Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.855668

53 (2015) 1377–1386
February

Taylor & Francis
Taylor & Francis Group

Groundwater protection from cadmium contamination by zeolite permeable reactive barrier

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Received 26 April 2013; Accepted 3 October 2013

ABSTRACT

This work studies the performance of zeolite permeable reactive barrier in removing cadmium from a contaminated shallow aquifer. Batch tests have been performed to characterize the equilibrium sorption properties of the zeolite in cadmium-containing aqueous solutions. A 1D numerical finite difference model has been developed to describe pollutant transport within groundwater taking pollutant sorption on the permeable reactive barrier (PRB), which is performed by Langmuir equation, into account. Numerical results show that the PRB starts to saturate after a period of time (~120 h) due to reduction of the retardation factor, indicating a decrease in the percentage of zeolite functionality. However, a reasonable agreement between model predictions and experimental results of Cd^{+2} concentration across the soil bed in the presence of zeolite permeable reactive barrier was recognized.

Keywords: Cadmium; Zeolite; Permeable reactive barrier; Groundwater; Transport

1. Introduction

The presence of toxic heavy metals in groundwater brings about significant changes in the properties of water resources and has to be avoided in order to preserve the environmental quality. These metals can be related to many anthropogenic sources, and their compounds are extremely toxic. Many heavy metals, such as mercury, chromium, and cadmium, accumulate in the aquatic food web reaching human beings through the food chain, and causing several pathologies [1].

The availability of fresh water of proper quality is a prerequisite for human well-being and the consequential social/economic development of communities. In the past,water requirements for humans were considerably lower than the available natural resources. Additionally, the negative impact on the quality of water resources 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.

In the middle and southern regions of Iraq, the fresh water situation is especially acute leading, among other drawbacks, to an increase in desertification. A number of factors are to blame; foremost of which are water-impoundment projects in river-source countries (Turkey and Iran) and scanty rainfall due to climate change.

During the last decades, world researchers focused on groundwater as a substitute or a complementary

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resource to surface water. However, groundwater quality is affected by pollutants seeping through the soil, either directly or indirectly via surface water. Iraq, an oil-producing country with numerous refineries and a network of oil/oil fractions pipelines as well as other industrial and agricultural facilities scattered all over its land mass, has a relatively high potential for its groundwater resources being/to be polluted. This necessitates researching into groundwater quality, pollutant migration, and control. A new promising technology in this regard is permeable reactive barrier technology (PRB) which can be implemented *in situ*. It is envisaged that this technology would have a significant positive impact on the quality of groundwater resources, particularly in the middle and southern regions of Iraq, making this resource a reliable complementary option to surface water.

Significant progress in the modeling and experimental studies of pollutant migration through groundwater in the presence of different types and configurations of PRB has been achieved in the last two decades [1–9]. The potential application of activated carbon in permeable adsorbing barrier (PAB) for the removal of cadmium was investigated. The adsorption isotherms of this material are experimentally determined and a theoretical model is proposed for the interpretation of experimental results [1]. A set of batch and column tests were conducted to determine the design factors for clinoptilolite, one of the natural zeolites, PRBs against the contaminated groundwater by ammonium and heavy metals [2]. Effects of cold temperature on the ion exchange equilibria of copper with clinoptilolite in natural and pretreated sodium forms were investigated [3]. Ion exchange characteristics of Cu^{+2} on the natural zeolite clinoptilolite at 2℃ and 22℃ to facilitate the development of a PRB to treat heavy-metal-contaminated waters in Antarctica were studied [4]. Phosphate-induced metal stabilization involving the reactive medium Apatite II was used in a subsurface PRB to treat acid mine drainage in a shallow alluvial groundwater containing elevated concentrations of Zn, Pb, Cd, Cu, SO_4, and NO_3 [5]. The use of surfactant-modified zeolite as permeable barrier materials to remove anionic contaminants from groundwater was studied [6]. Many other theoretical and experimental studies were achieved to study the performance of many types of reactive materials such as natural clinoptilolite, Na-modified clinoptilolite, zero valent iron, etc as PRB in remediation of contaminated groundwater [7–9].

