Al-Khwarizmi Engineering Journal, Vol. 16, No. 2, June, (2020)
P. P. 47- 55

Al-Khwarizmi Engineering Journal

Permeable Reactive Barrier of Coated Sand by Iron Oxide for Treatment of Groundwater Contaminated with Cadmium and Copper Ions

Mohammed B. Abdul-Kareem* **Ayad A.H. Faisal****
,Department of Environmental Engineering / University of Baghdad*
*Email:Mohammed.bahjet73@gmail.com
**Email:ayadabedalhamzafaisal@yahoo.com

(Received 12 January 2020; accepted 5 May 2020)
https://doi.org/10.22153/kej.2020.05.002

Abstract

In this research, coated sand iron-oxide (CSIO) has been used as a permeable reactive barrier (PRB) for removal of cadmium and copper ions from the contaminated groundwater. The prepared material has been manufactured by precipitation of nano-particles based this oxide type on the sand surfaces by impregnation process. Therefore, this technique can be considered the main objective of the present study. The description of sorption data for sorbate-sorbent under consideration by the Langmuir isotherm model was more valuable than the Freundlich model. The maximum adsorption capacity of CSIO reaches 1.9181 and 7.6425 mg/g for cadmium and copper respectively. COMSOL Multiphysics Version release 3.5 has a good ability in the simulation and prediction of the cadmium and copper transport through one-dimensional CSIO-PRB. The outcome of this investigation prove that the manufactured CSIO has significant capability in the delay of contaminants the migration through barrier packed with this material. The root means squared errors between predicted and measured data were not exceeded the 0.121; so, this means that there a good agreement between these data.

Keywords: Barrier technology, Heavy metals, Isotherm, COMSOL, Contamination.

1. Introduction

Ground- and surface- water contamination by hazardous compounds considers an urgent issue because it has negative impacts on public health and environment. Heavy metals are classified as one of hazardous compounds because they are non-biodegradable and tend to accumulate in living organisms, causing various biological disorders. Both cadmium and copper ions are presented in the effluents of several industries. Cadmium is one of the dangerous pollutants, originating from metal plating, metallurgical alloying, mining, ceramics, and other industrial operations [5,11]. Copper mining and smelting, brass manufacture, use of Cu-based agri-chemicals and electroplating industries are the major sources for pollution with this element [6,19].

The reclamation of the contaminated groundwater quality for standards specified by USEPA and WHO within acceptable time framework can be considered a big task because it is difficult and more expensive. A Pump-and-treat method is a historical technique that utilized for remediating the groundwater contaminated with different types of elements and compounds by extraction the polluted water to the ground surface and, then, treated it by conventional methods like adsorption, flotation, precipitation, and others. The resulted water from the treatment process can be disposed to water bodies, sewer system or reinjected to the aquifer. Unfortunately, the collected data related to this technique certified that this system is not effective, costly and not able to reclamation the contaminated water with acceptable periods of time. So, the permeable reactive barrier (PRB) technique is introduced as an alternative method for in-situ treatment of the contaminated groundwater. This technique has many advantages;1) passive (not need any exterior source of energy), 2) underground (not effect on the activities on the ground surface), safe (no contact between workers and contaminants) and others. The PRB is based on the idea of constructing a trench filled with the reactive material perpendicular on the direction of the flow where water will pass the barrier and contaminants can be entrapped within the barrier by physico-chemical and biological forces [5,19].

There are a significant number of studies that directed towards the use of different sorbents in the treatment of aqueous solutions polluted with heavy metals such as activated carbon, zeolite, waste foundry sand, sewage sludge, cement kiln dust, and others [9,17]. Precipitates of iron oxides have been used as promising sorbents for organic compounds metal elements [4,13]. The particles of iron oxide are fine powders and their separation from aqueous solution can be represented as a serious obstacle in the usage of this material for the treatment process. Several previous studies are suggested to achieve plantation for the iron oxide on the immobilized solid supporting bed like sand, silica, cement, granular activated carbon, biomass and others [3,14]. Accordingly, the importance of this work is manufacturing of iron-oxide nano-particles-immobilized sand and use it as PRBs for capturing the elements of cadmium and copper from contaminated water based on the set of the experiments and theoretical simulations.

