

**REMOVAL OF LEAD IONS FROM AQUEOUS SOLUTION USING GRANULAR IRON
SLAG BYPRODUCT AS PERMEABLE REACTIVE BARRIER**

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ABSTRACT

This study was aimed to investigate the possibility of using iron slag by product as reactive materials in the porous reactive barriers technologies to achieve the principles of sustainability. Results reveal that the maximum adsorption capacity of iron slag (=2.309 mg/g) can be calculated by Langmuir model because it is more representative for adsorption data. This means that the chem-sorption is predominant mechanism for sorption of lead ions where the dissolution of calcium oxide by hydrolysis and ion exchange can enhance the removal of lead ions by iron oxide surface sites. In addition, the results of continuous tests conducted for 140 hours certified that the longevities of the barriers is proportional straightforwardly with the bed depth but it changed inversely with initial concentration of metal ions and flowrate. Hydraulic conductivity was recognized to remain approximately constant and this certify that there is no precipitation occurred through the removal process. The COMSOL software was proved its ability in the description of the measured breakthrough curves with high agreement.

Key words: ground water; break through; contaminations; permeable reactive barriers, irons slag.

القزويني وفیصل

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إزالة أيونات الرصاص من المحلول المائي باستخدام المنتج الثانوي خبث الحديد الحبيبي للحماية كحاجز تفاعلي نفاذ

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المستخلص

يدرس هذا العمل إمكانية استخدام منتجات الخبث الحديدي الثانوي كمواد تفاعلية في تقنيات الحواجز التفاعلية المسامية لتحقيق مبادئ الاستدامة. تكشف النتائج أنه يمكن حساب السعة القصوى لامتماز خبث الحديد (= 2.309 مجم / جم) بواسطة نموذج Langmuir لأنه أكثر تمثيلاً لبيانات الامتصاص. وهذا يعني أن الامتماز الكيميائي هو الآلية السائدة لامتماز أيونات الرصاص، حيث يمكن أن يؤدي إذابة أكسيد الكالسيوم عن طريق التحلل المائي والتبادل الأيوني إلى تعزيز إزالة أيونات الرصاص عن طريق مواقع سطح أكاسيد الحديد. بالإضافة إلى ذلك، أثبتت نتائج الاختبارات المستمرة التي أجريت لمدة 140 ساعة أن طول عمر الحواجز يتناسب بشكل مباشر مع عمق الطبقة ولكنه يغير بشكل عكسي مع التركيز الأولي للأيونات المعدنية والتدفق. تم التعرف على التوصيلية الهيدروليكية لتصل ثابتة تقريباً وهذا يشهد بعدم حدوث أي ترسيب خلال عملية الإزالة. أثبت برنامج COMSOL قدرته في وصف منحنيات الاختراق المقاسة بدرجة عالية من التوافق.

الكلمات المفتاحية: المياه الجوفية؛ منحنيات اختراق التلوث. الحواجز التفاعلية نفاذية، خبث الحديد.

INTRODUCTION

Industrial waste water causes a lot of damage to the environments and negatively affects peoples' health. Heavy metal could be noticed from other toxic pollutant, because these metals are non-biodegradable and accumulates in the living tissue, so they concentrate throughout the foods chains (15,19). Lead is malleable, soft, bluish gray, heavy metal with relatively low melting points (327°C). Lead is distributed widely in lithospheres and also unfavorably present in hydrosphere and atmosphere. Lead is mostly found in the nature in minerals named galena Pb(II) and (PbS) represent its most commonplace forms in the environments. The lead concentrations in natural water are expanded primarily through anthropogenic activity. Larger numbers of industry like batteries manufacturing, petroleum, paints, ceramic, electric cables insulations, pesticide and plastic utilizes lead in different applications. These industrialized waste waters contain different lead quantity and they have higher abilities for contaminating the groundwater and surface waters. The metal of lead could cause many poisonous effects like distribution of hemoglobin synthesis, anemia and damage the kidneys and to nervous system, damages the brain; intense lethal doses to humans is 300-700 mg/kg and 0.8 mg lead/L of blood is regarded as thresholds for toxicity (12,27). The existence of immense lead levels in the environments result in long term health risk to the ecosystem and to humans. In the ground water, the sources of the problems are either internally by re-charging of the high polluted liquid to the aquifer like plumes or external from the spill and leakage or within the sources from the leach of polluted soil in the middle of ground-waters flowing (1,16). Restorations of the qualities of polluted ground water are considered to be a very complex and high-priced environmental problem. Common technologies utilized for the treatment of groundwater have been ex situ pump and treat system. This system drawn out ground water to the surfaces, treating it by varied method like adsorptions and either reintroduce the treated waters to the sub surfaces or discharging it to storms drains. Such techniques are costly, challenging, and mostly