Characteristics of the barrier (i.e. barrier material, geometry, alignment, and depth) are the most important factors that should be considered when designing a barrier. Thus, the significant characteristics of the present study are: (1) characterization of soil and zeolite reactive barrier for cadmium transport through groundwater flow and (2) demonstration of the governing equations and their solution procedure as representative of contaminant distribution through saturated soil and reactive permeable barrier.

2. Experimental work

2.1. Materials

Naturally Iraqi soil was used as a porous medium in the experiments conducted in the present study. Depending on the particle size distribution (ASTM D 422), the percentages of sand, silt, and clay were 90, 10 and 0% respectively. Accordingly, this soil can be classified as sand soil. The permeability of this sand, measured with a constant head permeameter, was 1.27×10^{-4} cm/s. The measured values of the porosity and bulk density were 0.51 and 1.29 g/cm^3, respectively.

ZSM-5 zeolite pellets with dimension (2 mm × 6 mm) manufactured by (Dwax company for synthetic zeolite) were used as reactive materials. The resins were washed with 1 M of NaOH and 1 M of HCl in order to remove possible organic impurities, and then they were washed with distilled water to remove all excess and basic. Finally the resins were dried for 24 h. Table 1 shows the composition and reported physico-chemical properties of the zeolite used in the present study.

Cadmium was selected as a representative of heavy-metal contaminants. To simulate cadmium contamination in water, a solution of $Cd(NO_3)_2{\cdot}2H_2O$ (manufactured by E. MERCK, Denmark) was prepared and added to the specimen to obtain representative concentration.

Table 1
Composition and physico-chemical properties of zeolite

Property	Value
SiO_2	34.48
Al_2O_3	29.94
L.O.I	15.05
Na_2O	13.40
CaO	2.52
TiO_2	1.70
Bulk density (g/cm^3)	0.58
Particle density (g/cm^3)	1.2
Porosity (n_B)	0.34
Cation exchange capacity (meq/100 g)	1.8

2.2. Batch experiments

Batch equilibrium tests are carried out to specify the best conditions of contact time, initial pH, initial concentration, resin dosage and shaking velocity. This means that these tests are suited to identify the activity of the reactive material and the sorption isotherm. Series of 250 ml-flasks are employed. Each flask is filled with 100 ml of cadmium solution which has an initial concentration of 50 mg/l. About 0.25 g of adsorbent was added into different flasks. The solution in each flask was kept stirred in the high-speed orbital shaker at 270 rpm for 3 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 amount of unsorbed metal ion still present in the solution. The measurements were carried out using atomic absorption spectrophotometer (Norwalk, Connecticut (USA)). These measurements were repeated twice and the average value has been taken. 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 (2, 4, 6.5, and 8), different values of initial Cd^{2+} concentration (50, 100, and 250 mg/l), amounts of adsorbent dosage (0.15, 0.25, 0.5, 1 and 2 g) and finally two values of shaking speed (200 and 270 rpm).

From the best experimental results, the amount of metal ion retained in the zeolite phase, q_e, was calculated using [10]:

$$q_{\mathrm{e}} = (C_0 - C_{\mathrm{e}})\frac{v}{m} \tag{1}$$

where q_{e} is the amount of heavy metal removed from solution (mg/g), C_{o} is the initial concentration of heavy metal in the solution before mixing with zeolite (mg/l), C_{e} is the equilibrium concentration of heavy metal left in the solution after the experiment (mg/l), V is the volume of solution in the flask (l), and m is the mass of zeolite in the flask (g).

The adsorption isotherms were produced by plotting the q_{e} against the C_{e} at constant temperature. There are two major adsorption isotherm equations available from the literature, namely the Langmuir model and the Freundlich model [11]. These models are commonly used for the description of sorption data. The equation that describes the Langmuir system is:

$$q_{\mathrm{e}} = \frac{abC_{\mathrm{e}}}{1 + bC_{\mathrm{e}}} \tag{2}$$

where a is empirical constant and b is the saturation coefficient (l/mg).

The Freundlich isotherm is quantified by:

$$q_{\mathrm{e}} = K_F C_{\mathrm{e}}^{1/n} \tag{3}$$

where K_F is the Freundlich sorption coefficient and n is an empirical coefficient.

