Iron Permeable Reactive Barrier for Removal of Lead from Contaminated Groundwater

Ayad Abdulhamza Faisal
Assistant Professor
College of Engineering
University of Baghdad
e-mail: ayadabedalhamzafaisal@yahoo.com

Talib Rasheed Abbas
Researcher
Ministry of Science and
Technology
e-mail: talibrshd@yahoo.com

Salim Hrez Jassam
Ph.D. student
College of Engineering
University of Baghdad
e-mail: hrez_salim@yahoo.com

ABSTRACT

The possibility of using zero-valent iron as permeable reactive barrier in removing lead from a contaminated groundwater was investigated. In the batch tests, 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 results proved that the best values of these parameters achieve the maximum removal efficiency of Pb^{+2} (=97%) were 2 hr, 5, 5 g/100 mL, 50 mg/L and 200 rpm respectively. The sorption data of Pb^{+2} ions on the zero-valent iron have been performed well by Langmuir isotherm model in compared with Freundlich model under the studied conditions.

Finite difference method and computer solutions (COMSOL) multiphysics 3.5a software based on finite element method were used to simulate the one-dimensional equilibrium transport of lead through sand aquifer with and without presence of barrier. The predicted and experimental results proved that the reactive barrier plays a potential role in the restriction of the contaminant plume migration and a reasonable agreement between these results was recognized.

Key words: zero-valent iron, lead, permeable reactive barrier, groundwater, migration.

الجدار الحديدي التفاعلي النفاذ لازالة الرصاص من المياه الجوفية الملوثة

سالم حريز جسام
طالب دكتوراة
كلية الهندسة-جامعة بغداد

طالب رشيد عباس
باحث
وزارة العلوم والتكنولوجيا

أياد عبد الحمزة فيصل
أستاذ مساعد
كلية الهندسة-جامعة بغداد

الخلاصة

تهدف الدراسة الحالية الى معرفة امكانية استخدام الحديد صفر التكافؤ كحاجز تفاعلي نفاذ في ازالة الرصاص من المياه الجوفية الملوثة. في اختبارات الدفعة تم دراسة تأثير عدة متغيرات تشغيلية مثل زمن التماس بين المادة المازة والممتزة (0-240 دقيقة), الدالة الحامضية (4-8), كمية المادة الممتزة (1-12 غم/100 مليلتر), التركيز الابتدائي للمعدن (50-250 ملغم/لتر), وسرعة الاهتزاز (0-250 دورة/دقيقة). أن افضل قيم لهذه المتغيرات والتي تم من خلالها الحصول على اعلى كفاءة ازالة للرصاص (97%=) هي 2 ساعة, 5, 5 غم/100 مليلتر,50 ملغم/لتر, و 200 دورة/دقيقة على التوالي. اظهرت نتائج الامتزاز للرصاص ان نموذج لانكمير هو الافضل في تمثيل بيانات الامتزاز مقارنة بنموذج فريندلج تحت الظروف التي تم دراستها.

تم استخدام طريقة الفروقات المحددة وبرنامج حاسوبي جاهز يعتمد على طريقة العناصر المحددة لتمثيل انتقال ملوث الرصاص باتجاه واحدة في الطبقة الرملية في حالة وجود وعدم وجود الجدار التفاعلي النفاذ. اثبتت النتائج المحسوبة من النماذج الرياضية والتجارب المختبرية ان هذه الجدران تلعب دور مهم في ازالة وتقييد حركة الملوث كما يوجد توافق معقول بين تلك النتائج.

1. INTRODUCTION

The permeable reactive barrier (PRB) technology has received acceptance as an effective passive remediation technology for the treatment of inorganic contaminants (such as cadmium, lead, mercury, nickel, zinc…etc) in groundwater. This technology combines subsurface fluid-flow with contaminant treatment by combinations of physical, chemical, biological or mixed processes. The medium most widely used in PRBs is the zero-valent iron (ZVI), which has proven very efficient, in particular, for heavy metals. The main advantage of a reactive barrier is the passive nature of the treatment: the contaminated groundwater moves under natural hydraulic gradient through the permeable reactive zone where the pollutant is degraded or immobilized. This method is found to be more cost-effective than pump and treat. It has been demonstrated potential to diminish the spread of contaminants which have proven difficult and expensive to manage with other cleanup methods, **Puls, et al., 1998**, **Di Natale, et al., 2008**, **Wilkin, et al., 2009**.

A considerable theoretical and laboratory-bench scale studies on ZVI and its potential for the treatment of heavy metals in water has been achieved. The kinetics of the cementation of lead from acidic solutions onto rotating iron discs have been studied over a large range of initial lead ion concentrations, disc rotation speeds and temperatures, **Makhloufi, et al., 2000**. The removal of organic and inorganic pollutants from groundwater by 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, **Geranio, 2007**. The reduction of hexavalent chromium by scrap iron was investigated in continuous system, using as reducing agent the following scrap iron shapes and sizes: (1) spiral fibers, (2) shavings, and (3) powder. The shape and size of scrap iron were found to have a significant influence on chromium and iron species concentration in column effluent, on column effluent pH and on Cr(VI) reduction mechanism, **Gheju, and Balcu, 2010**. A continuous column experiment was carried out under dynamic flow conditions in order to study the efficiency of low-cost PRBs to remove several inorganic contaminants from acidic solutions. A 50:50 w/w waste iron/sand mixture was used as candidate reactive media in order to activate precipitation and promote sorption and reduction–oxidation mechanisms, **Bartzas, and Komnitsas, 2010**. The optimal weight ratio between iron and pumice in nickel removal from contaminated groundwater in order to balance the preservation of the hydraulic conductivity (favoured by increasing the pumice content of the mixture) and the removal efficiency (favoured by increasing ZVI content) was evaluated, **Calabró, et al., 2012**. Groundwater flow velocity is found to have no effect on the adsorption performance of PRB, but it have effect on treating time because zinc is transported faster from its source to the PRB with greater groundwater flow velocity, **Riyapan, et al., 2012**. 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, **Suponik, 2013**. A study for groundwater flow and zinc transport modeling to assess the performance of the continuous and funnel and gate PRBs which having 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 2170 to 2248 and 1675 to 1803 days for continuous and funnel and gate PRBs, respectively, **Chalermyanont, et al., 2013**.

Accordingly, the significance of the present study was investigated the potentially using of ZVI as an inexpensive material in PRBs theoretically and experimentally for the removal of lead from simulated contaminated groundwater.

2. EXPERIMENTAL WORK
2.1 Materials

Naturally 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 93, 7 and 0 % respectively and this soil can be classified as sandy soil. The permeability of this sand, measured with a constant head permeameter, was **2.22** x 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 as scrap iron (iron filings of workshop). 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, 2010.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.

Lead was selected as a representative of heavy metal contaminants. To simulate the water's lead contamination, a solution of $Pb(NO_3)_2.2H_2O$ (manufactured by E. MERCK, Denmark) was prepared and added to the specimen to obtain representative concentration.

2.2 Batch Experiments

Batch equilibrium tests are carried out to specify the best conditions of contact time, initial pH, initial concentration of metal, ZVI dosage and agitation speed. Series of 250 mL flasks are employed and each flask is filled with 100 mL of contaminant solution. A constant weight of adsorbent was added into different flasks and the mixtures were agitated on a rotary shaker (Thermolyne, Maxi-Mix III, Type: 65800 (USA)) at 200 rpm for 4 hours. 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 metal ion still present in solution. The measurements were carried out using atomic absorption spectrophotometer (AAS) (Norwalk, Connecticut (USA)). The adsorbed concentration of metal ion on the ZVI was obtained by a mass balance.

