INFLUENCE OF LOW PERMEABLE BARRIER ON THE MIGRATION OF CADMIUM IONS IN THE SUBSURFACE MEDIUM

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Abstract

Interaction of cement kiln dust - aqueous solution contaminated with cadmium ions was investigated under the different operational conditions of batch tests to simulate the acetogenic phase in the sanitary landfill. The best values are time= 1 hr, dosage=0.7 g/100 mL and speed=250 rpm to obtain the maximum removal efficiency of 97.6%. Langmuir model has high ability in the representation of the sorption data with determination coefficient (R^2) equal to 0.97471 and the sorption capacity reached to 84.1 mg/g. Tests elucidated that the average coefficient of the hydraulic conductivity is equal to 9.7×10^{-15} m/s and this is suitable for low permeable barrier. Finally, COMSOL Multiphysics 3.5a package was able to represent the distribution of cadmium ions concentrations within the two-dimensional hypothetical problem for model packed with sand aquifer and CKD barrier.

Keywords: Cement kiln dust; Migration, Retardation; Contamination; Barrier.

Introduction

The liners used as barriers in the bottom of the sanitary landfills are represented the major component of the system applied to restrict the leachate migration. Several natural materials used in these barriers like clay, bitumen, geomembrane and others. Restriction of pollutant migration and resistance of the shrinkage and erosion are the main characteristics that must be available in the material consisted of this barrier. Historical records certified that the compacted clay is the mostly material used in the construction of liner because its availability, low cost and have a low permeability with high ability in the attenuation of contaminant concentration (Brandl, 1992). However, the clay may fail (i.e. crack) under the operation due to its high potential for swelling and certain types of leachate can be caused an increase in its hydraulic conductivity; accordingly, the finding the more suitable materials for being liners can be considered a main task for many new studies (Prashanth *et al.*, 2001). In this regard, solid waste materials resulted as byproducts from industrial and commercial activities can be tested as alternatives for clay such as waterworks sludge produced from water supply treatment plant, sewage sludge accompanied to the wastewater treatment plant processing, waste foundry sand associated to the production processes of steel industry and others.

So, the present study concentrated on the using cement kiln dust (CKD) which results as byproduct material from cement industry (Khanna 2009; Khaliefa, 2014) in the low permeable barrier for controlling the migration of contaminants presented in the leachate to protect the water resources near the sanitary landfills. This material is alkaline powder solid waste where the production of every ton of cement material will be accompanied with about 41 kg of CKD. Approximately 60% of the generated CKD can be recycled and the remaining quantity must manage (USEPA, 1993b); so, huge amounts of this waste will form a burden on the environment (Adaska and Taubert, 2008) and its usage in low barrier can be considered a good solution for this problem. The leachate is solution that contained a broad wide of pollutants like organic materials, ammonical nitrogen and heavy metals. This study is monitored the migration of cadmium ions as target pollutant in the subsurface medium with presence of CKD as low permeable barrier.

Previous studies signified that the contamination of aquifer will prohibit the use of its water for long periods of time reached to several decades and; in addition, the quickly reclamation of this aquifer may be impossible (Mason 2003). Heavy metals are among of the most hazardous inorganic water chemicals because they have extremely toxicity. These chemicals like cadmium have a good ability for accumulation in the web of aquatic food to reach the human beings and cause many pathologies. In Japan, the spreading of Itai-itai disease in the 1950s was attributed to the presence of cadmium element (resulted from base-metal mining) with high concentrations in water applied in the irrigation of rice fields (Kasuya *et al.*, 1992). The heavy metals in groundwater may be resulted from water infiltration through the polluted layers of the soil (Di Natale *et al.* 2008). Several studies (Abichou *et al.*, 2000; Anderson and Mesa, 2006; Bradshaw *et al.*, 2016; Widomski *et al.*, 2018) are directed to study the possibility of using different materials in the low permeable barriers. Also, solid wastes like municipal solid waste incineration ash, waste rock and others may be represented a familiar sources of the heavy metals through the leaching process. Finally, the main object of the present study is finding the performance of CKD as low permeable reactive barrier based on the set of batch tests with hypothetical simulation using COMSOL Multiphysics 3.5a (2008) for migration of the cadmium ions in the sand aquifer that contained of CKD barrier.
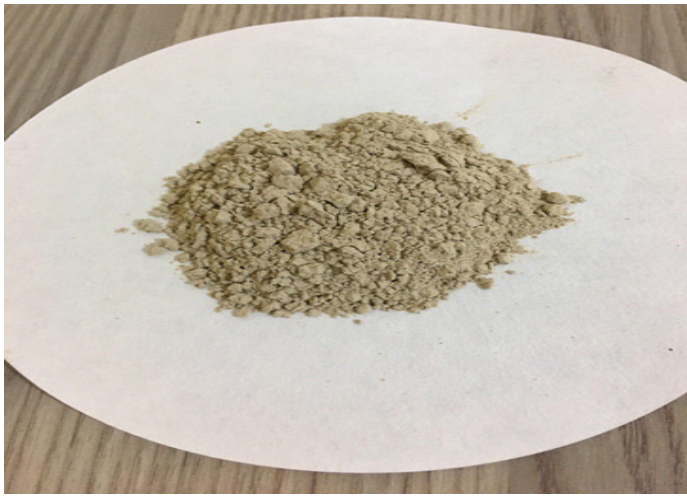
Materials and Methods