2.3. Continuous experiments

Fig. 1 shows the schematic diagram of the reactor setup used in the present study. This set-up is constructed of Perspex cylinder having height and diameter equal to 70 and 5 cm, respectively; the column is 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

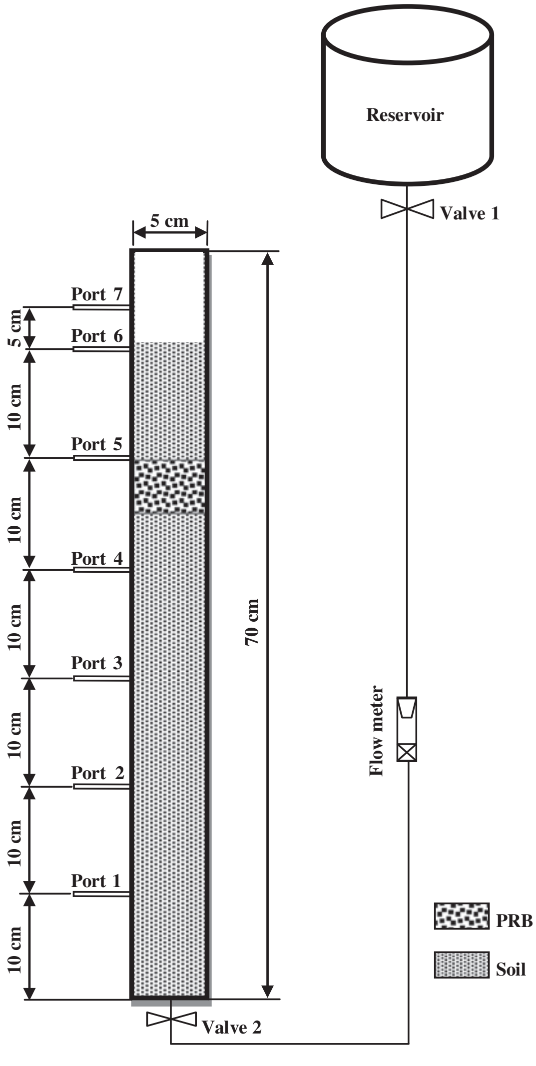

Fig. 1. Schematic representation of column test.

bottom. These ports are made of stainless steel fittings which are blocked with Viton stoppers. Sampling was carried out at specified periods from the sampling ports using needle which are inserted into the center axis of the column.

At the beginning of each test, the column was packed with 45 cm depth of soil specimen measured from the bottom. Then, zeolite with depth of 15 cm was placed at the top surface of the packed soil. Again, 5 cm of the soil was added above the zeolite. 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 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 a constant temperature, 25 ± 1℃.

The contaminated solution with Cd^{+2}, which simulated the contaminated groundwater, was introduced into the column from certain reservoir. The flow rate from this reservoir, which is placed at the elevation higher than the level of column outlet, was controlled by valve 1, valve 2 and flow meter. Three values of flow rate (5, 10, and 15 ml/min) are selected and about 11–15 l of artificial contaminated water was flushed out of the column for each experiment.

Monitoring of Cd^{+2} concentrations along the length of the column in the effluent from sampling ports was conducted for a period of 15 h. Water samples were taken regularly (after 5, 10, and 15 h) from these ports. For sampling the ports, three needles were connected to the three ends of Viton stoppers covering port 2, port 4, and port 6 in each test. However, these selected sampling locations may be changed periodically to comprise the ports (1, 3, and 5) during the same test. In addition to specifying only three locations 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 the disruption of flow within the column. The samples were immediately introduced in poly-ethylene 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. The volumetric water discharge through the column cross section was constant over time and set as the experimental values. The pollutant inlet concentration was set constant. All tubing and fitting for the influent and effluent lines should be made of an inert material. Information from the column study can be used along with the site characterization and modeling to help in designing the field-scale PRB.