2. Experimental Work

2.1 Materials

Quartz sand with initial porosity of 36% was brought from a local market and washed carefully with distilled water before the use. The $Cd(NO_4)_2.4H_2O$ and $Cu(NO_4)_2.3H_2O$ (manufactured by HIMEDIA, India) were dissolved in distilled water to prepare the aqueous solutions contaminated with 1000 mg/L of cadmium and copper ions respectively. This solution was used to prepare the required concentration of used metals; however, the pH of the solution was changed by the addition of 0.1 M of hydrochloric acid or sodium hydroxide. The heavy metals concentrations were measured using atomic absorption spectrophotometer (AAS, AA-7000 Shimadzu, Japan).

2.2 Preparation of Coated Sand and Equilibrium Experiments

To prepare the sand coated with nano-particles of iron oxide (CSIO), the method of modified precipitation was applied [15]. The amount of 1 g sand was added to 50 mL of a solution containing 2 g $Fe(NO_3)_2$. To ensure the occurrence of precipitation, the NaOH was added to raise the pH of the mixture. This mixture must be agitated for the duration of three hours; then, it is dried for four hours at 105°C and thereafter the unattached iron oxide can be removed by successive washing until the pH of the wash water stabilized within the range of (7–8). The coated solids must put in the oven for drying for twenty-four hours at 105°C and stored until usage in the sorption tests. The coating process was assessed under the effects of solution pH and sand/ferric nitrate ratios based on the achieved maximum removal efficiency of cadmium ions. The required concentration of the solutions contaminated with metal ions was obtained by dilution of stock solution. The removal efficiency was calculated by applying the initial (C_o) and final (C_e) concentration before and after the sorption process respectively as follows [7,10]:

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \qquad \ldots(1)$$

The isotherm data were obtained by taking 50 mL with different concentrations (5-100) mg/L of Cd(II) and Cu(II) solutions and distributed into different conical flasks at pH =5. The 1 g of coated sand by iron oxide (CSIO) must distribute on the conical flasks which agitated by the shaker for three hours at room temperature to enhance the transport of metal ions from the liquid phase to solid phase until the reaching of equilibrium status. These sorption measurements are fitted with the Langmuir and Freundlich isotherm models that represented by Eqs. 2 and 3 respectively [1,7,8, 16,18]:

$$q_e = K_f C_e^{1/n} \qquad \ldots(2)$$

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \qquad \ldots(3)$$

where q_e was the amount of metal ions adsorbed at equilibrium (mg/g). The constants K_f and $1/n$ are Freundlich constants which reflect the adsorption capacity and intensity respectively. Also, the b and q_{max} are affinity constant (L/mg) and maximum adsorption capacity (mg/g) for Langmuir isotherm respectively.

2.3 Continuous Study

The diagram for column setup utilized for representation the contaminant transport is illustrated in Figure 1. This setup consists of three Perspex columns and each column has dimensions of height = 50 cm and diameter = 2.5 cm. Each column was supplied with ports P1, P2 and P3 at distances of 10, 20, and 30 cm as clear in this figure. The ports were assembled with stainless steel fittings and Viton stoppers can be for blockage them. By using the syringes, the water samples have been taken periodically from the column center. Each column was packed with 30 cm of CSIO and this bed must saturate with distilled water by feeding it from the bed bottom in the upward direction. Using a constant head tank with a flow-meter and four valves, the contaminated solution was introduced into the beds for the Column-1, -2 and -3. The flow rates of (5, 10, and 15 mL/min) with an initial concentration of (10, 20, and 30 mg/L) are tested in the present experimental program. The concentrations of Cd(II) and Cu(II) at locations are identical in ports P1, P2 and P3 and measured by AAS for a period not exceeded 13 days. The measurements are also included the monitoring of the accumulative aqueous solution volume with time and results proved that the flow rate values remained constant through each experiment.