ineffective in taking off enough contaminations for restoring the ground water for standard of drinking water in agreeable time frames (9,11). As substitution methods, (PRBs) permeable reactive barrier has appeared in the forefronts, play increasingly substantial roles in the passive interceptions and in situ treatments of ground water as components of restorative integral program. New horizon open in the technologies of remediation that can permit more polluted site to be effectively remediated by using natural ground water protections (26,28). The reactive material utilized as the cores elements in the PRB technologies are different and have developed across wide ranges bases on the variations of the targets contaminant and treatments mechanism. This material should be easily available, financially effective, non hazardous material for ensuring that the ground water isn't contaminated secondly, they should keep their re-activity for longer periods, of homogeneous particles sizes for preventing clogging. They should be made of particle larger enough for ensuring that the ground water flowing isn't restricted (6,22). Activated carbon, zeolite and other conventional sorbents have been used for the treatment of contaminated streams. Although these sorbents are suitable for removal of inorganic/ organic pollutants, the high cost limited their widespread uses (17,30). Hence, finding the non-conventional materials with low cost that have a good ability in the reduction of the pollution became the good topic for many studies. Byproducts resulted from different industries such as fly ash, bottom ash, and iron slag as well as agricultural wastes like rice husk and tree bark can be tested to find their suitability for the PRB. The possibility of using iron slag byproduct resulted from steel-making process as reactive material for PRB will be the substantial point for the present study to specify its suitability to retard the migration of lead ions in groundwater.

MATERIALS AND METHODS

The experiments for the removal of Pb^{+2} ions from artificial contaminated water was conducted using the by-product granular iron slag as a sorbent in the laboratory column tests for simulation of PRB. These sorbents were

supplied by iron and steel factories in Talee'a city/ Babil Governorate/ Iraq. The chemical and physical property have been calculated and introduced in Table 1. The sizes of the particles of the irons slag were ranging from 0.6 to 1 mm. For non-spherical particle, the particles diameters are defined as the equal diameters of spherical particles with similar volumes. As approximations, the diameter of particles might be measured from the geometrics means of the two in sequence sieves opening without introducing serious errors. The geometrics means diameters are presented by, $d_{gm} = (d_1 d_2)^{1/2}$, in which d_1 are the diameters of the lower sieves on which the particle is retain and d_2 are the diameters of the up sieves where the particle passes (2,3). The irons slag were cleaned before using with distill water for removing fine powders and dry after that in ovens at 383 K for 24 h; from that time after, it is put in desiccators till the use. Figures 1 illustrate the shapes of this slag after and before grinding. A buffer lead solutions with concentrations of (1000 mg/L) were made using $Pb(NO_3)_2$ salts. A 1.5985 g of these salts were melted in (1L) of distill water and the particular concentrations were calculated using (AAS) Atomic Absorptions Spectrophotometer. The prepared solutions were used at room temperature and used as stocks solutions. The pH of these solutions is modified by the addition 0.1M HNO_3 or 0.1M NaOH as needed.

Table1. Chemical and physical property of iron slag

Properties	Values
Bulk density (kg/m^3)	2026.4
Real density (kg/m^3)	3413.8
BET Surface area (m^2/g)	0.2571
Porosity	0.41
Hydraulic conductivity ($m s^{-1}$)	2.69×10^{-3}
Average particle diameter (mm)	0.775
pH	8.0
Ash content (%)	10

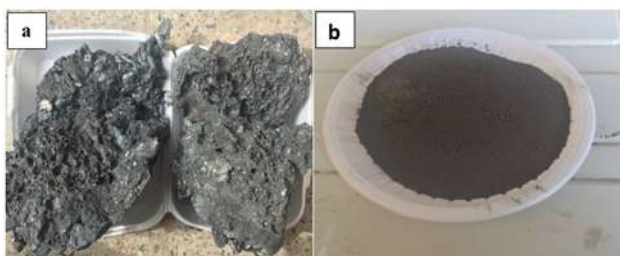


Figure1. Sample of a) raw and b) prepared iron slag

Experimental procedure

Batch experiments were applied for obtaining the equilibriums data and for specifying the sorption isotherm models that suite for describing those data. The number of 250 mL conical flasks could be used and 100 mL solutions of metals with metal solution with initial concentration ranged from 50 to 250 mg/L was put in each flask. Particular iron slag quantities (5.0 g) were put to the flasks and the solution was kept stirred on a high-speed orbital shaker at 250 rpm for 2 hours. Samples of 20 mL are drawn from each flask, and filtered using type filters paper (CHM, F2042-150) to separate the sorbent. A 10 mL of the filtered solutions were pipetted out to analysis for determining the concentrations of the remain contaminant using (AAS) Atomic Absorption Spectrophotometer. The quantity of ions sorbed on the solid phase (i.e. iron slag) was determined by mass balance. The adsorptions isotherms were acquired by plotting the weights of the adsorbed solutes for each unit weights of granular irons slag (q_e) against the equilibriums concentrations of the solutes in the solutions (C_e) (4,30). Langmuir and Freundlich model (11) were used for representing these relationships at fixed temperature and pH. Model of Freundlich (1906) was the early popular sorption isotherm equations and could be written as follow:

$$q_e = K_F C_e^{1/n} \quad (1)$$

where K_F is a constant related to the maximum adsorption capacity of the sorbent and n is represented the intensity of sorption. Langmuir model (1916) could be written as follow:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