Kinetic studies were investigated with different values of initial pH (4, 5, 6 and 8), ZVI dosage (1, 3, 5, 10 and 12 g per 100 mL), initial metal concentration (50, 100, 150, 200 and 250 mg/l) and agitation speed (0, 50, 100, 150, 200 and 250 rpm). The amount of metal ion retained in the ZVI, q_e (mg/g), was calculated as follows, **Wang, et al., 2009**:

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

where C_o is the initial concentration of lead in the solution before mixing with ZVI (mg/L), C_e is the equilibrium concentration of lead remaining in the solution (mg/L), V is the volume of solution in the flask (L), and m is the mass of ZVI in the flask (g).

Langmuir (Eq. (2)) and Freundlich (Eq. (3)) models are used for the description of sorption data as follows, **Watts, 1998**:

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

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

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

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 setup 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), 65 cm (port 7) from the bottom. These ports should be constructed of stainless steel fittings which blocked with Viton stoppers. Sampling was carried out at specified periods from sampling ports using needle to be inserted into the center axis of the column.

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 the air in front of it. As a result of this procedure, **Ujfaludi, 1986**, no difficulties with entrapped air were encountered. The up flow column test was performed at constant temperature, 25ºC.

The contaminated solution with Pb^{+2}, which simulated the contaminated groundwater, was introduced into the column from storage tank controlled by pump, flowmeter and three valves A, B and C. Four values of flow rate (5, 10, 15 and 20 mL/min) are applied.

Monitoring of Pb^{2+} concentration along the length of the column in the effluent from sampling ports was measured for a period of 12 hrs. Water samples were taken regularly after 2, 4, 6, 8, 10 and 12 hrs. 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 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. All tubing and fitting for the influent and effluent lines should be composed of an inert material.

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, by using conductivity meter at port 7 (z_o=65 cm). In this case, the value of D_L is given by the following formula, **Ujfaludi, 1986**:

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

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), $t_{0.16}$ 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 Investigation of Sorption Parameters
3.1.1 Effect of contact time and initial pH

Fig. 2 shows the effect of contact time on the percentage removal of lead using 5 g of ZVI added to 100 mL of metal solution at 25ºC. The percentage removal for different values of pH was rapid in the beginning but it gradually decreased with time until it reached equilibrium. The plots reveal that maximum removal efficiency of the lead after about 2 hr of shaking. The rate of removal is higher in the beginning due to the presence of large number of sites available for the sorption processes.

The sorption of Pb^{+2} on the ZVI was examined at different pH ranging 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 below pH_{PZC}, protons are sorbed on the functional group that causes the iron surface to have a net positive charge and, thus, inhibit cation sorption. At above pHpzc, the oxygen atom stays deprotonized and the surface prevails to have a net negative charge, thus, enhancing cation sorption, **Rangsivek, 2010**. However, the maximum removal efficiency of this metal was achieved at initial pH of 5.

3.1.2 Effect of initial lead concentration

Fig. 3 explains that the removal efficiency increased inversely with the initial metal concentration. It is clear that the removal efficiency of Pb^{+2} decreased from 97% to 75% with increasing the initial metal concentration from 50 to 250 mg/L. This plateau represents saturation of the active sites available on the ZVI samples for interaction with lead ions. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution, **Selvarani, and Prema, 2010**.

3.1.3 Effect of ZVI dosage

The dependence of lead 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. 4**). It can be observed that removal efficiency improved with increasing sorbent dosage from 1 g to 5g at a fixed initial metal concentration. This was expected due 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, **Rahmani, et al., 2010**.

3.1.4 Effect of agitation speed

The effect of agitation speed on removal efficiency of lead ions was studied by varying the speed of agitation from 0 (without shaking) to 250 rpm and keeping other parameters equal to best ones obtained in the previous steps. Fig. 5 shows that about 10% of the metal ion was removed before shaking and that Pb^{+2} uptake increase 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 97% of lead ions have been removed. The results also indicate that a shaking with 200 rpm is sufficient to ensure that all the surface binding sites are made readily available for metal uptake. Results proved that there is no significant change in ions removal after 200 rpm. 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 reactive media, **Faisal, and Hmood, 2013**.

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.

3.1.5 Sorption isotherms

The sorption isotherms were produced by plotting the amount of lead 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, **Hamdaouia, and Naffrechoux, 2007**, **Kumar, and Kirthika, 2009**. The data of the batch tests are fitted with linearized form of Langmuir and Freundlich models. Accordingly, the equations of these models will be;

$$q_e = \frac{0.481 C_e}{1 + 0.117 C_e} \qquad R^2 = 0.9926 \tag{5}$$

$$q_e = 0.81 C_e^{0.381} \qquad R^2 = 0.9836 \tag{6}$$

It is clear that these models are provided the best representation of lead sorption onto ZVI reactive material. However, the Langmuir model was chosen to describe the sorption of solute onto solid in the partial differential equation governed the transport of a solute undergoing equilibrium sorption through permeable reactive barrier in the continuous mode.

3.2 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 are taken a linear relationship as follows:

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

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

These equations are taken the general 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.

3.3 Theoretical Modeling

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

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

where D_z is the dispersion coefficient in the direction z, V_z is the velocity of flow, 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. For the flow of contaminated groundwater through the sandy soil, the value of R will be assumed equal to 1 which is reasonable for this type of soils. 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, **Elango, 2005**:

$$R = 1 + \frac{\rho_d}{n}\left(\frac{ab}{(1+bC)^2}\right) \tag{11}$$

$$R = 1 + \frac{\rho_d}{n_B}\left(\frac{0.302}{(1+0.203 C_{PbB})^2}\right) \tag{12}$$

where n_B is the porosity of the barrier. To present theoretical verification for column test described previously, Eq. (10) can be applied for sandy soil aquifer in the regions where $0 \leq z \leq 40$ cm and 50 cm $\leq z \leq$ 65cm. The same equation can be applied for ZVI barrier in the region where 40 cm $\leq z \leq$ 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 was applied to the partial differential equation (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 problem was solved by using the COMSOL Multiphysics 3.5a software which is based on finite element method.

Fig. 6 reports the concentration lines of lead in the aquifer without presence of PRB at different values of contaminated groundwater flow rate after many time intervals. These concentrations are calculated from numerical methods described above and they are compared with those calculated by analytical solution given by, **Holzbecher, 2007**:

$$C(z,t) = \frac{C_o}{2}\left\{\text{erfc}\left(\frac{z-V_z t}{\sqrt{4D_z t}}\right) + \exp\left(\frac{z V_z}{D_z}\right)\text{erfc}\left(\frac{z+V_z t}{\sqrt{4D_z t}}\right)\right\} \tag{13}$$

where erfc(-) is a complimentary error function. It is clear that there 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 reaching the normalized concentration of solute (C/C_o) to 1 at the outlet of column was not exceeded 3 hr. Also, it seems that the increased value of flow rate will increase the velocity of flow for same cross sectional area of soil specimen and, consequently, this will increase the velocity of contaminant plume propagation.

The predicted concentrations of Pb^{+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 lead concentration level reaching the outlet of the column is around zero (**Figs. 7 and 8**). It is clear from these figure in comparison with **Fig. 6** 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. It is clear from these

figures that there is a reasonable agreement between the predicted FDM, COMSOL and experimental results for Pb^{+2} concentrations.

4. CONCULSIONS

1)   Equilibrium contact time, initial pH of the solution, initial metal concentration, ZVI dosage and agitation speed were most the parameters affected on the sorption process between lead ions and ZVI. The best values of these parameters that will achieve the maximum removal efficiency of Pb^{+2} (=97%) were 2 hr, 5, 50 mg/L, 5 g/100 mL, and 200 rpm respectively.

2)   Lead sorption data on the ZVI were correlated reasonably with Langmuir and Freundlich sorption isotherm equations. However, Langmuir model with highest coefficient of determination (R^2) was chosen in the solute transport model through the PRB.

3)   One dimensional numerical model, solved by explicit finite difference method 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 because the decreasing of 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 are effective and efficient tools in description of pollutant transport phenomena.