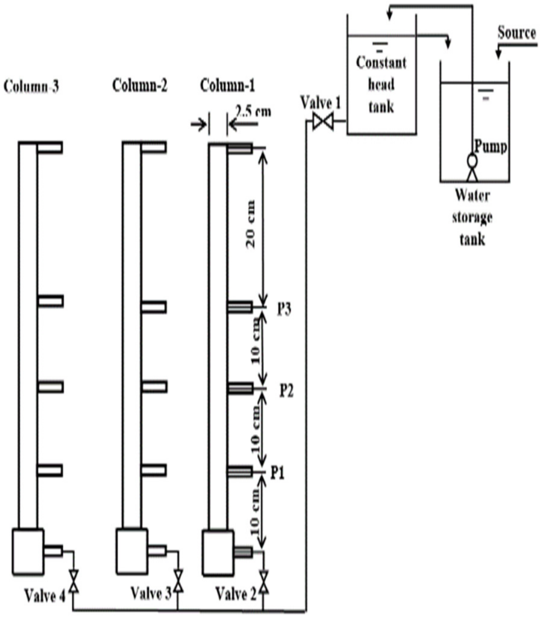


Fig. 1. Laboratory-scale column setup.

3. Results and Discussion

3.1 Preparation of CSIO

The pH effect of aqueous solution associated with $Fe(NO_3)_2$ concentration and also the mass of sand on the removal efficiency for Cd(II) ions were evaluated as showen in Figure 2. This figure proved that the increase of $Fe(NO_3)_2$ solution pH from 5 to 12 can cause a significant increase in the removal efficiency by CSIO. The precipitation of ferric hydroxide on the solid particles surfaces was achieved by changing the pH to became > 3 (11). In addition, the removal efficiency be CSIO was approximately stabilized the pH 11; so, this value can be chosen for the coating of sand by iron oxide. Then, the mass of sand used in the coating process was changed within the range from 0.5 to 10 g added to 50 mL of solution contained on 2 g of $Fe(NO_3)_2$. The removal efficiency of Cd(II) ions was increased with an increase in the sand dosage from 0.5 to 5 g (0.25 to 2.5 sand dosage /ferric nitrate). The washing after ending the process of preparation can be applied to remove the uncoated iron oxide. Therefore, the sand dosage of 5 g (2.5 sand dosage /ferric nitrate) was proposed for the achieving of the coating process.

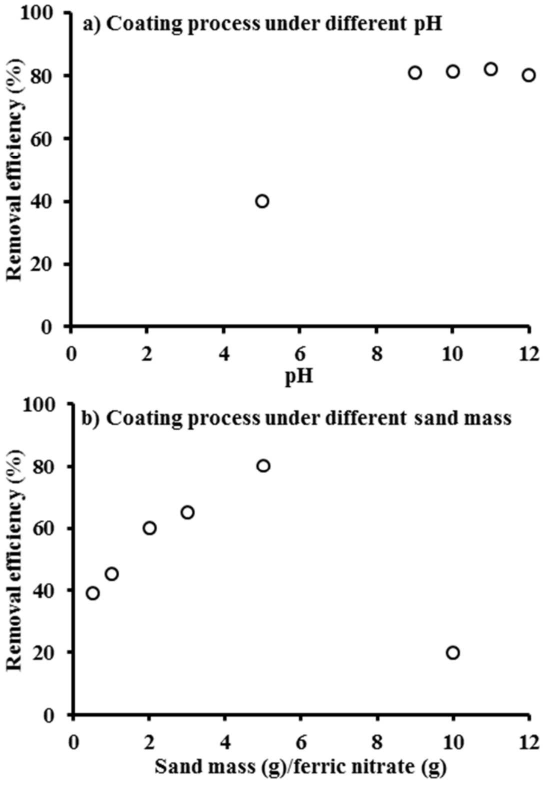


Fig. 2. Effect of a) pH and b) sand mass on the Cd(II) removal efficiency onto CSIO.

3.2 Sorption Isotherms

Langmuir and Freundlich's models are fitted with sorption data for the interaction of cadmium and copper ions with CSIO for q_e (mg/g) with C_e (mg/L) as shown in Figure 3. The fitted constants with statistical measures have been calculated from nonlinear regression - Microsoft Excel (2016) [1,7,8, 16,18] as listed in Table 1. This figure in conjugation with a determination coefficient (R^2) and the sum of squared errors (SSE) elucidated that the model of Langmuir is more representative of sorption data.

Table 1,
Values of parameters for models of Langmuir and Freundlich for removal of cadmium and copper onto CSIO.