In which q_{max} is the maximum adsorption capacity (mg/g) and b is the dissociation coefficient of the solute–adsorbent complex. The b represents the affinity between the solute and the adsorbent-meaning that a higher b value corresponds to a higher affinity (5,14).The adsorber continuous setup used in the present study was constructed of four identical acrylic columns in row configuration with the dimension of lengths 50.0 cm, inners diameters 5.0 cm, and walls thicknesses 0.5 cm (Figure 2). Columns experiment is assumed that the migrations of contaminants in the one dimension and these simulations are

presented the real operations of PRB for analyzing both hydraulic performances and reactivity depended on the longevities of the beds, pH and hydraulic conductivity, calcium concentrations. The columns were packed with reactive material only (i.e. iron slag) without introduce any aquifer because the aim of the continuous tests is to evaluate the efficacy of this material as PRB in the elimination of contaminant concentration. The packed beds were fed with distill water which fed from the bottoms of the columns and force up-ward to avoid the entrapped air. The up flows columns tests were conducted at the temperatures of the room. After the iron slag bed saturated with distilled water, the contaminated water was introduced with certain value of flow rate in the upward directions through the columns depend on the applications of constants heads. The volume of treated water is periodically observed through specific period (e.g., 15

minutes, 30 minutes, 1 hour . . . etc.) and this volume with hydraulics gradients could be used for calculating the hydraulics conductivity coefficient as functions of the time. 5 sampling port designate as P is situated at 0 cm (inlet or P1), 10 cm (P2), 20 cm (P3), 40 cm (P4) and 50 cm (outlet or P5) along the packed columns (Figure 2). While conducting the experiments, the syringe used for gathering the sample from the central axes of the columns for measuring the lead ion and benzaldehyde concentration. Continued experiment was kept going for durations of 140 h. and the choices of these periods are connected with the evolutions of contaminants break through curve. Steady volumes (10 mL) of the solutions were filtered and withdrawn, using filter papers (CHM, F2042-150) and the pH meters were utilized for measuring the acidities of these sample.

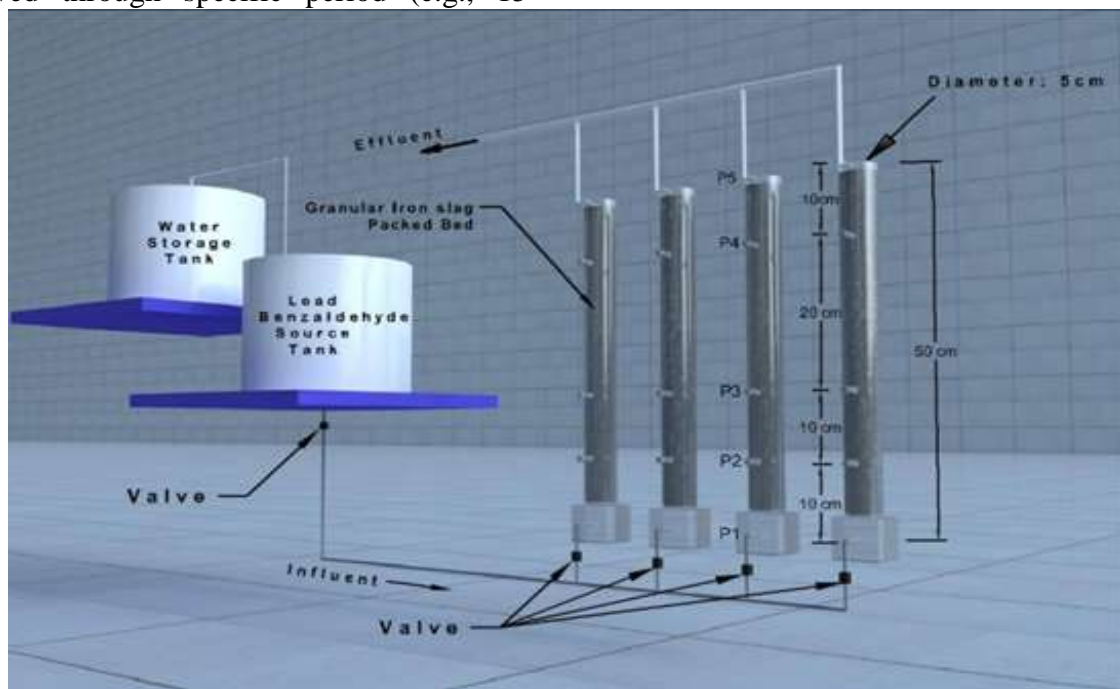


Figure2. Schematic representation of experimental set-up used in the continuous tests.