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 0.3, 0.6 or 0.9 l/hr. Electrical conductivity was measured with time, as a representative of concentration, by conductivity meter at port 7 (z_o = 65 cm). In this case, the value of D_L is given by the following formula [12]:

$$D_L = \frac{1}{8}\left[\frac{(z_0 - Vt_{0.16})}{(t_{0.16})^{0.5}} - \frac{(z_0 - Vt_{0.84})}{(t_{0.84})^{0.5}}\right]^2 \tag{4}$$

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), $t_{0.16}$ and $t_{0.84}$ are the arrival times of C/C_0 = 0.16 and 0.84 relative concentration values, respectively.

3. Results and discussion

3.1. Effect of shaking time and initial pH of solution

Fig. 2 shows the effect of contact time on cadmium exchange using 0.25 g of zeolite added to 100 ml of metal solution for batch tests at 25 ± 1℃. Equilibrium for the purposes of this study was taken as having been reached when the cadmium removal efficiency values plateau.

It is clear from the same figure that the adsorption rate was very fast initially and it is increased with increasing contact time until it reaches the equilibrium time. This may be due to a decrease in mass transfer coefficient of the diffusion controlled reaction between resins and metal ions. This is a crucial parameter for the optimal removal of ions from the contaminated water [13]. Also this may be due to the presence of large number of resin sites available for the adsorption of metal ions. As the remaining vacant surfaces decrease, the adsorption rate slowed down due to the formation of repulsive forces between the metals on the solid surfaces and in the liquid phase [14]. However, further increase in contact time had no significant effect on cadmium removal.

It is seen from Fig. 2 that the increase in the metal removal as the pH increases (i.e. as the solution becomes more basic) can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in

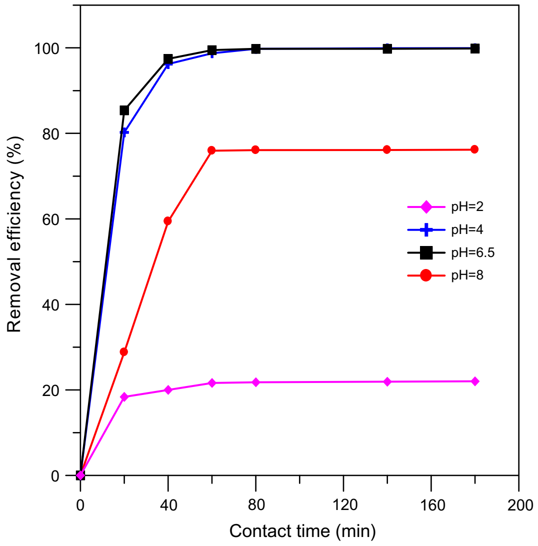

Fig. 2. Effect of shaking time and initial pH on removal efficiency of cadmium on zeolite as a function of contact time (Co = 50 mg/l; dose = 0.25 g; speed = 270 rpm; $T = 25 \pm 1$℃).

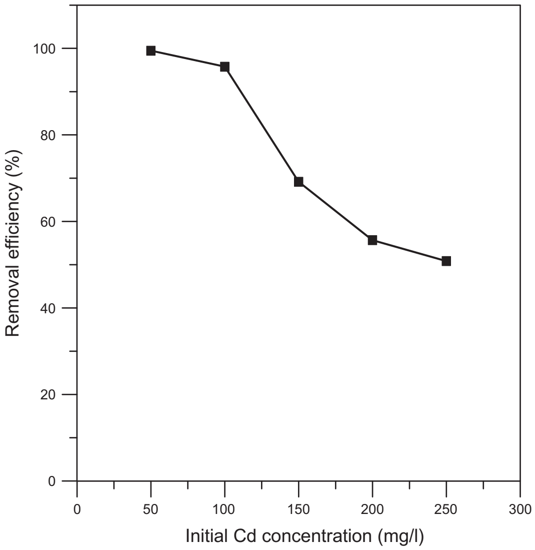

Fig. 3. Effect of initial concentration on removal efficiency of cadmium on zeolite (pH = 6.5; dose = 0.25 g; speed = 270 rpm; contact time = 1 h; $T = 25 \pm 1$℃).

positive surface charge, which results in a lower columbic repulsion of the sorbing metal. However, further increase in pH values would cause a decrease in the removal efficiency. This may be attributed to the formation of negative cadmium hydroxides $Cd(OH)_2^-$ which are precipitated from the solution making true sorption studies impossible. In addition, at low pH values an excess of protons can compete effectively with the Cd^{+2} ions for binding sites on zeolite surface. This effect has been attributed to the surface binding of low-affinity surface sites as high-affinity ones begin to reach saturation, leading to a reduction in the removal efficiency. It is clear from this figure that the time required to reach equilibrium in batch systems is equal to 1 h, although the initial pH of the solution was varied from 2 to 8. Also, the maximum removal efficiency of cadmium was achieved at an initial pH of 6.5.