5. REFERENCES

➢ Bartzas, G., and Komnitsas, K., 2010, *Solid Phase Studies and Geochemical Modeling of Low-Cost Permeable Reactive Barriers*, Journal of Hazardous Materials, Vol. 183, PP. 301-308.

➢ Calabró, P. S., Moraci, N., and Suraci, P., 2012, *Estimate of the Optimum Weight Ratio in Zero-Valent Iron/Pumice Granular Mixtures Used in Permeable Reactive Barriers for the Remediation of Nickel Contaminated Groundwater*, Journal of Hazardous Materials, Vol. (207-208), PP. 111-116.

➢ Chalermyanont, T., Chetpattananondh, P., and Riyapan, N., 2013, *Numerical Modeling of Permeable Reactive Barriers to Treat Heavy-Metal Contaminated Groundwater*, 6th PSU-UNS International Conference on Engineering and Technology (ICET_2013), Novi Sad, Serbia, University of Novi Sad, Faculty of Technical Sciences.

➢ Di Natale, F., Di Natale, M., Greco, R., Lancia, A., Laudante, C., and Musmarra, D., 2008, *Groundwater Protection from Cadmium Contamination by Permeable Reactive Barriers*, Journal of Hazardous Materials, Vol. 160, PP. 428–434.

➢ Elango, L., 2005, *Numerical Simulation Groundwater Flow and Solute Transport*, Allied Publishers Pvt. Ltd., 751, Anna Salai, Chennai-600002, ISBN:81.

➢ Faisal, A. A., and Hmood, Z. A., 2013, *Groundwater Protection from Cadmium Contamination by Zeolite Permeable Reactive Barrier*, Desalination and Water Treatment, doi: 10.1080/19443994.2013.855668.

➢ Geranio, L., 2007, *Review of Zero Valent Iron and Apatite as Reactive Materials for Permeable Reactive Barrier*, Term Paper SS 07/08, major in Biogeochemistry and Pollutant Dynamics, Department of Environmental Sciences ETH Zurich.

➢ Gheju, M., and Balcu, I., 2010, *Hexavalent Chromium Reduction with Scrap Iron in Continuous-Flow System. Part 2: Effect of Scrap Iron Shape and Size*, Journal of Hazardous Materials, Vol. 182, PP. 484-493.

➢ Hamdaouia, O., and Naffrechoux, E., 2007, *Modeling of Adsorption Isotherms of Phenol and Chlorophenols onto Granular Activated Carbon Part I. Two-Parameter Models and Equations Allowing Determination of Thermodynamic Parameters*, Journal of Hazardous Materials, Vol. 147, PP. 381–394.

➢ Holzbecher, E., 2007, *Environmental Modeling Using MATLAB*, Springer Berlin Heidelberg New, ISBN: 978-3-540-72936-5.

➢ Kumar, P. S., and Kirthika, K., 2009, *Equilibrium and Kinetic Study of Adsorption of Nickel from Aqueous Solution onto Bael Tree Leaf Powder*, Journal of Engineering Science and Technology, Vol. 4, PP. 351-363.

➢ Makhloufi, L., Saidani, B., Hammache, H., 2000, *Removal of Lead Ions from Acidic Aqueous Solutions by Cementation on Iron*, Water Research, Vol. 34, No. 9, PP. 2517-2524.

➢ Puls, R. W., Powell, R. M., Blowes, D. W., Vogan, J. L., Gillham, R. W., Powell, P. D., Schultz, D., Sivavec, T. M., and Landis, R., 2011, *Permeable Reactive Barriers Technologies for Contaminant Remediation*, Washington, D.C.: United States Environmental Protection Agency, Report # EPA/600/R-98/125.

➢ Rahmani, A. R., Ghaffari, H. R., and Samadi, M. T., 2010, *Removal of Arsenic (III) from Contaminated Water by Synthetic Nano-size Zero Valent Iron*, World Academy of Science, Engineering and Technology, Vol. 38, PP. 737-740.

➢ Rangsivek, R., 2010, *Removal of Dissolved Metals from Storm Water Runoff by Zero-Valent Iron*, Ph.D. Dissertation, University of Berlin.

➢ Riyapan, N., Chalermyanont, N., and Chetpattananondh, P., 2012, *Performance Prediction of a Permeable Reactive Barrier for Remediation of Groundwater Contaminated with Zinc*, phoenix.eng.psu.ac.th/qa/Reference54/GradPaper/5210120078.pdf.

➢ Selvarani, M., and Prema, P., 2010, *Removal of Toxic Metal Hexavalent Chromium [Cr(VI)] from Aqueous Solution Using Starch – Stabilized Nano-scale Zero Valent Iron as Adsorbent: Equilibrium and Kinetics*, International Journal of Environmental Sciences, Vol. 2, PP. 1962-1975.

➢ Suponik, T., 2013, *Groundwater Treatment with the Use of Zero-Valent Iron in the Permeable Reactive Barrier Technology*, Physicochem. Probl. Miner. Process., Vol. 49, PP. 13-23.

➢ Ujfaludi, L., 1986, *Longitudinal Dispersion Tests in Non-uniform Porous Media*, Hydrological Sciences Journal - des Sciences Hydrologiques, Vol. 31, No. 4, PP. 467-474.

➢ Wang, S., Nan, Z., Li, Y., and Zhao, Z., 2009, *The Chemical Bonding of Copper Ions on Kaolin from Suzhou, China*, Desalination, Vol. 249, PP. 991–995.

➢ Watts, R. J., 1998, *Hazardous Wastes: Sources, Pathways, Receptors*, John Wiley and Sons, Inc.

➢ Wilkin, R. T., Acree, S. D., Ross, R. R., Beak, D. G., and Lee, T. R., 2009, *Performance of a Zero-Valent Iron Reactive Barrier for the Treatment of Arsenic in Groundwater: Part1. Hydro-geochemical Studies*, Journal of Contaminant Hydrology, Vol. 106, PP. 1-14.

NOMENCLATURE
a = empirical constant, L/g.
b = saturation coefficient, mg/g.
C/C_o = normalized concentration.
C_e = equilibrium concentration, mg/L.
C_o = initial concentration of metal, mg/L.
D^* = effective molecular diffusion coefficient, m^2/sec
D_{mech} = mechanical dispersion coefficient, m^2/sec
D_z = dispersion coefficient in the direction z, m^2/sec.
K_F = Freundlich sorption coefficient.
m = mass of zero-valent iron in the flask, g.
n = porosity.
q_e = amount of solute removed from solution, mg/kg.
R = retardation factor.
t = travel time, sec.
V = volume of solution in the flask, L.
V_z = velocity of flow in the direction z, m/sec.
α_L = longitudinal dispersivity, cm.
ρ_b = bulk density of the soil, g/cm^3.