Model	Parameter	Value Cd(II)	Cu(II)
Langmuir	q_{max} (mg/g)	1.9181	7.6425
	b (L/mg)	0.3639	0.0559
	R^2	0.9928	0.9804
	SSE	0.0178	0.5496
Freundlich	K_f	0.5450	0.8536
	$1/n$	0.3170	0.4634
	R^2	0.9657	0.9278
	SSE	0.0740	2.0936

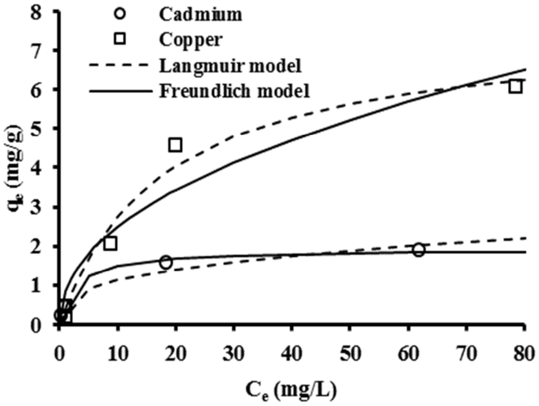


Fig. 3. Isotherms models for cadmium and copper ions sorption onto CSIO.

3.3 Breakthrough Curves

The breakthrough curves for the propagation of cadmium and copper fronts measured at certain locations along the CSIO packed columns are plotted in Figures 4 to 6 under the different values of initial concentration and flow rate. A significant decrease in the concentrations of contaminants can be recognized due to the change of depth from 10 to 30 cm for all magnitudes of initial concentration and flow rate. Remaining of the polluted water for the long duration within the bed may be the cause for this result; however, this was improved the sorption process. With time, the barrier functionality decreases significantly because of the decrease of retardation factor due to saturate of the bed with sorbed metals. For initial concentration at a certain location, plotted results signified that the migration of the metal front relates directly with the flow velocity; so, the higher flow rate means faster transport for contaminant and this accompanies with decreasing of time required for achieving the state of equilibrium. Also, the increase of initial metal concentration will enhance the saturation of the bed with this contaminant more quickly due to the increase of the mass transfer driving force. The shapes of breakthrough curves are to be sharper due to the increase of metal concentration [12].

To represent the experimental measurements mathematically, the advection - dispersion equation (Eq.4) can be solved numerically by the finite element method through the application of COMSOL Multiphysics 3.5a (2008). This equation plots the contaminant transport in the column packed with CSIO porous medium and it can be written as follows:

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} = R \frac{\partial C}{\partial t} \qquad \ldots(4)$$

where C is the contaminant concentration, D_z is the dispersion coefficient, V_z is the flow velocity. Because the sorption of solute onto CSIO is more represented by the Langmuir model, the retardation factor (R) is expressed as follows:

$$R = 1 + \frac{\rho_b}{n}\left(\frac{1.9181*0.3639}{(1+0.3639C)^2}\right) \quad \text{cadmium} \qquad \ldots(5)$$

$$R = 1 + \frac{\rho_b}{n}\left(\frac{7.6425*0.0559}{(1+0.0559C)^2}\right) \quad \text{copper} \qquad \ldots(6)$$

where n is the porosity and ρ_b is the bulk density.

To complete the modeling process, the dispersivity must be calculated for the medium under consideration. Experimental measurements for the coefficient of longitudinal dispersion (D_L) versus velocity (V) through CSIO can be described by the following linear relationship [9]:

$$D_L = 6.49\,V + 0.5325 \quad R^2=0.996 \qquad \ldots(7)$$

By similarity of this equation with the following formula, dispersivity (α) can be evaluated:

$$D_L = \alpha\,V + D^* \qquad \ldots(8)$$

where D^* is the coefficient of effective molecular diffusion.

The outputs of solution for physical problem are illustrated in Figure 1 by applying COMSOL on the Eq.4 and are plotted together with the experimental measurements as shown in Figures 4 to 6. All magnitudes of CSIO with initial and boundary conditions for the present problem are listed in Table 2. The predicted concentrations of cadmium and copper ions by the numerical solution for different flow rates, initial concentrations and bed depth showed that the contaminant plume is hindered by CSIO and the contaminant concentration levels reaching the outlet of the column may be low in the initial times and then increased with the time. Satisfactory matching between the predicted values and experimental results for cadmium and copper concentrations was observed with root mean squared errors [2] that did not exceed 0.121.