Materials

The Al-Kufa cement factory, Al-Najaf city, Iraq was the source of CKD used in the present study. The main constituents of this sorbent are inserted in Table 1 and its physical appearance can be imaged in Figure 1. The specific surface area of CKD was found equal to 0.52 m^2/g measured according to ASTM C 204-05 using the Blaine-air permeability apparatus (Sreekrishnavilasam *et al.* 2006).

The quartz sand with size of 0.6-1 mm was used to simulate the aquifer. It washed thoroughly with distilled

water, dried using the oven for 2 hours under 105˚C, then used. The bulk density, porosity and hydraulic conductivity coefficient have value of 1.7335 g/cm^3, 0.31, and 4.1×10^{-4} m/s respectively with d$_{50}$ equal to 0.7674 mm.

Table 1 : The chemical composition of CKD.

Constituents	Composition (wt. %)
SiO_2	15.05
Al_2O_3	4.43
Fe_2O_3	2.23
CaO	43.99
MgO	1.64
SO_3	6.02
Na_2O	0.69
K_2O	4

Fig. 1. Physical appearance of cement kiln dust used in this study.

Contaminant

To prepare the water sample with cadmium concentration of 1000 mg/L, 2.744 g of $Cd(NO_3)_2.4H_2O$ dissolved in one liter of distilled water and this solution was kept at room temperature. The solution was used as stock solution to prepare any specific concentration of cadmium by dilution and its pH adjusted to became 3 to represent the acetogenic phase of leachate by adding 0.1 M HNO_3 or NaOH as required.

Batch experiments

They were carried out to determine the best conditions that required to achieve the maximum removal efficiency of pollutant. These conditions included contact time, adsorbent dosage, initial metal concentration and agitation speed for certain value of initial concentration and initial pH of the solution. Series of 250 mL flasks are employed and each flask is filled with 100 mL of cadmium solution which has initial concentration (C_o) of 50 mg/L. The CKD dosages (m) of (0.05, 0.1, 0.3, 0.5, 0.7, 0.9 and 1 g) were added to the different flasks and they have been stirred in the high-speed orbital shaker (Edmund Buhler SM25, German) at 250 rpm for 1 hour. A fixed volume (20 mL) of the solution was withdrawn from each flask and filtered using filter paper type (JIAO JIE 102) to separate the adsorbent; then, fixed volume (V =10 mL) of the clear solution was utilized for the determination of the amount of unsorted metal ion still present in solution (C_e). The measurements were carried out to concentration of cadmium using atomic absorption spectrophotometer (AAS, Sens AA, Australian). Different values of contact time (0, 50, 100, 150, 200 and 250) and

agitation speed (50, 100, 150, 200 and 250 rpm) for initial pH of 3 and initial concentration of 50 mg/L. The quantity of adsorbed contaminant (q_e) was established by the mass balance using the following equation (Gheju and Miulescu, 2007):

$$q_e = (C_0 - C_e)\frac{v}{m} \qquad ....(1)$$

The removal efficiency (R) for all contaminants was determined by:

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad .... (2)$$

Models of Sorption

They related between the contaminant concentration sorbed on the solid phase of the sorbent (q_e, mg/g) and concentration remaining in the liquid phase (C_e, mg/L). The sorption models have many mathematical relationships like Langmuir, Freundlich and others. In the present, the first model with following formula is used to represent the sorption data (Hamdaoui and Naffrechoux, 2007; Foo and Hameed, 2010):

$$q_e = \frac{q_{max}bC_e}{1+bC_e} \qquad .... (3)$$

where b and q_{max} are the affinity constant (L/mg) and the maximum adsorption capacity (mg/g) respectively. These constants are very important in the description the retardation factor (i.e. reaction term) in the contaminant (advection-dispersion) transport equation in the hypothetical problem adopted in the present study.