Table 1. Measured parameters, related constants and conditions used in the modeling of lead 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
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 Pb^{+2} (mg/l)	zero
Boundary conditions	Concentration of Pb^{+2} @ z=0 (mg/l)	50
	Advective flux ($\frac{\partial c}{\partial z}$) @ z=65 cm	zero
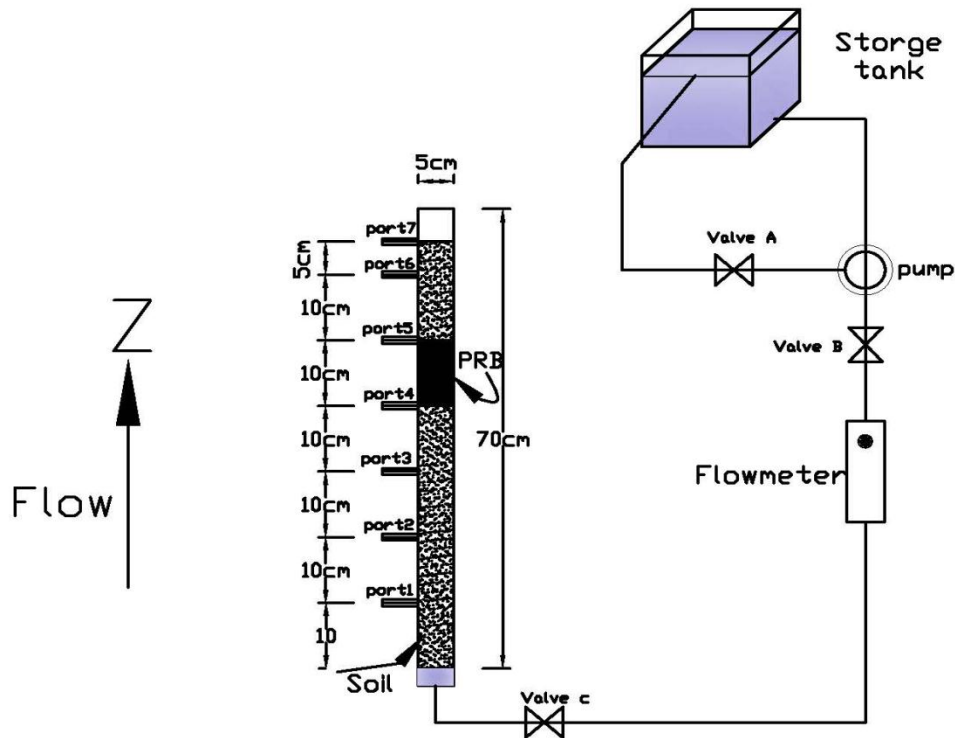
Figure 1. Schematic diagram of the laboratory-scale column.
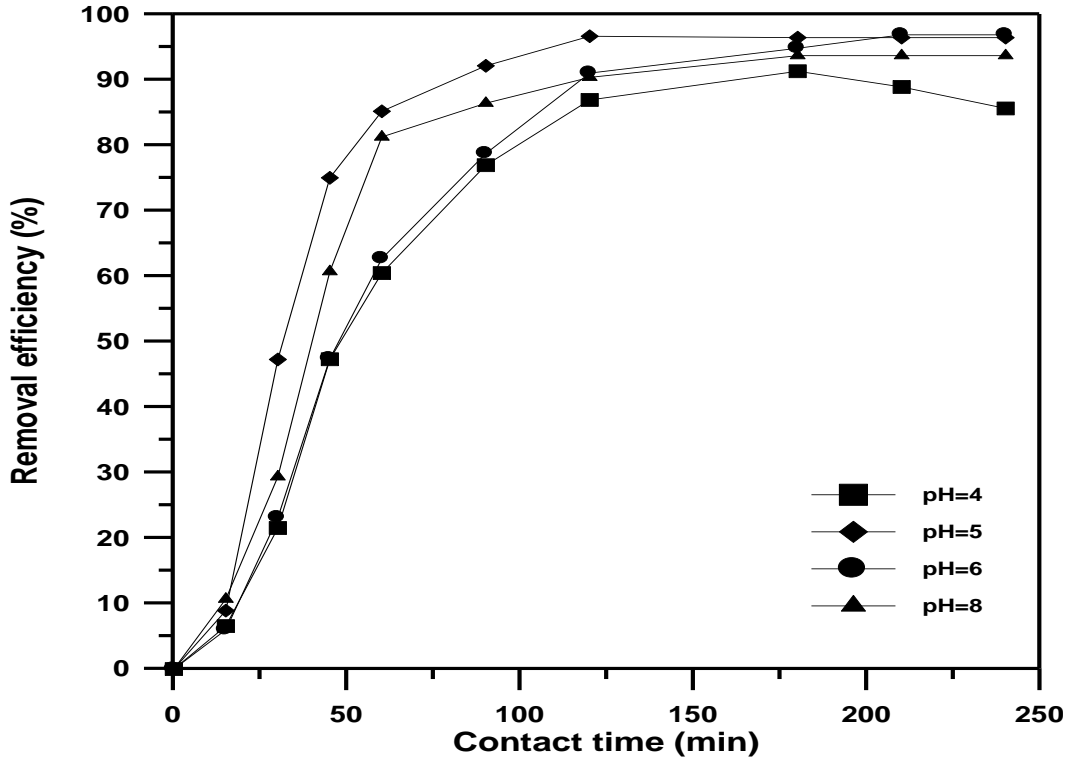
Figure 2. Effect of contact time and initial pH on removal efficiency of lead on ZVI (C_o= 50 mg/L; dosage=5 g/100 mL; agitation speed= 200 rpm; T= 25°C).
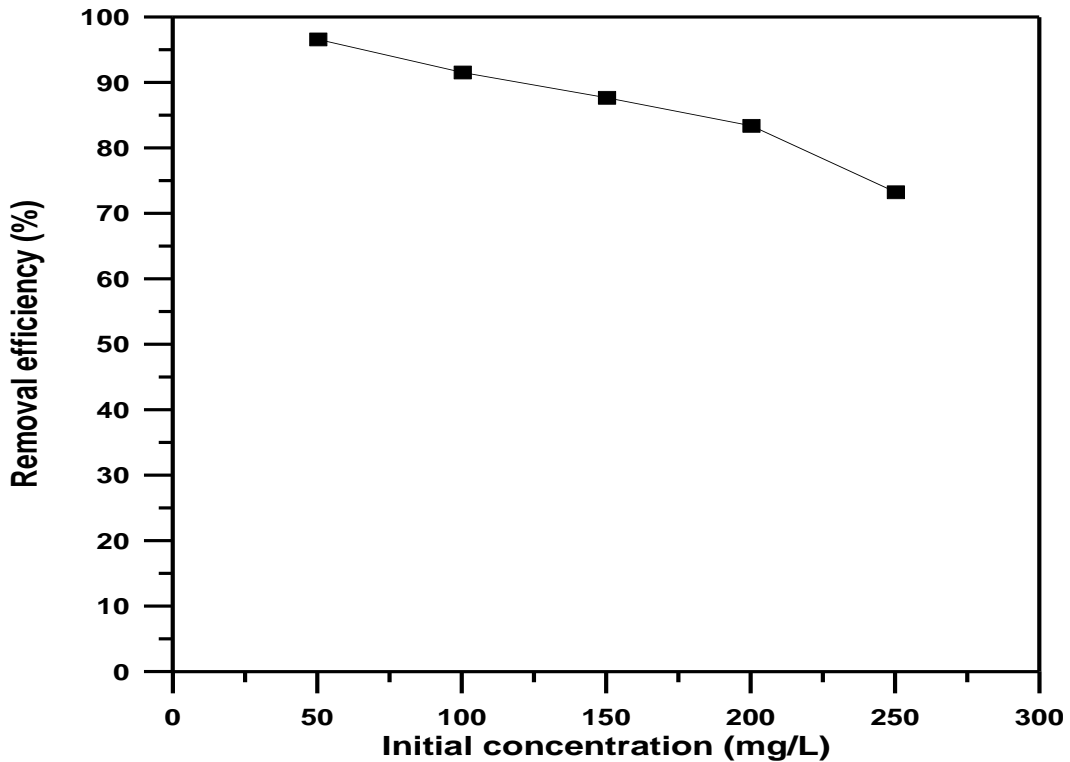
Figure 3. Effect of initial concentration on removal efficiency of lead on ZVI (pH=5; dosage=5 g/100 mL; agitation speed= 200 rpm; contact time=2 hr; T= 25°C).
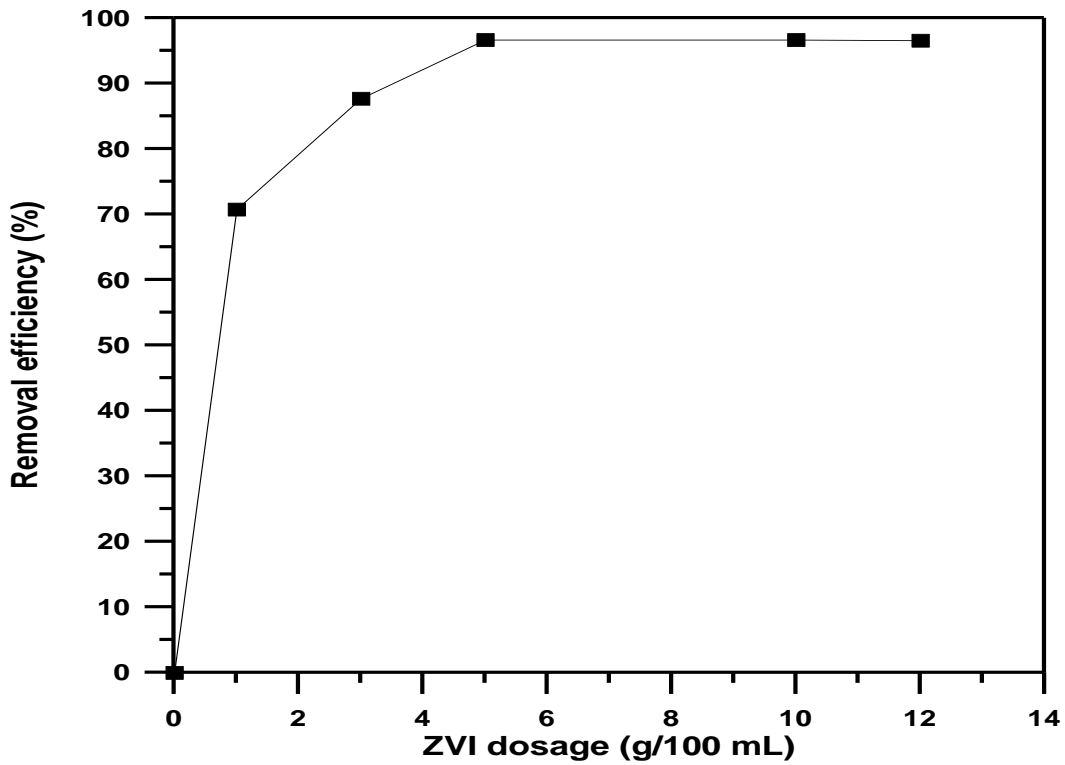
40