3.2. Effect of initial cadmium concentration

Fig. 3 illustrates the removal of Cd^{+2} ions by zeolite as a function of initial metal ion concentration. The results show that there was a higher removal of the metal in the first values of initial concentration. This removal was decreased with an increase in the initial concentration up to 200 mg/l and beyond this value, there is not a significant change in the amount of adsorbed metal ions. This plateau represents saturation of the active sites available on the zeolite samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the zeolite at equilibrium (the adsorption capacity) rapidly increases at the low initial metal ions concentration and then it begins to a slight increase with increasing metal concentration in aqueous solutions in the length between 200 and 250 mg/l. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution [15].

3.3. Effect of resin dose

The dependence of Cd^{+2} sorption on adsorbent dosage was studied by varying the amount of zeolite from 0.15 to 2 g added to 100 ml of metal solution for batch tests, while keeping other parameters as follows; $C_0 = 50$ mg/l, pH = 6.5, shaking speed = 270 rpm and contact time = 1 h. Fig. 4 presents the Cd^{+2} removal efficiency as a function of different amounts of zeolite. It can be observed that removal efficiency of the Cd^{+2} improved with increasing adsorbent dosage from 0.15 to 0.25 g for a fixed initial metal concentration. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites. This also suggests that after a certain dose of adsorbent (0.25 g), the maximum adsorption sets in and hence the amount of Cd^{+2}

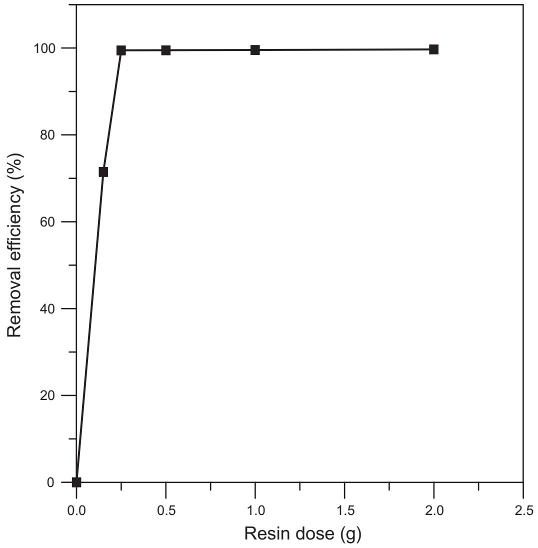

Fig. 4. Effect of resin dosage on removal efficiency of cadmium (Co = 50 mg/l; pH = 6.5; speed = 270 rpm; contact time = 1 h; T = 25 ± 1˚C).

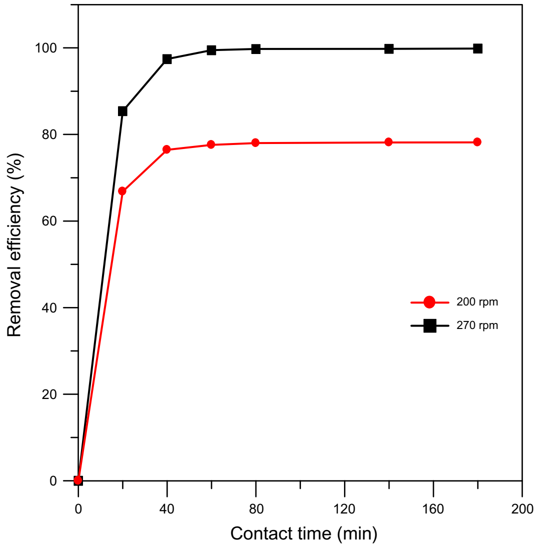

Fig. 5. Effect of agitation speed on removal efficiency of cadmium as a function of contact time (Co = 50 mg/l; pH = 6.5; resin dose = 0.25 g/100 ml; T = 25 ± 1˚C).

bound to the adsorbent and the amount of Cd^{+2} in solution remains constant even with further addition of the dose of adsorbent.