Hypothetical Problem for Description the Cadmium Transport

The geometry of the hypothetical model is assumed to be consisted of sand aquifer and CKD barrier with alignment and dimensions plotted in Figure 2. The transport of cadmium ions in the 2D bed is based on the solving of the groundwater equation (Eq.4) for steady state system and the transient advection-dispersion equation (Eq. 5) simultaneously. These equations are written as follows (Faisal and Ahmed, 2014):

$$\frac{\partial}{\partial x}\left(Kx\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(Ky\frac{\partial h}{\partial y}\right) = 0 \qquad .... (4)$$

$$D_x\frac{\partial^2 C}{\partial x^2} + D\frac{\partial^2 C}{\partial y^2} - V_x\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{\rho_b}{n}\frac{\partial q}{\partial t} \qquad .... (5)$$
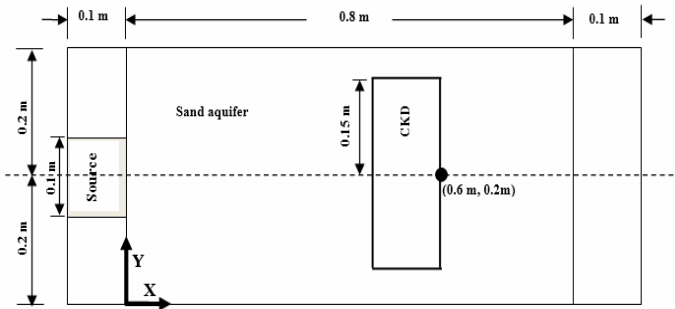
where K is the hydraulic conductivity coefficient (m/s), D is the dispersion coefficient (m^2/s), V is the seepage velocity (m/s), h is the hydraulic head (m), ρ_b is the bulk density (kg/m^3). The Langmuir model must be incorporated with the last equation to describe the adsorption process in the transport of the contaminant and the resultant equation can take the following form:

$$D_x\frac{\partial^2 C}{\partial x^2} + D_y\frac{\partial^2 C}{\partial y^2} - V_x\frac{\partial C}{\partial x} = R\frac{\partial C}{\partial t} \qquad .... (6)$$

and R will be;

$$R = 1 + \frac{\rho_d}{n}\left(\frac{q_m b}{(1+bC)^2}\right) \qquad \text{.... (7)}$$
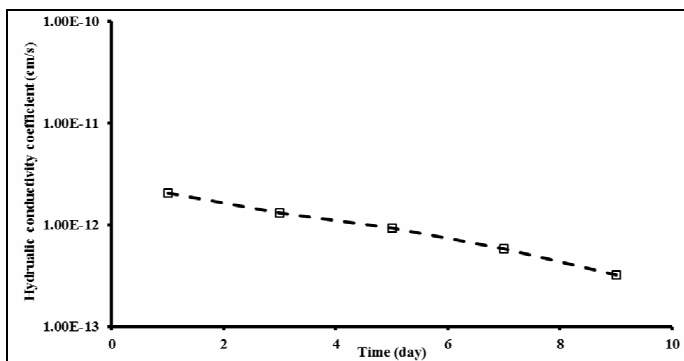
where R is the retardation factor.

Fig. 2 : Geometry of the hypothetical problem model for aquifer with CKD barrier solved as plotted by COMSOL Multiphysics 3.5a to find the migration of cadmium ions.

Results and Discussion

Coefficient of hydraulic conductivity

The "falling head permeameter" utilized in the measurement of the hydraulic conductivity coefficient for CKD material. The experiment was beginning by saturating the porous medium sample with tap water for duration not less than 2 days; so, this test actually measures the water passing through this material. Figure 3 plots the relationships between the hydraulic conductivity and elapsed time for CKD. It is clear that the coefficient of hydraulic conductivity was decreased with the time from 2.05×10^{-12} until approximately stabilized on the value of 3.22×10^{-13} cm/s after contact time of 9 days. Due to the high density of the present reactive materials, this will cause the slowed flow within the internal pores and, consequently, the coefficient of hydraulic conductivity (K) will be low (Worthington and Soley, 2017). Also, the average value for coefficient of hydraulic conductivity for CKD was equal to 9.7×10^{-13} cm/s which lower from the familiar values of clay and this can be considered a good point in the selection of CKD as alternative material for clay in the low permeable barrier.
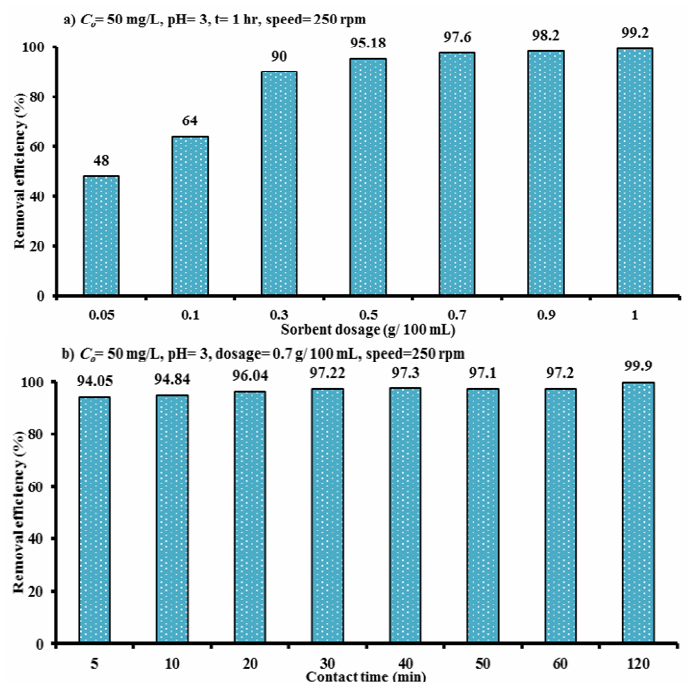