Figure 4. Effect of ZVI dosage on removal efficiency of lead (C_o=50 mg/L; pH=5; agitation speed= 200 rpm; contact time=2 hr; T= 25°C).
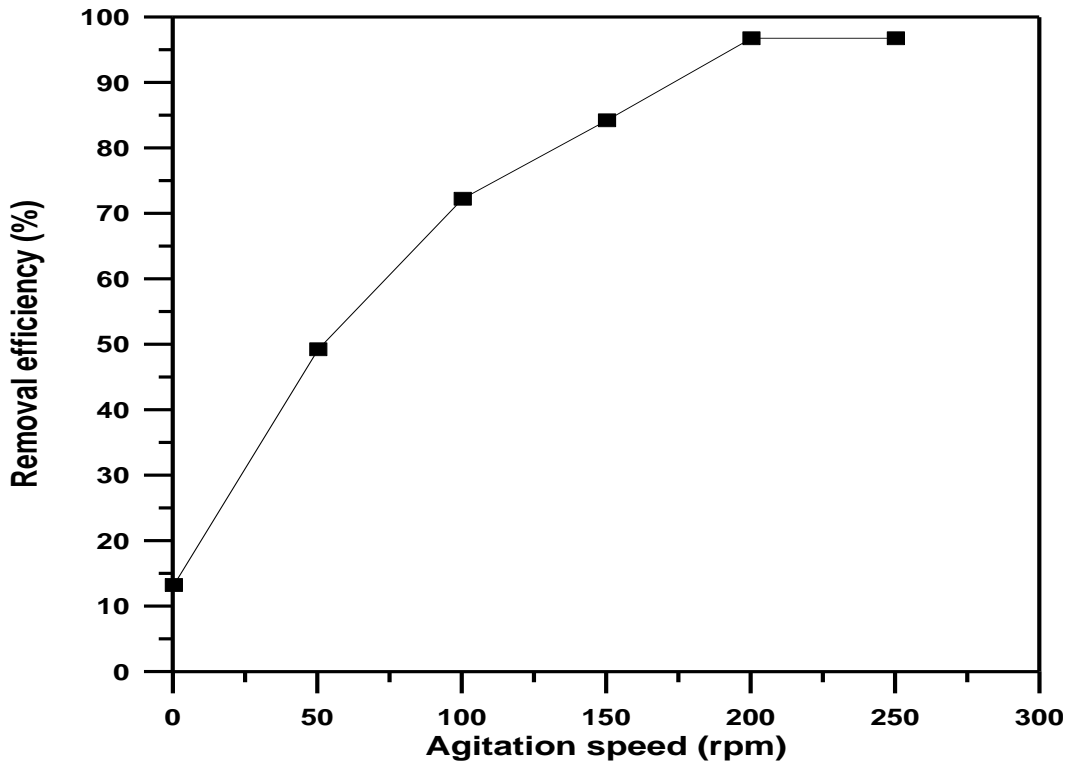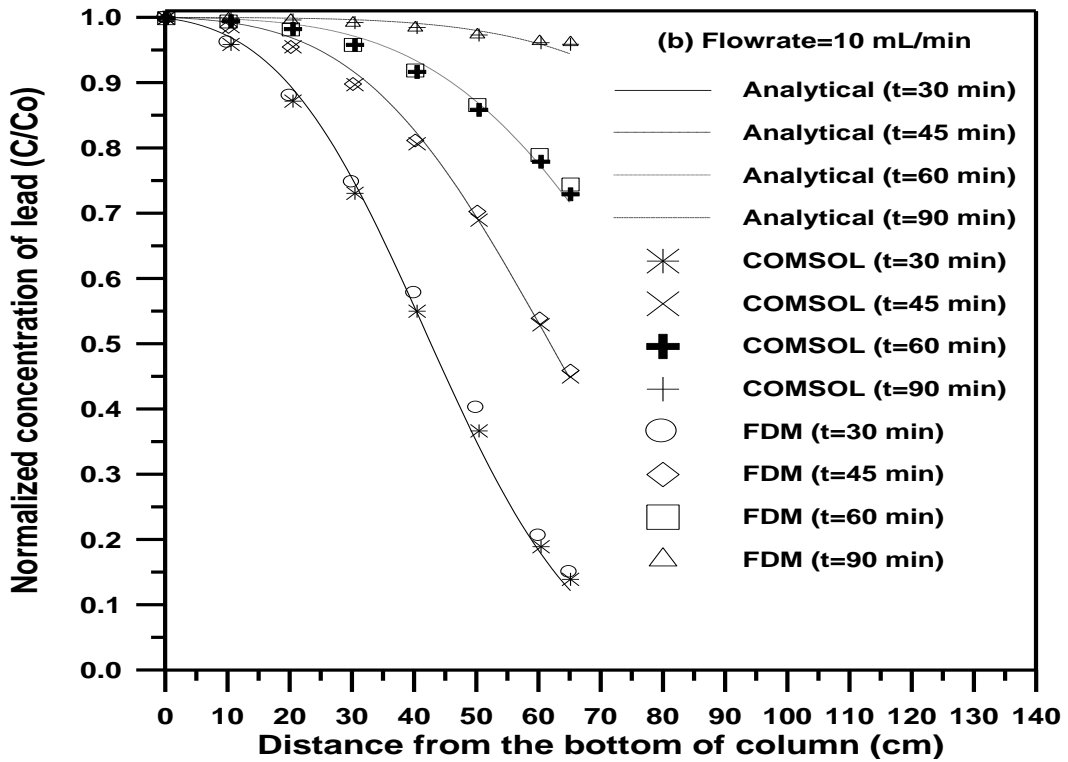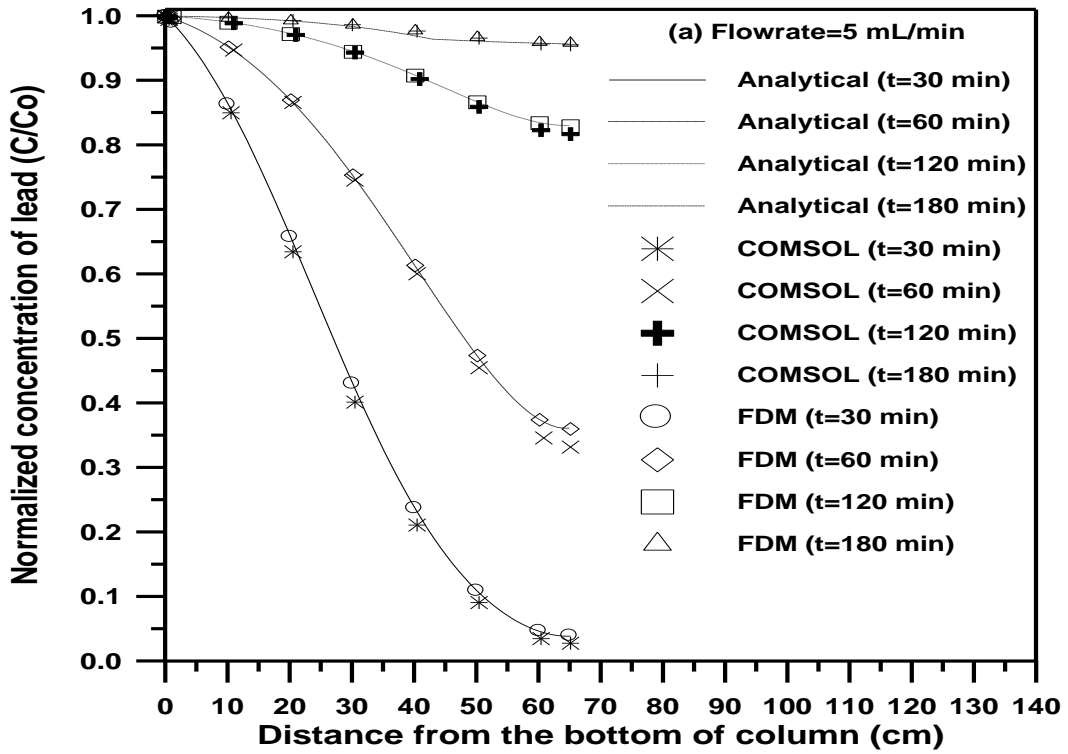