Contaminant transport and breakthrough curves

A dimensional masses transportation of solutes in the saturated zones of the soils that are known is (ADE) advection dispersion equations could be written as follow (20):

$$D_z \frac{\partial^2 c}{\partial z^2} - V_z \frac{\partial c}{\partial z} \pm \frac{r}{n} = \frac{\partial c}{\partial t} \quad (3)$$

The same forms of the ADE depend on the masses transfer process accounted for in the terms r . The most dominant masses mechanism of transfer happening during

masses transportation is adsorption that presents the important mechanisms for the operations of reactive permeable barrier. Embodying sorption could be gained by using Linear Langmuir, or Freundlich isotherm. The rates expressions r equals to the products of time derivatives of q and dry masses densities, ρ_b . so,

$$r = \rho_b \frac{\partial q}{\partial t} \quad (4)$$

For unidirectional flow, Eq.2 could be included with Eq.1 like this:

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial q}{\partial t} \quad (5)$$

The terms $\frac{\rho_b}{n} \frac{\partial q}{\partial t}$ are the rates of alteration in contaminants concentrations because of the sorption process, in which q is the ion concentration adsorbed on the reactive media represented by granular iron slag in this study. Under equilibrium condition, in which the sorption occur spontaneously and local equilibriums between the liquids and solids phases are kept, the Langmuir isotherm equations (Eq.2) relate the solutes concentration in aqueous and solids phase could be incorporated with Eq.5 and the resultants is Eq.6:

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial (q_m b C)}{\partial t} \quad (6)$$

These equations could be made easier as:

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = \left(1 + \frac{\rho_b}{n} \left(\frac{q_m b}{(1+bC)^2} \right) \right) \frac{\partial C}{\partial t} \quad (7)$$

where n is the porosity of sorbent in the packed column, ρ_b is the bulk density of the bed (kg/cm^3), q_m is the higher adsorptions capacities (mg/g), and b represents the affinity constants. The effects of retarding the transportation of adsorb species relative to the advective front could be defined by retardation factors (R) like this:

$$R = 1 + \frac{\rho_b}{n} \left(\frac{q_m b}{(1+bC)^2} \right) \quad (8)$$

Therefore, the general forms of 1D advection dispersion equations taking the sorption into consideration for equilibrium cases of solute transportation in the saturated zones could be like this:

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = R \frac{\partial C}{\partial t} \quad (9)$$

RESULTS AND DISCUSSION

Adsorption isotherm

The adsorption isotherms are the essential prerequisites for the design of adsorption systems and they are depended on the equilibrium data. These isotherms are functions correlated between the sorption capacity (q_e) and equilibrium metal concentration in the bulk solution phase (C_e) (13). The measured sorption data are fitted with non-linear forms of Freundlich and Langmuir model illustrated in Figure. 3 where the coefficients of the model have been determined using Origin 2018 software. The non-linear analysis was utilized to reduce the

percentage of errors in comparison with linearization of Freundlich and Langmuir isotherms for description of lead ions sorption onto granular iron slag. The coefficients of the isotherm models and statistical measure like coefficients of determinations (R^2), Chi square, and sum of squared error (SSE) are mentioned in Table 2. Based on the statistical constants, Langmuir isotherm model is more representative for description the sorption of lead ions onto granular iron slag. It is clear that the present sorbent has maximum adsorption capacity reached to 2.309 mg/g . The good fit of the data with the Langmuir isotherm stated that the uniform surface of the active sites is dispersed on the iron slag (8). The meaning of this is that the adsorptions happen at specific homogenous site within the adsorbents and there are no lateral interactions between the sorbed molecules (7). Further analyses of Langmuir isotherm could be made using the dimensionless equilibrium parameters R_L that are measured from the divisions of 1 onto the $(1+bC_o)$. The values of R_L are between 0 and 1 for better adsorptions, while $R_L > 1$ represent undesirable adsorptions, for $R_L = 1$ adsorptions are linear and if $R_L = 0$, it is irreversible (25,26). The dimensionless parameters, R_L founded in the ranges of 0–1 that confirm the desirable adsorptions processes for the removal of lead ion.

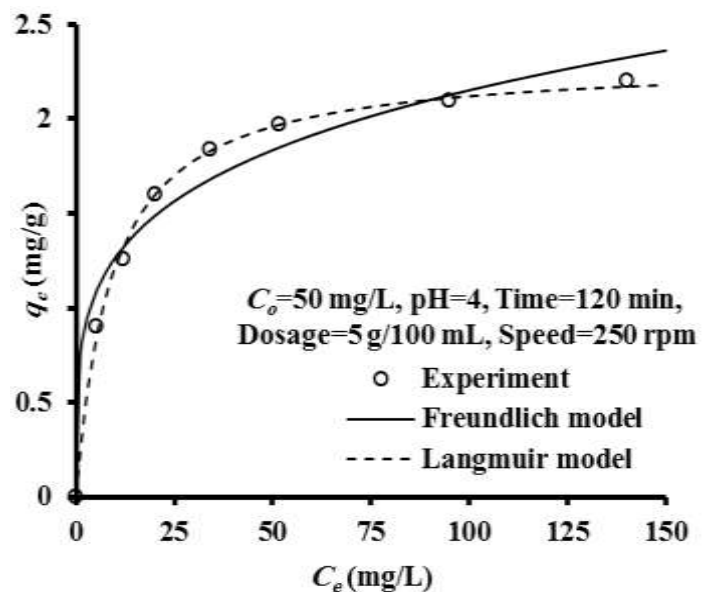


Figure3. Concurrence between the experimented results and values predict by isotherm model for adsorption capacity of lead ions onto granular iron slag.