3.4. Effect of agitation speed

Fig. 5 shows that about 77% of the cadmium ions were removed at a shaking speed equal to 200 rpm when the contact time at equilibrium and that Cd removal increases with the increase in shaking speed. There was gradual increase in metal ions removal when agitation speed was increased from 200 to 270 rpm at which about 99.5% of Cd ions have been removed at equilibrium time. These results can be associated to the fact that the increase in the agitation speed improves the diffusion of metal ions towards the surface of the adsorbent. 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. This figure also shows that best equilibrium was reached at the agitation speed of 270 rpm. Therefore, higher uptake of metal ions could be possible at this speed of agitation as it will assure that all the sites are made readily available for metal ions uptake. However, greater availability of functional groups on the surface of adsorbent, which is required for the interaction of adsorbent and Cd^{+2}, significantly improved the binding capacity and the process proceeded rapidly. This result is important, as the agitation speed and, consequently, the equilibrium time is one of the important parameters for an economical contaminated water treatment system.

3.5. Sorption isotherms

The batch equilibrium technique is often used to determine the adsorption characteristics of various materials such as zeolite by plotting their adsorption isotherms. The adsorption isotherms were produced by plotting the amount of cadmium 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.

However, the data of the batch tests are fitted with a linearized form of Langmuir model and Freundlich model. Hence, the equations of these models will be;

$$q_e = \frac{14.355C_e}{1 + 0.29C_e} \quad R^2 = 0.9887 \tag{5}$$

$$q_e = 26.168C_e^{0.13349} \quad R^2 = 0.9033 \tag{6}$$

The comparison of the experimental values with the values of q_e obtained by these models (Eqs. 5 and 6) is shown in Fig. 6. It is clear that the Langmuir isotherm model provided the best correlation when compared with Freundlich isotherm model for cadmium adsorption on the zeolite. Accordingly, the Langmuir isotherm model was used to describe the sorption of solute on solid in the partial differential equation that

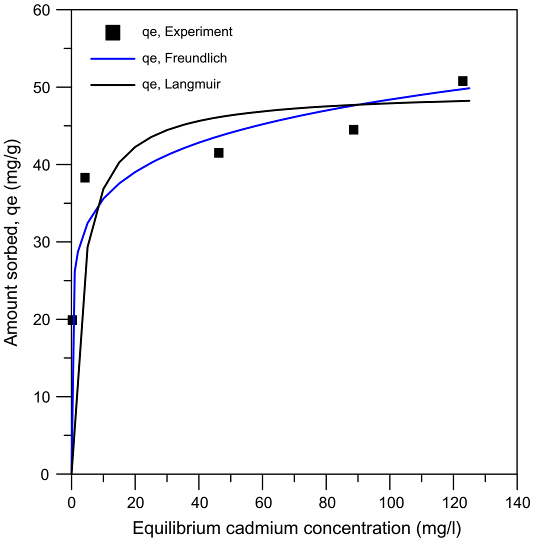

Fig. 6. Comparison of the experimental results with the *qe* values obtained by Langmuir and Freundlich models for Cd^{+2} removals on zeolite adsorbent.

governed the transport of a solute undergoing equilibrium sorption through permeable reactive barrier 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 zeolite are taken a linear relationship as follows:

$$\text{For soil,} \quad D_L = 9.96678V + 0.395667 \quad R^2 = 0.993 \tag{7}$$

$$\text{For zeolite,} \quad D_L = 17.0019V + 0.0033 \quad R^2 = 0.9393 \tag{8}$$

These equations have taken the general form of longitudinal hydrodynamic dispersion coefficient as follows:

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

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

3.7. Theoretical modeling

One dimensional mass transport of solute in the saturated zone of the soil which well-known advection-dispersion equation can be established as follows:

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

where R is known as the retardation factor since it has the effect of retarding the transport of adsorbed species relative to the advection front.