Figure 5. Effect of agitation speed on removal efficiency of lead (C_o=50 mg/L; pH= 5; ZVI dosage=5 g/100 mL; contact time= 2 hr; T= 25°C).
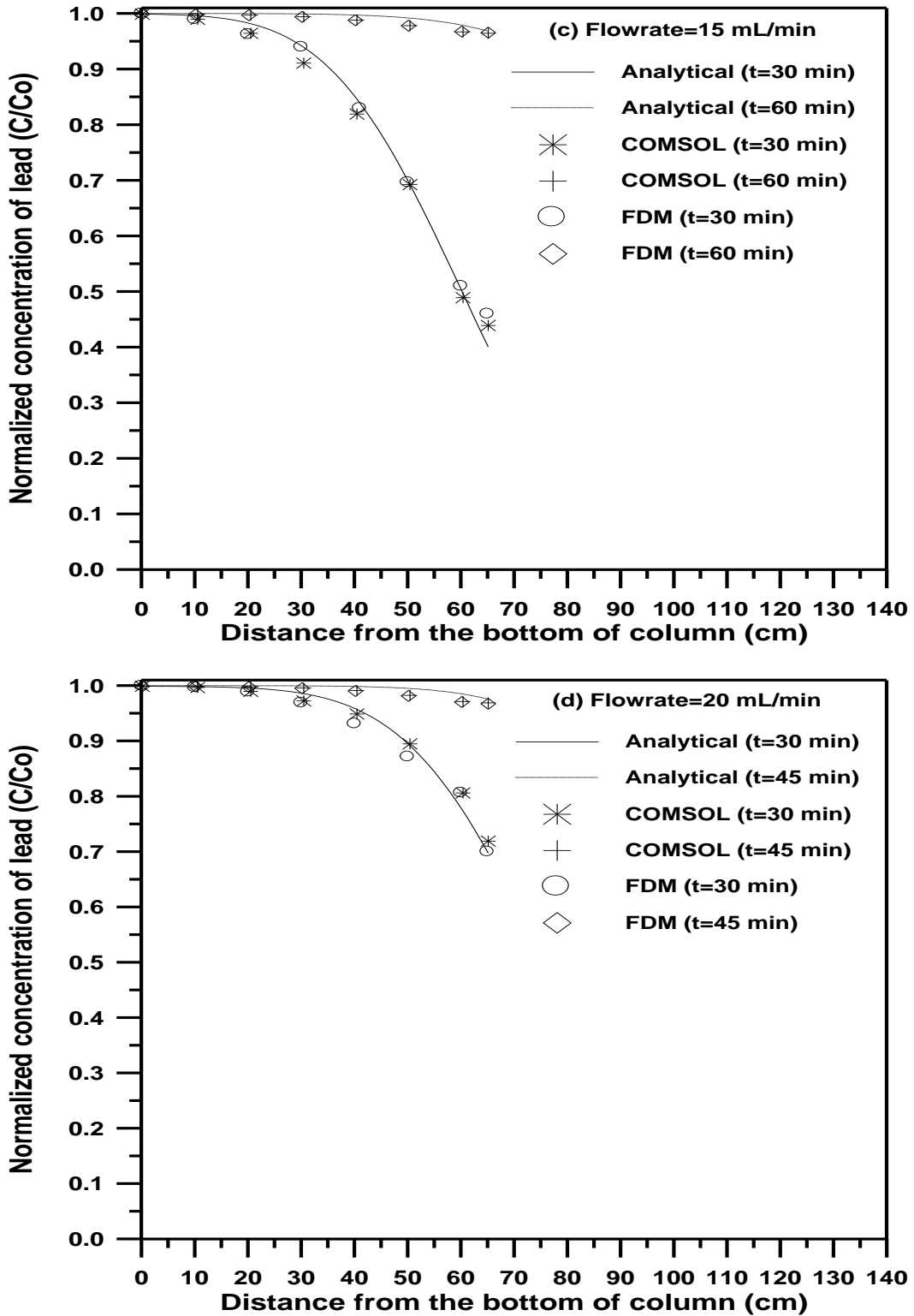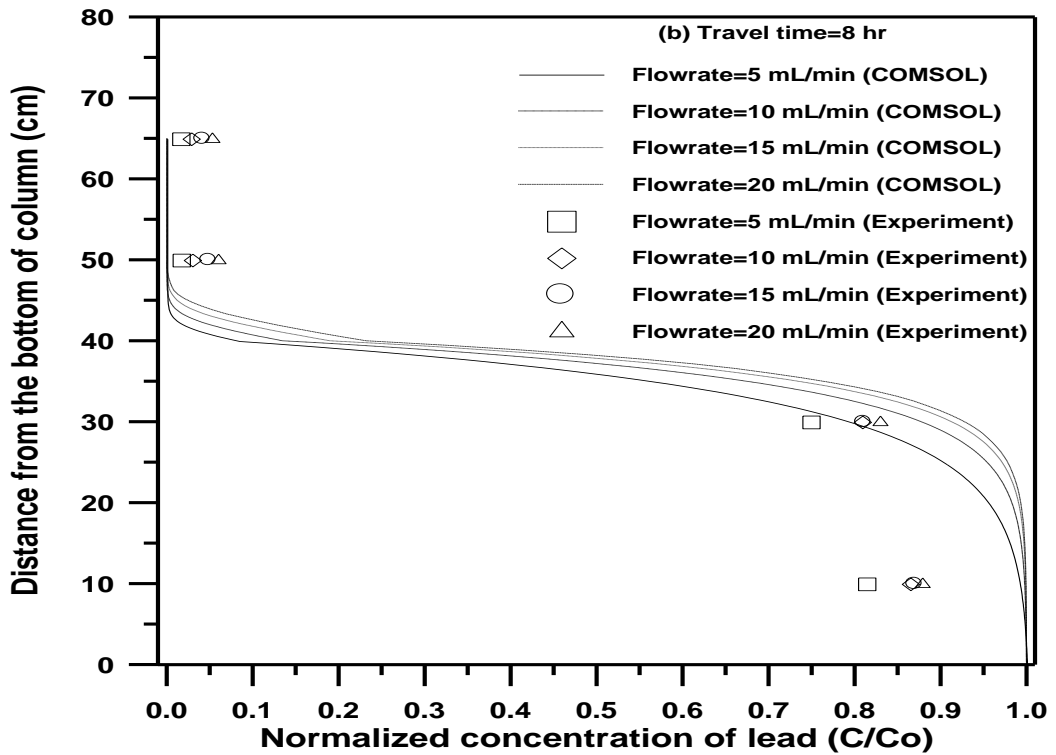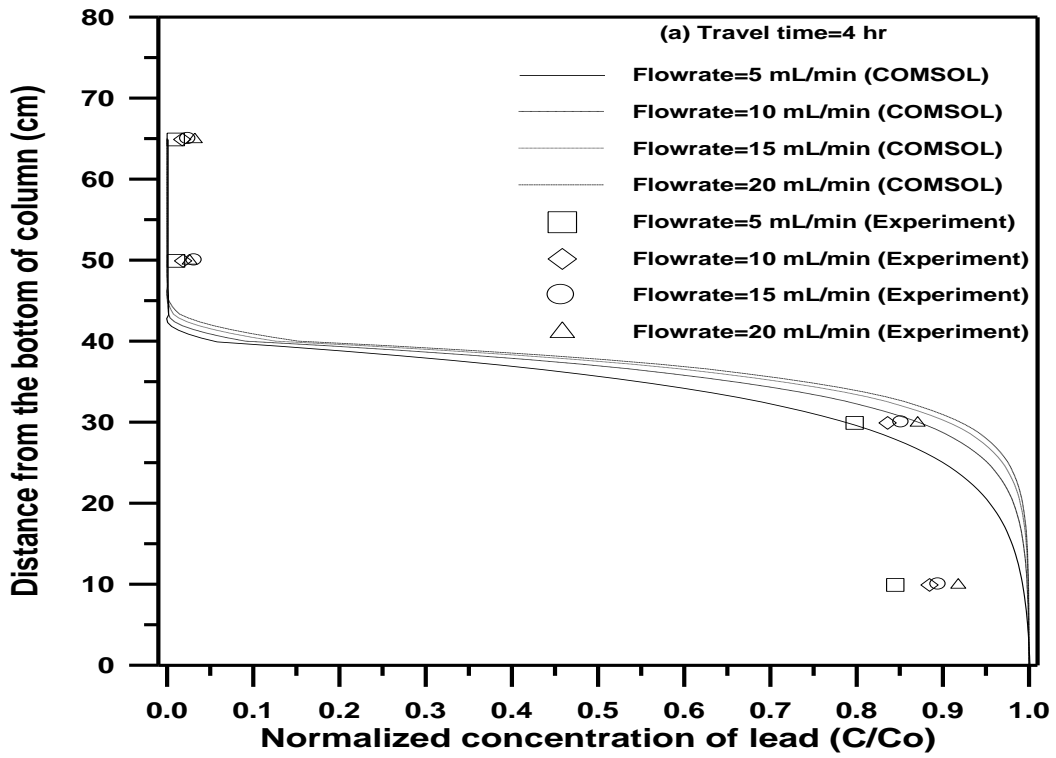
41