Table 2. Constants and statistical measures of isotherm model for sorption of lead ions onto granular iron slag

Model	Parameter	Value
Freundlich	K_F (mg/mg)(L/mg) ^{1/n}	0.7479
	N	4.3570
	R^2	0.9739
	Chi-square (χ^2)	0.0168
	SSE	0.1005
Langmuir	q_{max} (mg/g)	2.309
	b (L/mg)	0.1123
	R^2	0.9974
	Chi-square (χ^2)	0.0017
	SSE	0.0102

Effect of flow rate, initial concentration and bed depth

The effect of flow rate on the sorption of lead ions onto granular iron slag was investigated with two value of flowing rates 5 and 10 mL/min for initial concentrations of 50, 100 and 150 mg/L. Breakthrough curves have been obtained by normalizing the contaminant concentration from the results already obtained from the experimental values. The experimental breakthrough curves for the lead ions uptake corresponding to adopted flow rates for different times and locations (i.e. ports) along each column packed are shown in figures 4 and 5. It is clear that the increase of flowing rates decreases the break through time and the curve become steep. This means that the residences time isn't enough and this causes the leaving of contaminated solutions before happening of equilibriums. This behavior may be due to diffusions limitation of the solutes into the pore of the sorbents at high flowing rate (18).

The same figures illustrated that the effects of initial concentrations on the propagation of contaminant front. It is clear that the higher concentration leads to the fast appearances of the contaminants fronts and bed exhaustions happened. High retentions rates and, therefore, early saturations results from great concentrations gradients and small masses transfer resistances at high concentrations (21,23). Lastly, it was obvious from this figure that the rise of reactive materials (i.e. bed depth) increases the capacities of sorption of the beds for lead ion under similar operational condition. The process also depending on the surface area and cation exchange capacity of material The Eq. 9 was solved numerically using COMSOL Multiphysics program which based on the finite element method. Parameter and constant of the granular irons slag utilized in the one dimensional solutes transports modeling are assessed either through laboratories test or approximations utilizing literatures data. Anyway, the parameter utilized in the current simulations (i.e. systems property, systems dimension, boundaries and initial condition) were shows in Table 3. A comparison between the anticipated values by COMSOL and experimented result for Pb⁺² concentration of ion in the middle of the migrations of the contaminants plumes at varied time interval for specific flowing rates were shows in Figure 4 and 5. It is obvious that there are good agreements between the models prediction and experimental result with coefficients of determinations (R^2) not lesser than 0.99.