For the flow of contaminated groundwater through the sand soil, the value of R will be assumed equal to 1 which is reasonable for this type of soil. On the other hand, the sorption of solute on zeolite barrier is governed by Langmuir sorption isotherm and the retardation factor is expressed as follows:

$$R = 1 + \frac{\rho_d}{n_B} \left(\frac{14.355}{(1 + 0.29 C_{cdB})^2} \right) \tag{11}$$

where n_B is the porosity of the barrier. To present theoretical verification for column test described previously, Eq. 10 can be applied for sand soil aquifer in the regions where $0 \le z \le 45$ cm and 60 cm$\le z \le 65$ cm. The same equation can be applied for zeolite barrier in the region where $45 \le z \le 60$ cm. However, parameters and constants related to the sand soil and zeolite as well as initial and boundary conditions adopted here for this verification are reported in Table 2.

An explicit method among finite difference methods was applied to the PDE describing the transport of contaminant through saturated zone of the sand soil and zeolite barrier. The equation was formulated with the following procedure: 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.

Fig. 7 reports the concentration lines of cadmium in the aquifer at different values of contaminated groundwater flow rate after the time interval equal to 0.5 h without using PRB. It is clear from this figure that the propagation of contaminated plume is very fast and the time required for reaching the concentration of cadmium in the outlet of column to the constant concentration applied to the left boundary (i.e. 50 mg/l) has not exceeded 1 h. Also, it seems that the increased value of flow rate will increase the velocity of flow for the same cross sectional area of soil specimen and, consequently, this will increase the velocity of cadmium plume propagation. The concentration of the contaminated plume reaching the outlet may attain concentration levels higher than 20 mg/l

Table 2
Summary of PRB application example parameters

Item	Parameter	Value or description
Aquifer characteristics	Aquifer bed depth before barrier (cm)	45
	Aquifer bed depth after barrier (cm)	5
	Porosity of aquifer (n_A)	0.51
	Longitudinal dispersivity (α_L, cm)	9.96678
PRB characteristics	Adsorbing medium	Zeolite
	Barrier bed depth (cm)	15
	Porosity of barrier (n_B)	0.34
	Longitudinal dispersivity (α_L, cm)	17.0019
Numerical model parameters	Number of nodes	65
	Time step size (min)	0.001
	Initial concentration of Cd^{2+} (mg/l)	Zero
Boundary conditions	Concentration of Cd^{2+} @ $z = 0$ (mg/l)	50
	$\frac{\partial c_{cd}}{\partial z}$ @ $z = 65$	Zero
	$C_{CdA}(45, t) = C_{CdB}(45, t)$	–
	$C_{CdA}(60, t) = C_{CdB}(60, t)$	–

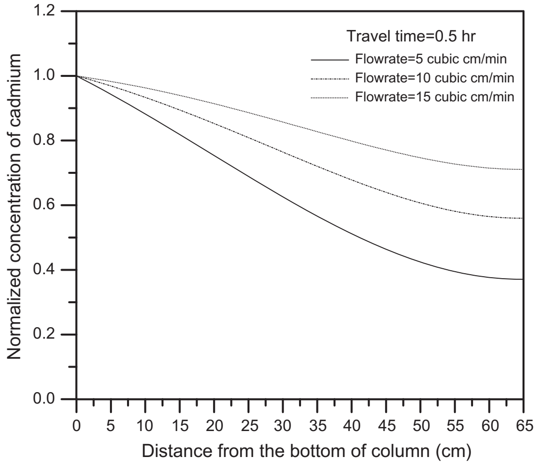

Fig. 7. Cadmium concentration distribution in the groundwater along the length of the soil column without using PRB after 0.5 h.

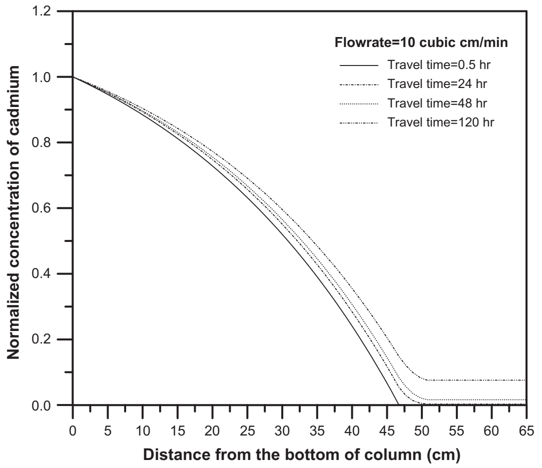

Fig. 8. Cadmium concentration distribution in the groundwater along the length of the soil column with using PRB at different time intervals.

and largely above the 0.005 mg/l quality limit prescribed for surface waters or drinking water [1].