(a) Flowrate=5 mL/min

(b) Flowrate=10 mL/min

Figure 6. Comparison between analytical and numerical solutions of conservative solute transport along the length of the soil column without using PRB at different time intervals for flow rate equal to; a) 5, b) 10, c) 15, d) 20 cm^3/min.
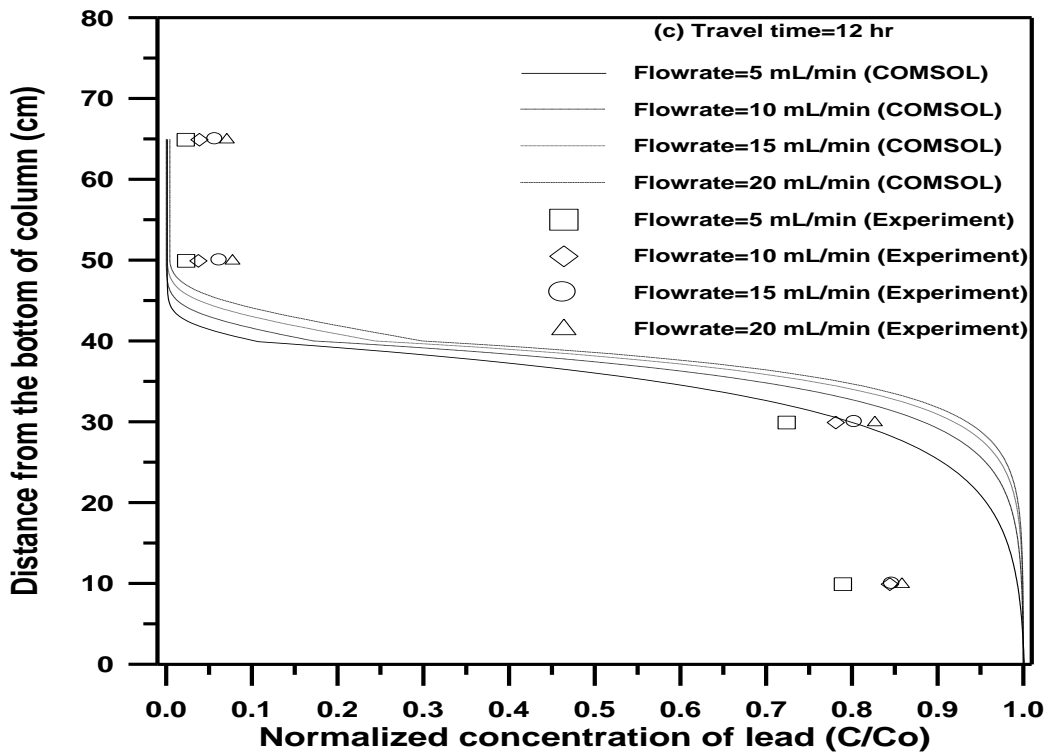
43

(a) Travel time=4 hr

Flowrate=5 mL/min (COMSOL)
Flowrate=10 mL/min (COMSOL)
Flowrate=15 mL/min (COMSOL)
Flowrate=20 mL/min (COMSOL)
□   Flowrate=5 mL/min (Experiment)
◇   Flowrate=10 mL/min (Experiment)
○   Flowrate=15 mL/min (Experiment)
△   Flowrate=20 mL/min (Experiment)

Distance from the bottom of column (cm)

Normalized concentration of lead (C/Co)

(b) Travel time=8 hr

Flowrate=5 mL/min (COMSOL)
Flowrate=10 mL/min (COMSOL)
Flowrate=15 mL/min (COMSOL)
Flowrate=20 mL/min (COMSOL)
□   Flowrate=5 mL/min (Experiment)
◇   Flowrate=10 mL/min (Experiment)
○   Flowrate=15 mL/min (Experiment)
△   Flowrate=20 mL/min (Experiment)

Distance from the bottom of column (cm)

Normalized concentration of lead (C/Co)