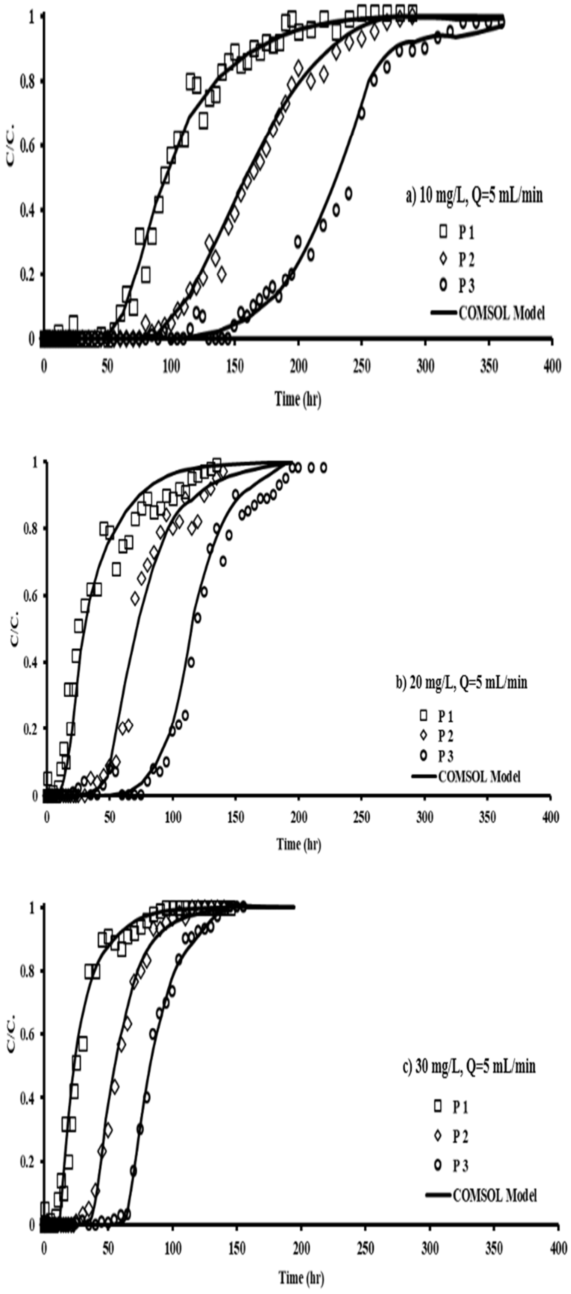


Fig. 4. Comparison between model predictions and experimental measurements for the normalized concentration of cadmium under the effects of initial concentration and bed depth.

