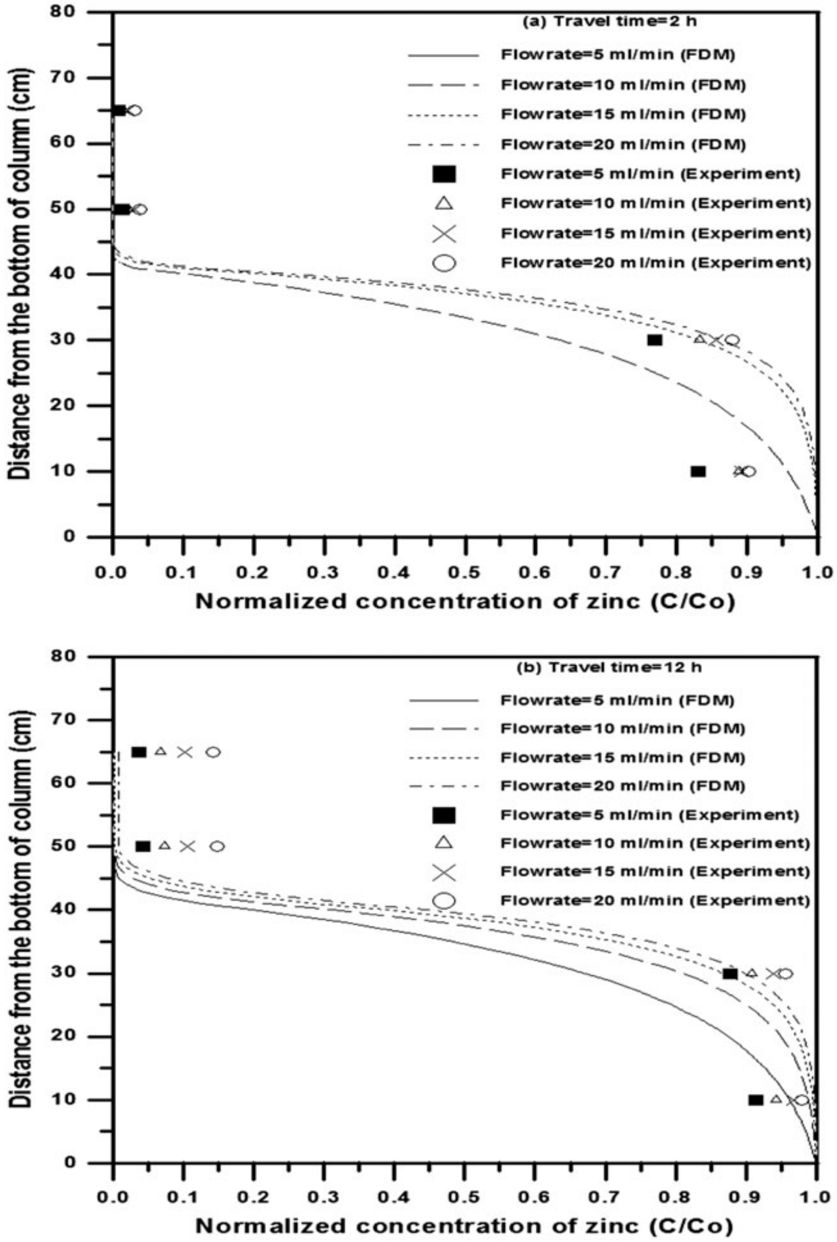

Fig. 8. Comparison between FDM solution and experimental results of Zn^{+2} concentrations in groundwater for two values of travel time.

4. Conclusions

(1) Equilibrium contact time, initial pH of the solution, initial metal concentration, ZVI dose, and agitation speed were the most significant parameters affecting sorption process efficiency of zinc ions by ZVI. The best values of these parameters that achieved the maximum removal efficiency of Zn^{+2} (=91%) were 3 h, 5, 50 mg/l, 10 g/100 ml, and 200 rpm, respectively.

(2) Zinc sorption data on the ZVI were applied to the Langmuir and Freundlich isotherm equations to test the fitness of these equations. These data were correlated reasonably well by the Langmuir sorption isotherm with coefficient of determination (R^2) equal to 0.9887.

(3) One-dimensional numerical model, solved by explicit FDM and COMSOL Multiphysics 3.5a under equilibrium condition, was used to describe pollutant transport within groundwater and the pollutant sorption on the PRB. The results proved that the iron barrier is efficient technique in the restriction of contaminant plume. However, the functionality of the barrier was decreased with time due to reduction in retardation factor. This may be due to formation of iron hydroxide and intermediate rust particles. These particles in turn may affect the longevity of an iron PRB by deposition and filling of the pores. This could eventually reduce the porosity of the reactive zone, and thereby block the flow path and reduce the efficiency of a PRB. A reasonable agreement between predicted and experimental results proved that these models were effective and efficient tools in description of pollutant transport phenomena.

(4) The results of this study demonstrated the possibility of using ZVI as an inexpensive material in PRB for removing zinc from polluted groundwater. Further work is needed to investigate the means required to sustain the functionality of the barrier during a reasonable operation period.

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