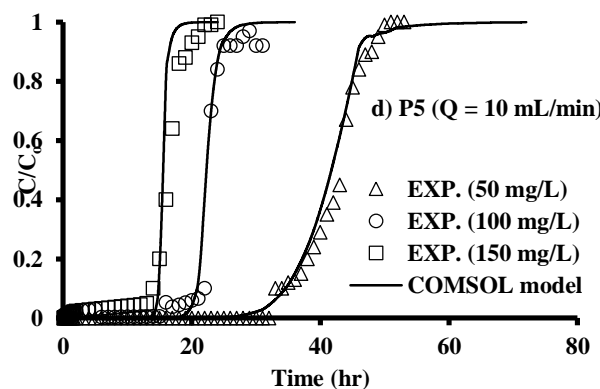
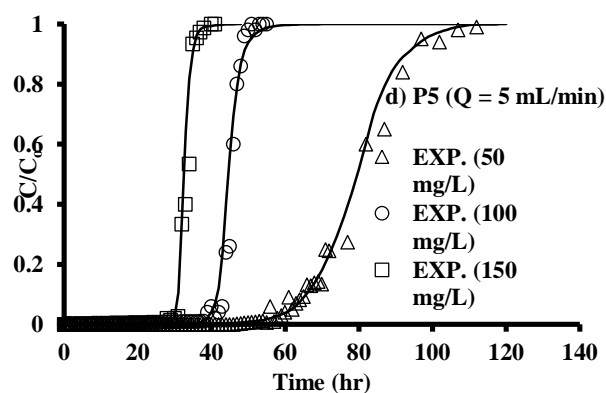
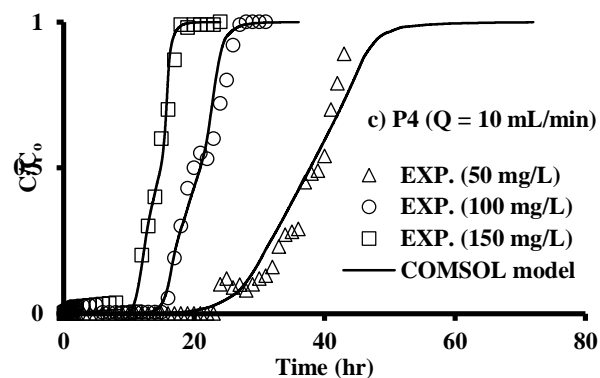
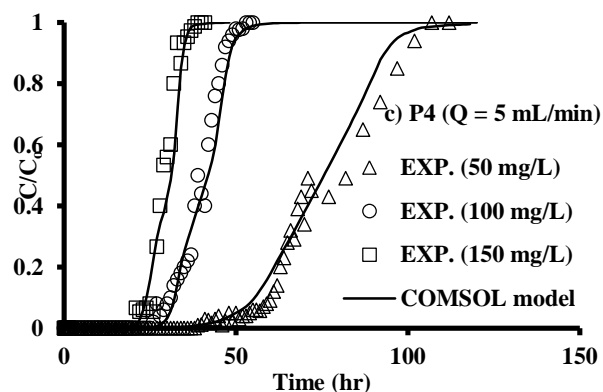
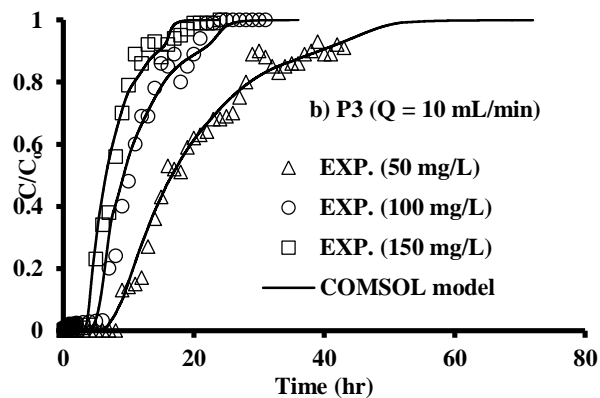
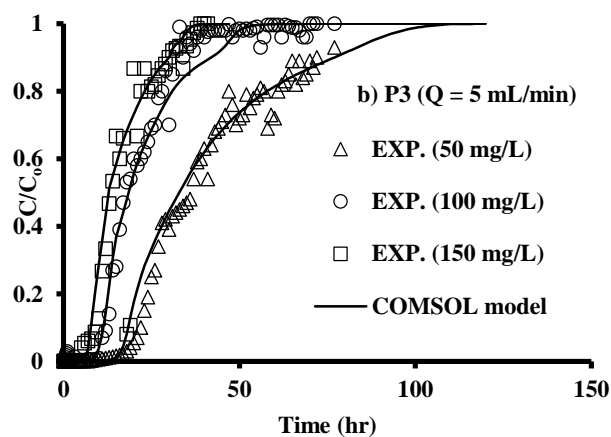
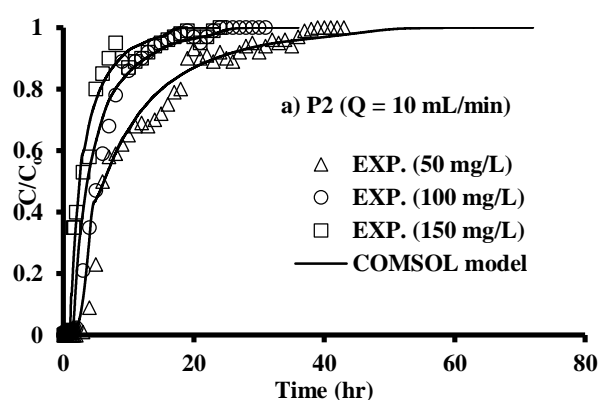
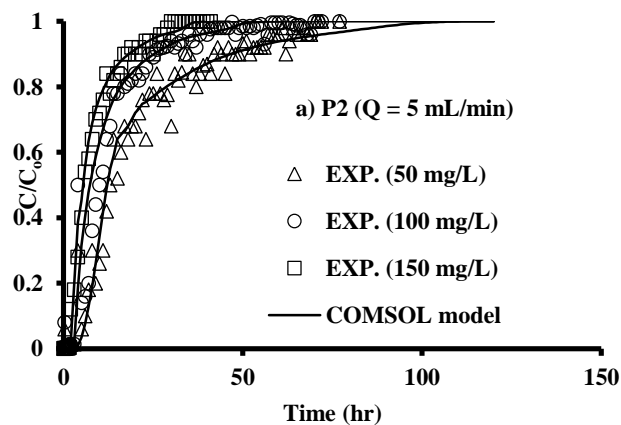


Figure4. Experimental and COMSOL predictions of breakthrough curves for Pb²⁺ ions at different values of initial concentration with flow rate= 5 m L/min

Figure5. Experimental and COMSOL predictions of breakthrough curves for Pb²⁺ ion at different values of initial concentration with flow rate= 10 mL/min

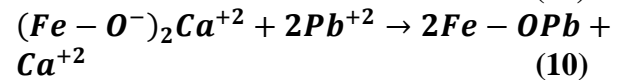
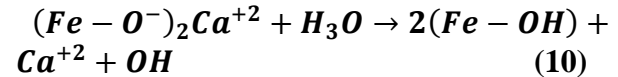
Table3. Measured parameters and related constants used in the modeling of Pb⁺² ion transport in 1D columns