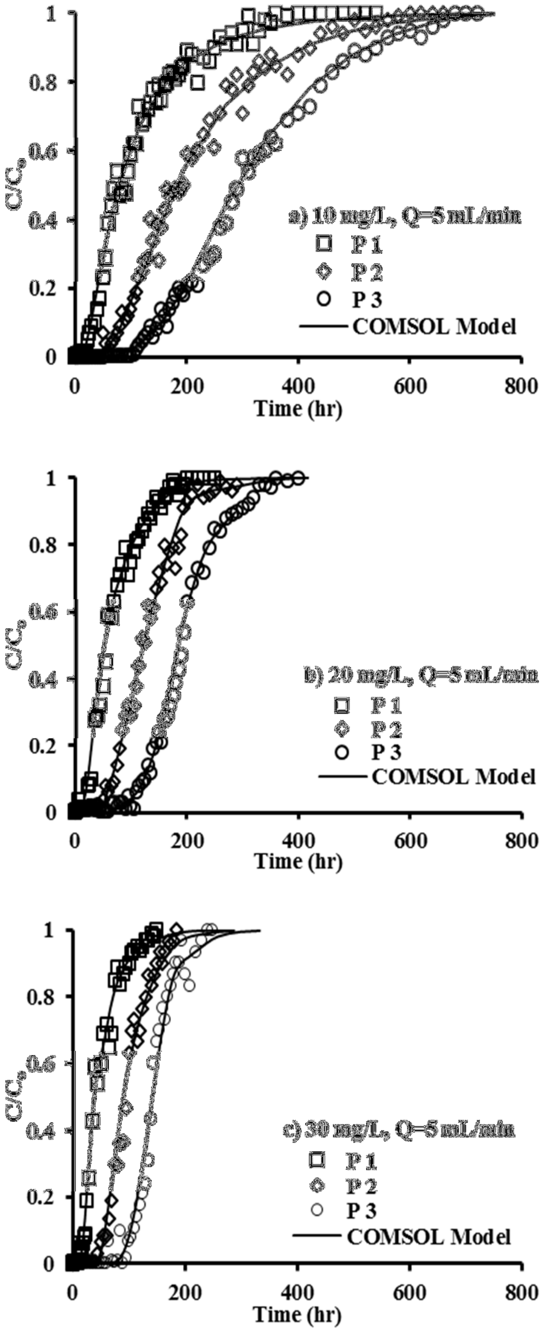
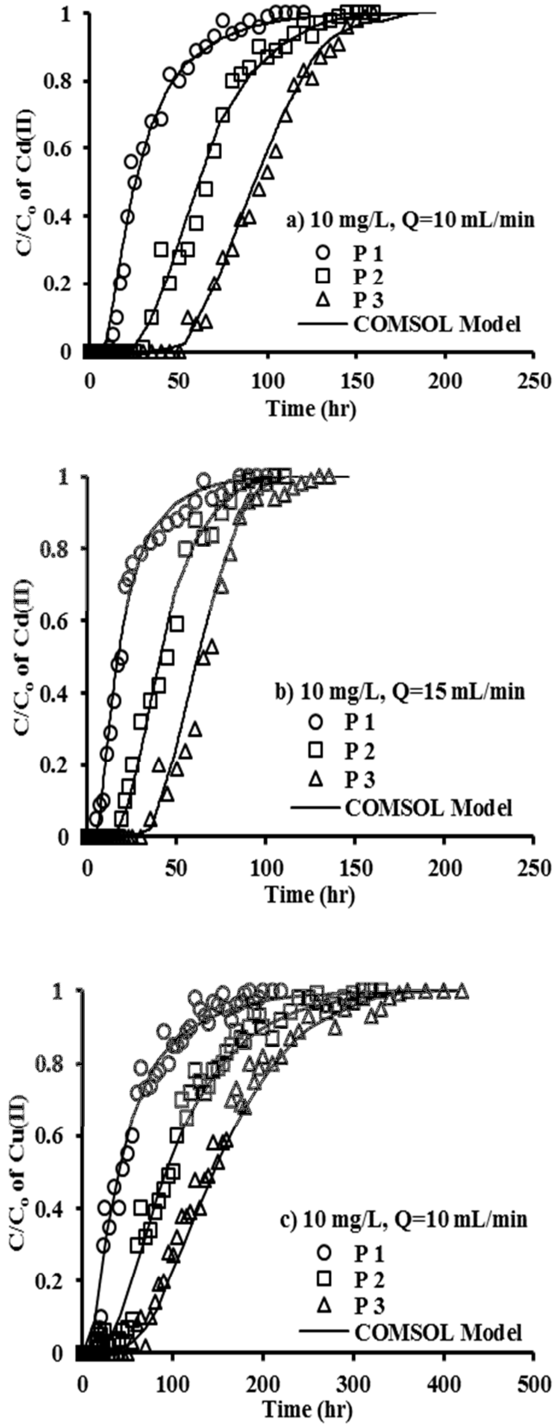


Fig. 5. Comparison between model predictions and experimental measurements for normalized concentration of copper under the effects of initial concentration and bed depth.



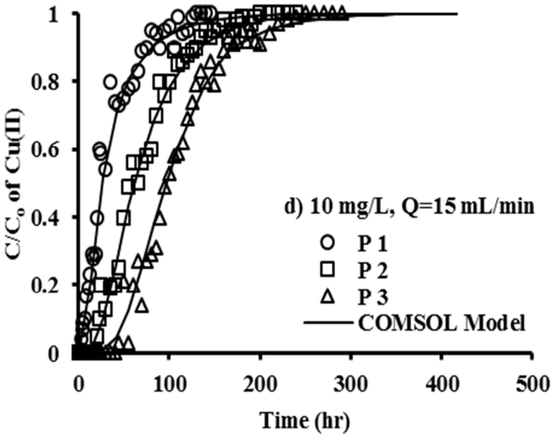


Fig. 6. Comparison between model predictions and experimental measurements for the normalized concentration of cadmium and copper under the effects of flow rate and bed depth.

Table 2,
The information utilized in the simulation of contaminant transport in a column packed with CSIO.