Numerical results proved that the introduction of the PAB hindered the contaminant plume and the cadmium concentration level reaching the outlet is around zero at 24 h for different values of contaminated groundwater flow rate. Fig. 8 illustrates the important role of the barrier in restricting the propagation of contaminant plume. However, this barrier starts to saturate with increasing the travel time and this means that the cadmium retardation factor was reduced, indicating a decrease in the percentage of zeolite functionality for cadmium retardation. This explains the increase of effluent concentration of cadmium from PRB with increased the travel time.

Comparison between the predicted and experimental results for cadmium concentration during the migration of the contaminant plume for simulated problem adopted here at a time interval equal to 15 h for different values of flow rate are depicted in Fig. 9. A reasonable agreement between these results can be observed. These concentrations seem to be almost identical however they are slightly different. The highest percentage of difference encountered between the predicted and experimental concentrations has not exceeded ± 20%. However, any variation between the

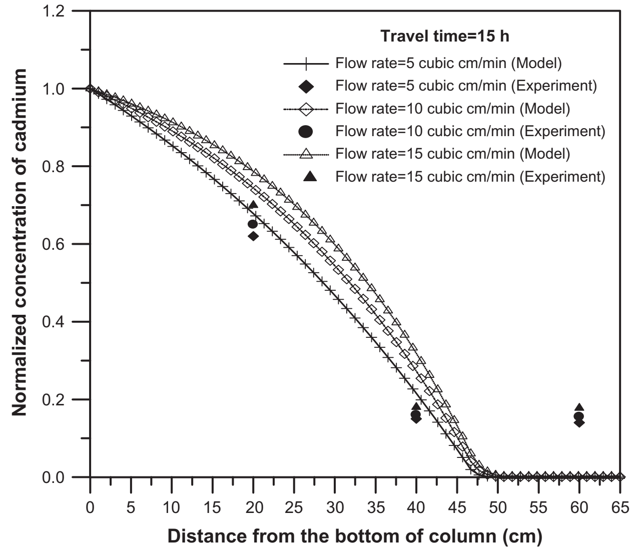

Fig. 9. Comparison between model predictions and experimental results for Cd^{+2} concentrations in groundwater for travel time equal to 15 h.

model predictions and experimental results could be attributed to the many causes such as neglecting the salts (such as calcite or carbonate) adsorption and their adsorption competition with the cadmium over the solid surface of the particles. Also, the competition between the dissolved salts in the groundwater from soil and cadmium in the zeolite barrier is not considered in the present mathematical modeling. This may explain the deviation of experimental results from the model prediction at 60 cm.

4. Conclusions

(1) The interactions between cadmium ions and zeolite have been investigated. The batch results indicated that several factors such as contact time, initial pH of the solution, initial metal ion concentration, resin dose and agitation speed affect the adsorption process. However, the best values of these factors will achieve the maximum removal efficiency of Cd^{+2} were 1 h, 6.5, 50 mg/l, 0.25 g/100 ml, and 270 rpm, respectively.

(2) The experimental equilibrium data obtained were applied to the Langmuir and Freundlich isotherm equations to test the fitness of these equations. The experimental data for cadmium sorption on the zeolite were correlated reasonably well by the Langmuir adsorption isotherm with a coefficient of determination (R^2) equal to 0.9887 in comparison with the Freundlich isotherm model (R^2 = 0.9033).

(3) A 1D numerical model is used to describe pollutant transport within groundwater and the pollutant adsorption on the PRB. Numerical results show that the PRB starts to saturate after a period of time (~120 h) due to reduction of the retardation factor, indicating a decrease in percentage of zeolite functionality. Also, reasonable agreement between model predictions and experimental results of the total concentration distribution of Cd^{2+} species across the soil bed was recognized.

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