Parameters	Values
Barriers beds depth (cm)	50
Porosities of barriers (n_B)	0.41
Longitudinal dispersivity (α_L , cm)	18.08
Bulk densities (g/cm ³)	2.0264
Initial concentrations (mg/L)	Zero
Concentrations @ z=0 (mg/L)	50, 100,150
Advective fluxes ($\frac{\partial c}{\partial z}$) @ z=50 cm	Zero

Monitoring of hydraulic conductivity and calcium concentrations

Hydraulic conductivities of the beds packed in the columns at specific period of time were measured by the law of Darcy depends on the accumulate volumes of water treated and the value of hydraulic gradient plotted in the Figures 6. It is obvious that the hydraulic conductivity was approximately remain constant during the duration not exceeding 70 hr. and this means that there is not formed precipitates within the packed bed. Figure. 7 and 8 illustrate the variation of calcium content as functions of time in the transportation of ground water polluted with Pb⁺² ions at varied value of initial concentrations with flowing rates value of 5

and 10 mL/min respectively. The calcium occupies these sites and when calcium oxide dissolved in the aqueous solutions both hydrolyses and ions exchange process begins. Under acidic best condition (i.e. pH of 4), the calcium change by the lead ions and the hydrogen according to the following reactions:



The reactions happen before saturation when the ions of lead are completely eliminated with increase of final pH values to reach 6.4. Accordingly, the elimination processes depend primarily on the release of calcium ions within the slag and they replaced by lead ions.

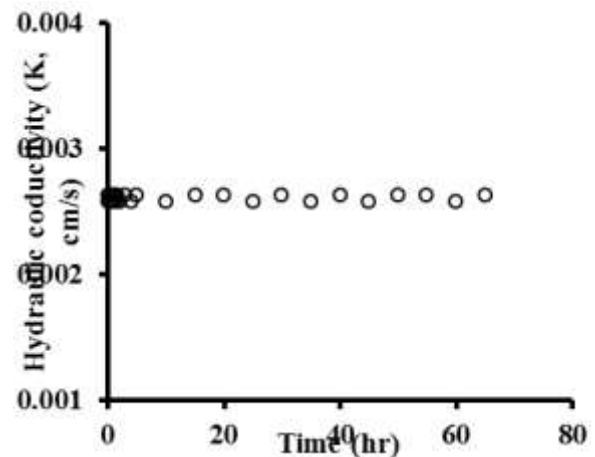


Figure6. Variations of hydraulic conductivities as functions of traveling time in the transportation of groundwater polluted with lead ions

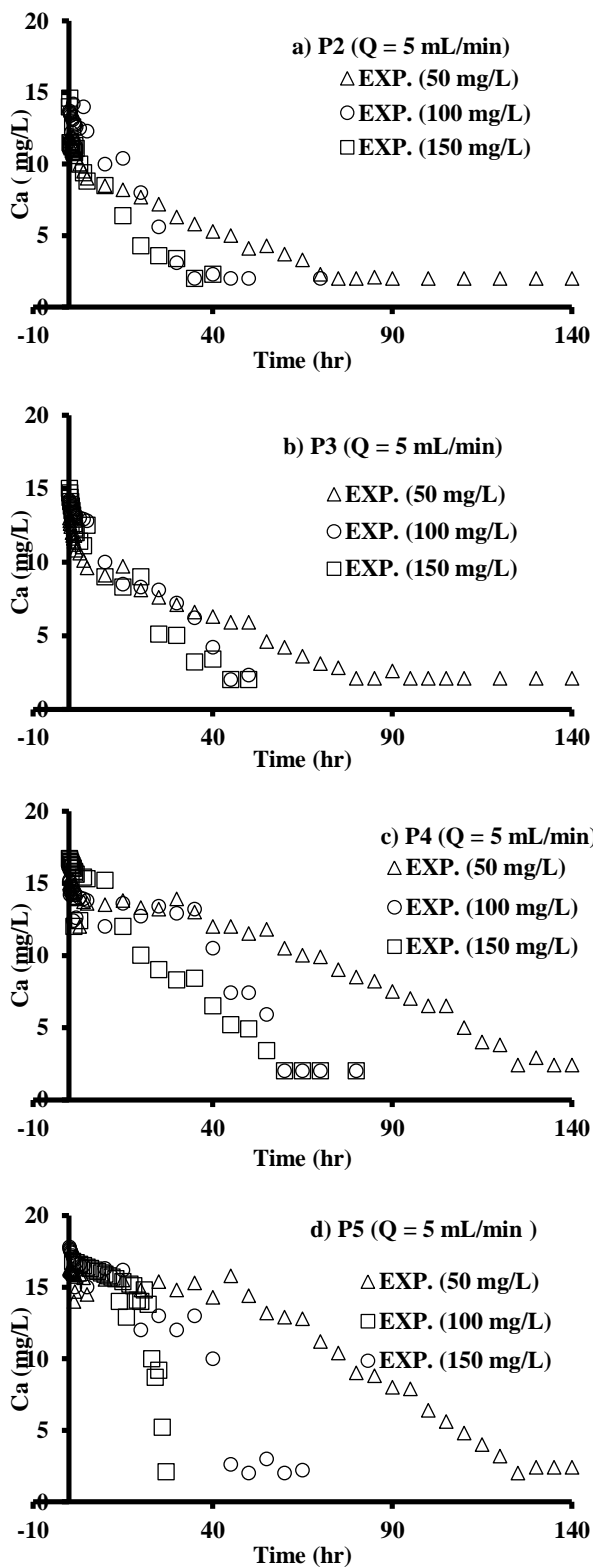


Figure7. Variation of calcium concentration dissolved in effluent water as a function of time due to the transport of aqueous solution contaminated with Pb^{+2} ions at different values of initial concentration with flow rate= 5 mL/min