Item	Parameter	Value
CSIO	Depth (cm)	30
	Porosity (n)	0.45
	α_L^* (cm)	6.49
	ρ_b (g/cm^3)	1.363
Initial condition	C_o^{**} (mg/L)	Zero
Boundary conditions	Conc. @ z=0 (mg/L)	10, 20, 30
	Advective flux @ z=30 cm	Zero

*Longitudinal dispersivity, **Initial concentration

4. Conclusions

Coated sand by iron oxide (CSIO) that prepared by plantation of nano-sized-iron oxide onto immobilized-sand through simple impregnation process proved its ability in the remediation of contaminated water. Mainly, CSIO was applied in the permeable reactive barrier for removal of cadmium and copper ions from aqueous solutions in the batch and continuous tests. The sorption data were described in better form by the Langmuir isotherm model in comparison with the Freundlich model where the coefficient of determination (R^2) was more than 0.98. The maximum adsorption capacities for cadmium and copper onto CISO reached to

1.9181 and 7.6425 mg/g respectively. The results of COMSOL Multiphysics 3.5a certified that the barrier is efficient in the delay of contaminant migration due to a decrease of both flow rate and inlet concentration as well as the increase of bed depth. However, a good agreement between the predicted and experimental results was observed with root mean squared errors not exceeded 0.121.

5. References

[1] Abd Ali, Z.T., Naji, L.A., Almuktar, S.A.A.A.N., Faisal, A.A.H., Abed, S.N., Scholz, M., Naushad, M., Ahamad, T., 2020. Predominant mechanisms for the removal of nickel metal ion from aqueous solution using cement kiln dust. J. Water Process Eng. 33, 101033. https://doi.org/10.1016/j.jwpe.2019.101033

[2] Bair, E.S., 2016. Applied Groundwater Modeling-Simulation of Flow and Advective Transport. Groundwater 54, 756–757. https://doi.org/10.1111/gwat.12464

[3] Benjamin, M.M., Sletten, R.S., Bailey, R.P., Bennett, T., 1996. Sorption and filtration of metals using iron-oxide-coated sand. Water Res. 30, 2609–2620. https://doi.org/10.1016/S0043-1354(96)00161-3

[4] Choo, K.H., Kang, S.K., 2003. Removal of residual organic matter from secondary effluent by iron oxides adsorption. Desalination. https://doi.org/10.1016/S0011-9164(03)80014-0

[5] Davis, T.., Volesky, B., Vieira, R.H.S.., 2000. Sargassum seaweed as biosorbent for heavy metals. Water Res. 34, 4270–4278. https://doi.org/10.1016/S0043-1354(00)00177-9

[6] Doula, M., Ioannou, A., Dimirkou, A., 2000. Thermodynamics of copper adsorption-desorption by Ca-kaolinite. Adsorption. https://doi.org/10.1023/A:1026513032260

[7] Faisal, A.A.H., Al-Wakel, S.F.A., Assi, H.A., Naji, L.A., Naushad, M., 2020. Waterworks sludge-filter sand permeable reactive barrier for removal of toxic lead ions from contaminated groundwater. J. Water Process Eng. 33, 101112. https://doi.org/10.1016/j.jwpe.2019.101112

[8] Faisal, A.A.H., Alquzweeni, S.S., Naji, L.A., Naushad, M., 2020. Predominant Mechanisms in the Treatment of Wastewater Due to Interaction of Benzaldehyde and Iron Slag Byproduct. Int. J. Environ. Res. Public Health 17, 226. https://doi.org/10.3390/ijerph17010226

[9] Faisal, A.A.H., Hmood, Z.A., 2013. Groundwater protection from cadmium contamination by zeolite permeable reactive barrier. Desalin. Water Treat. 1–10.https://doi.org/10.1080/19443994.2013.855668

[10] Faisal, A.A.H., Naji, L.A., 2019. Simulation of Ammonia Nitrogen Removal from Simulated Wastewater by Sorption onto Waste Foundry Sand Using Artificial Neural Network. Assoc. Arab Univ. J. Eng. Sci. 26, 28–34. https://doi.org/10.33261/jaaru.2019.26.1.004

[11] Hajialigol, S., Taher, M.A., Malekpour, A., 2006. A New Method for the Selective Removal of Cadmium and Zinc Ions from Aqueous Solution by Modified Clinoptilolite. Adsorpt. Sci. Technol. 24, 487–496. https://doi.org/10.1260/026361706780154437