44

Figure 7. Comparison between COMSOL solutions and experimental results of Pb^{+2} concentrations in groundwater for different values of travel time.
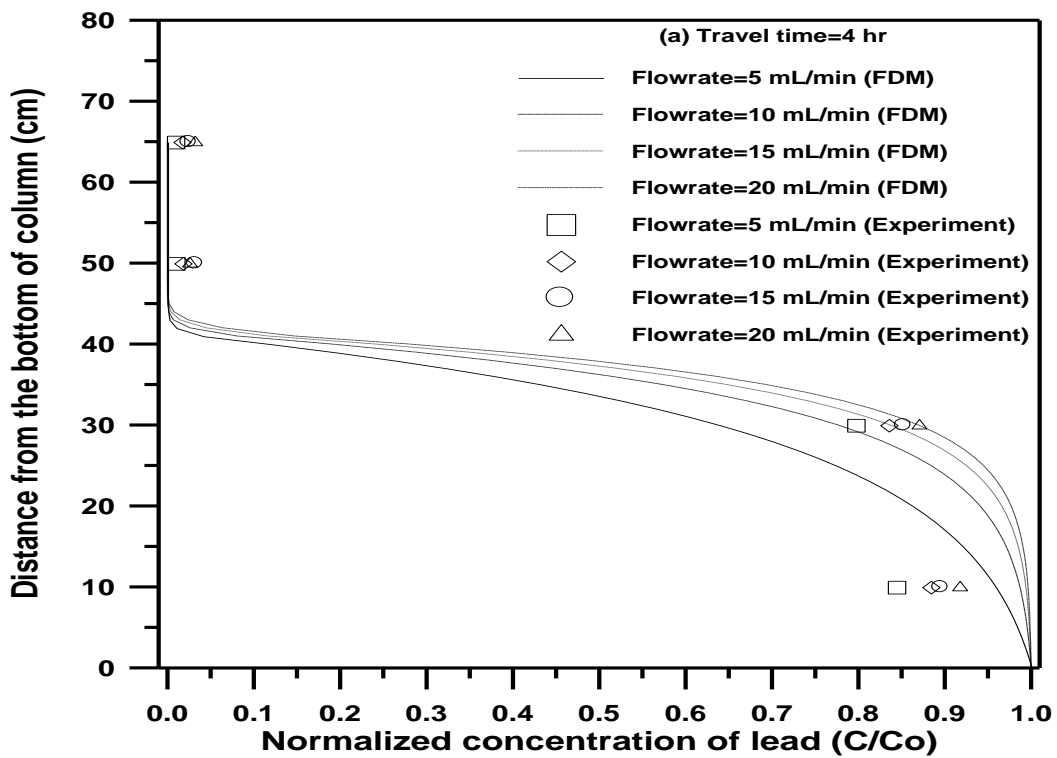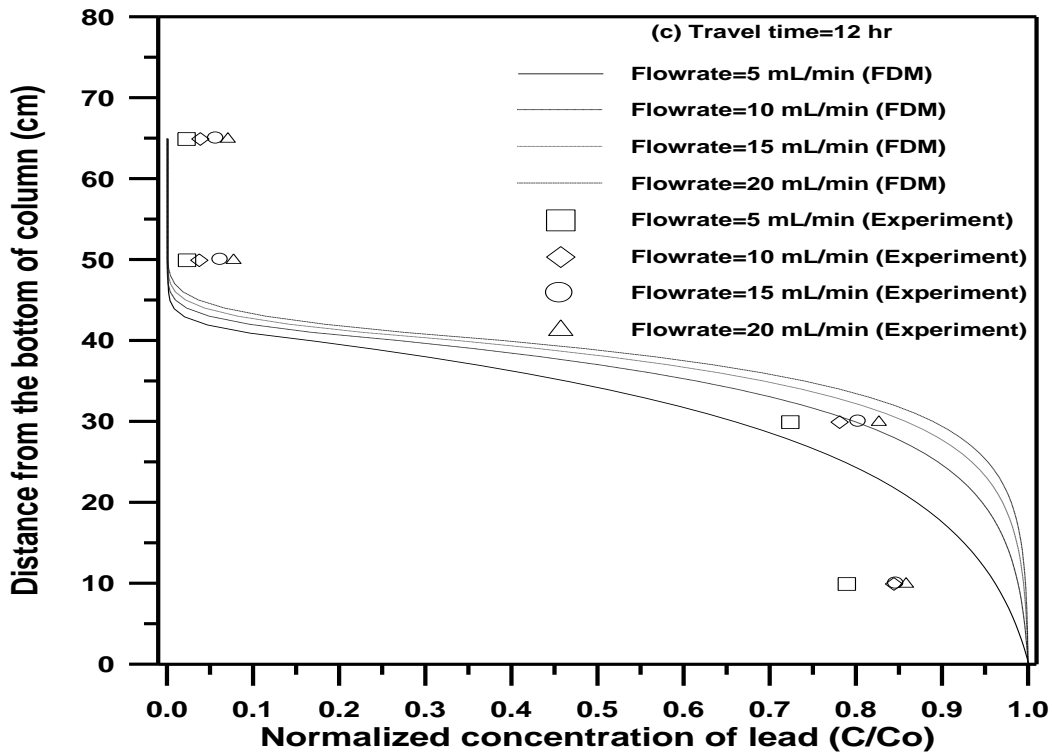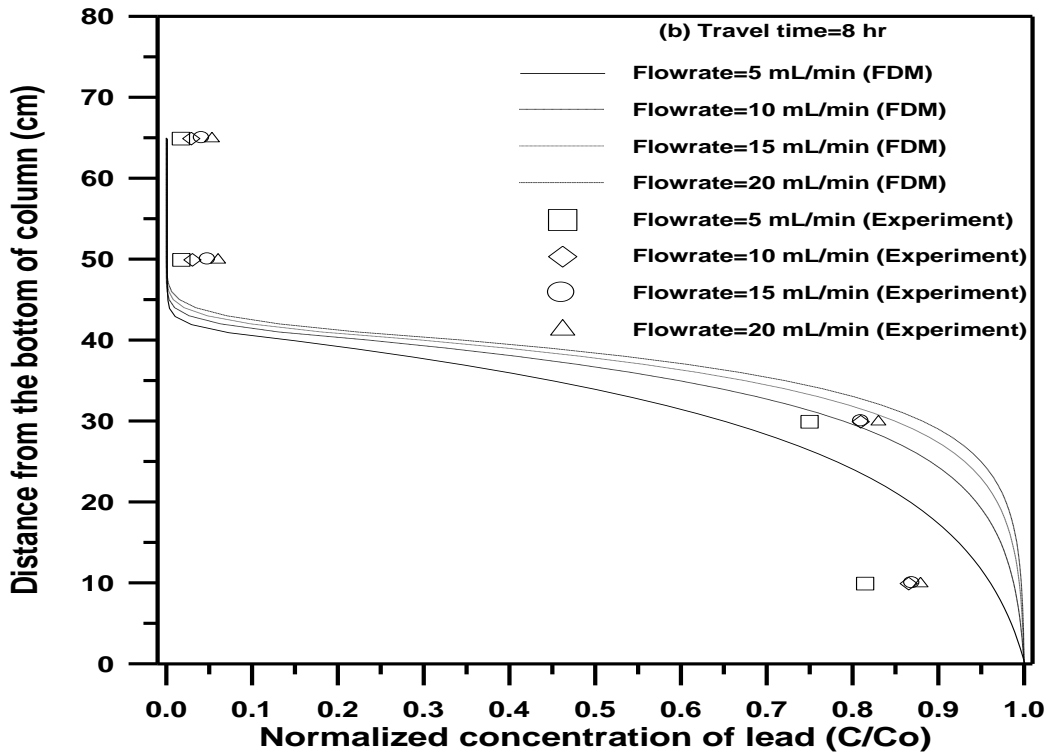
Figure 8. Comparison between FDM solutions and experimental results of Pb^{+2} concentrations in groundwater for different values of travel time.