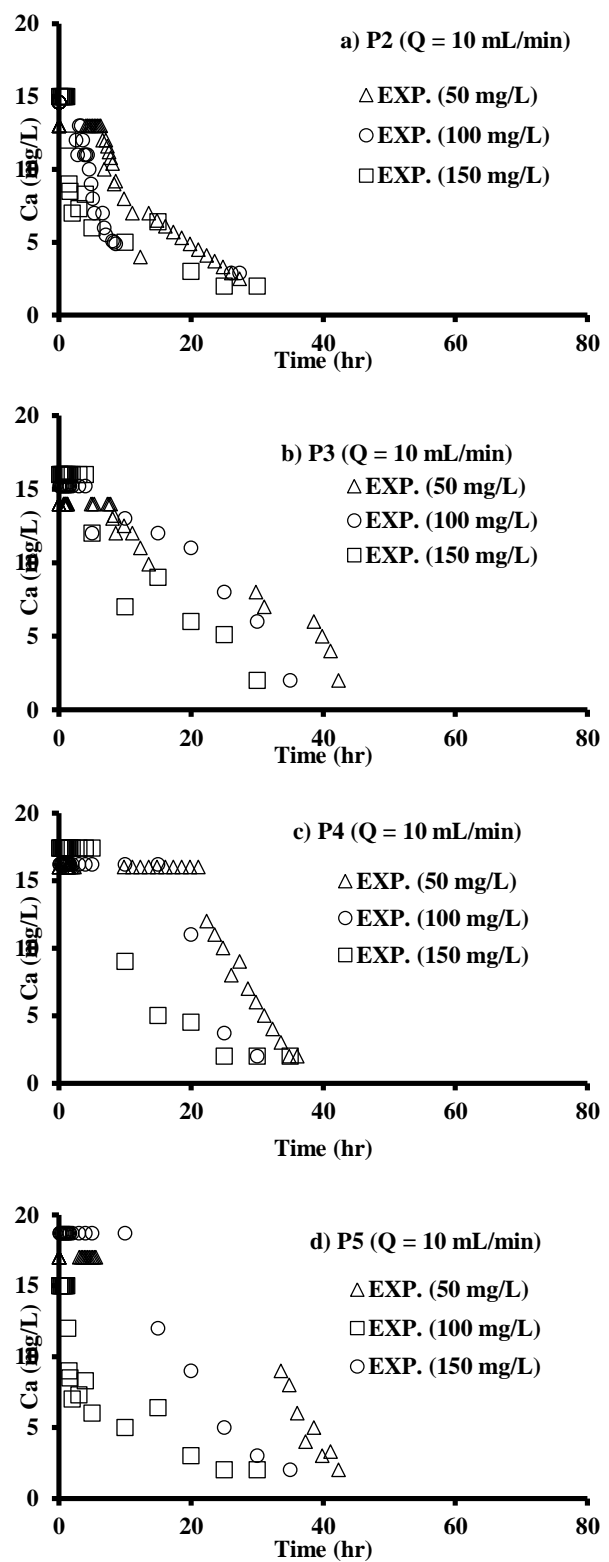


Figure8. Variation of calcium concentration dissolved in effluent water as a function of time due to the transport of aqueous solution contaminated with Pb^{+2} ions at different values of initial concentration with flow rate= 10 mL/min

The results proved that the iron slag byproduct material has a good ability in the elimination of the lead ions from contaminated water and it can be used effectively in the permeable reactive barrier technology. Results signified that the best conditions for the interaction of iron slag and solution contaminated with lead ions were pH of 4, contact time of 120 min, sorbents dosages of 5 mg/ 100 mL, and agitations speeds of 250 rpm to achieve the higher adsorption capacities of 2.309 mg/g. Langmuir isotherm model was found more representative for sorption data in comparison with Freundlich model. The Langmuir model was combined with advection-dispersion equation to plot the breakthrough curves at certain points along the packed bed using COMSOL Multiphysics 3.5a. The results revealed that the low initial concentration of lead ions, low flowrate and high packed depth will increase the longevity of the barrier; however, the hydraulic conductivity remained approximately constant and this means there is no precipitation process. Also, there is a good matching between experimental results and predications of COMSOL model with R^2 greater than 0.99. Finally, the iron oxide surface sites are the predominant in the removal of lead ions due to dissolve of calcium oxide and this will enhance both the hydrolysis and ion exchange.

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