[12] Han, R., Zou, L., Zhao, X., Xu, Y., Xu, F., Li, Y., Wang, Y., 2009. Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper(II) from solution in fixed bed column. Chem. Eng. J. 149, 123–131. https://doi.org/10.1016/j.cej.2008.10.015

[13] Jeong, Y., Fan, M., Singh, S., Chuang, C.L., Saha, B., Hans van Leeuwen, J., 2007. Evaluation of iron oxide and aluminum oxide as potential arsenic(V) adsorbents. Chem. Eng. Process. Process Intensif. https://doi.org/10.1016/j.cep.2007.05.004

[14] Kundu, S., Gupta, A.K., 2005. Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC). J. Colloid Interface Sci. 290, 52–60. https://doi.org/10.1016/j.jcis.2005.04.006

[15] Lee, S., Laldawngliana, C., Tiwari, D., 2012. Iron oxide nano-particles-immobilized-sand material in the treatment of Cu (II), Cd (II) and Pb (II) contaminated waste waters. Chem. Eng. J. 195–196, 103–111. https://doi.org/10.1016/j.cej.2012.04.075

[16] Naji, L.A., Jassam, S.H., Yaseen, M.J., Faisal, A.A.H., Al-Ansari, N., 2019. Modification of Langmuir model for simulating initial pH and temperature effects on sorption process. Sep. Sci. Technol. 1–8. https://doi.org/10.1080/01496395.2019.1655055

[17] Phuengprasop, T., Sittiwong, J., Unob, F., 2011. Removal of heavy metal ions by iron oxide coated sewage sludge. J. Hazard. Mater. 186, 502–7.

https://doi.org/10.1016/j.jhazmat.2010.11.065.

[18] Saad, N., Abd Ali, Z.T., Naji, L.A., AAH Faisal, A., 2019. Development of Bi-Langmuir model for description initial pH and temperature effects on the sorption of cadmium onto waste foundry sand. Environ. Eng. Res. https://doi.org/10.4491/eer.2019.277

[19] Yu, B., Zhang, Y., Shukla, A., Shukla, S.S., Dorris, K.L., 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption - Removal of copper. J. Hazard. Mater. https://doi.org/10.1016/S0304-3894(00)00278-8

الحاجز التفاعلي النفاذ المكون من رمال مطلية بأوكسيد الحديد لمعالجة المياه الجوفية الملوثة بأيونات الكادميوم والنحاس

محمد بهجت عبد الكريم* اياد عبد الحمزة فيصل**
*،**قسم الهندسة البيئية / جامعة بغداد
*البريد الالكتروني: Mohammed.bahjet73@gmail.com
**البريد الالكتروني:ayadabedalhamzafaisal@yahoo.com

الخلاصة

ان تصنيع رمال مطلية بأوكسيد الحديد من خلال ترسيب الجزيئات النانوية لذلك الاوكسيد على سطوح الرمال واستخدامها في الحاجز التفاعلي النفاذ لإزالة ايونات الكادميوم والنحاس من المياه الجوفية الملوثة الهدف الرئيسي للدراسة الحالية. تم توصيف بيانات الامتزاز نتيجة تفاعل المادة المازة مع المادة الممتزة قيد الدراسة بشكل جيد من خلال نموذج لانكمير والذي كان أفضل من نموذج فراندلش. لقد وجد ان اعلى قيم لقابلية الامتزاز باستخدام الرمال المطلية بأوكسيد الحديد وصلت الى 1.9181 و٧.٦٤٢٥ ملغم/غم لكل من الكادميوم والنحاس على التوالي. اثبت برنامج COMSOL Multiphysics 3.5a قدرته على محاكاة والتنبؤ بانتقال الكادميوم والنحاس من خلال حاجز تفاعلي نفاذ ذو البعد الواحد والمكون من رمال مطلية بأوكسيد الحديد. أثبتت النتائج ان المادة المصنعة المستخدمة ضمن هذا الحاجز لها القدرة على تأخير انتقال الملوثات. لوحظ ان جذر معدل مجموع الأخطاء بين النتائج المتوقعة والمقاسة لا يتجاوز 0.121 وهذا يعني وجود توافق جيد بين تلك البيانات.