Fig. 3 : Variation of hydraulic conductivity coefficient for CKD reactive material.

Batch experiments

- **Contact time:** Figure 4(a) plots the variations of removal efficiencies for cadmium ions onto CKD versus the contact time under the conditions of C_o= 50 mg/L, pH= 3, dosage= 0.7 g/ 100 mL, speed=250 rpm. This figure reveals that the sorption rate is very fast within the first five minutes and at which the efficiency approaches to 94.05%. Thereafter, the rate was gradually slowed and efficiency approximately stabilized beyond 1 hr at 97.6%. The presence of sufficient numbers of the binding sites on the adopted sorbent may be the main

reason for high rate of sorption process and its decrease with elapsed time can be resulted from the occupation of these sites by cadmium ions (Rashid and Faisal, 2019)..
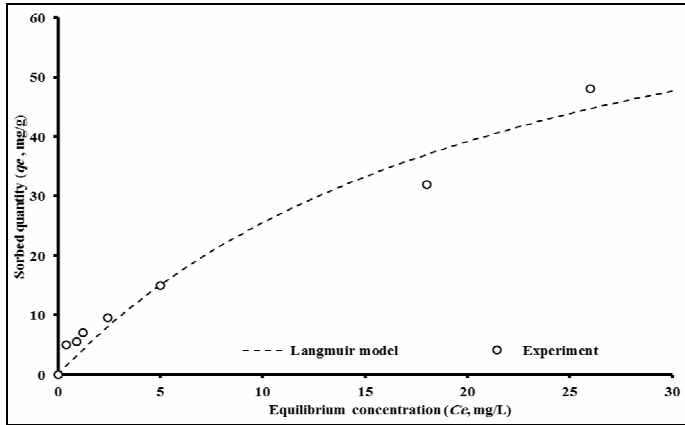
- **Sorbent dosage:** The sorption of cadmium ions as function of CKD masses can be studied by variation of the dosage from 0.05 to 1 g added to 100 mL of the contaminated aqueous solution. The relationships between the metal ions removal efficiencies and sorbent dosages of CKD are plotted in Figure 4(b). It can be seen that the increase of sorbent mass will improve the removal efficiency and this may be attributed to available greater vacant sites. Also, this figure certifies that the sorption efficiency was increased from 48 to 90% due to increase of dosage from 0.05 to 0.3 g/ 100 mL. Beyond the 0.3 g/ 100 mL, slow increase in the efficiency can be recognized; so, the dosage was chosen of 0.7 g/ 100 mL to obtain of the fair value of removal efficiencies for cadmium ions that reached to 97.6%. An increase in the sorbent dosage beyond 0.7 g/ 100 mL will not have significant effect on the adsorption capacity because the metal concentrations in the aqueous solution and sorbent dosage reached to the equilibrium status (Abd Ali *et al.*, 2019).

- **Agitation speed:** This speed was changed within the range extended from 50 to 300 rpm and the measured corresponding removal percentages of the cadmium ions have been measured under the operational conditions of C_o= 50 mg/L, contact time= 1 hr, initial pH= 3, and dosage= 0.7 g/ 100 mL. The slight increase in the sorption efficiency from 91.8 to 100% was recorded due to change of agitation speed from 50 to 300 rpm. This means that the reactivity of CKD is very high due to generate two mechanisms namely adsorption and precipitation responsible of the removal process; so, the agitation speeds within the adopted range not have significant effect on the removal process. For practical purposes, the choice speed of 250 rpm as best value for batch tests is satisfactory for two sorbents under consideration.

Fig. 4 : The trend of the relationships related between the removal efficiencies of the cadmium ions a) contact time, and b) sorbent dosage.

Isotherm models

Figure 5 shows the Langmuir isotherm model that fit the sorption data to describe the removal of cadmium ions onto CKD reactive material. Constants of this model are listed in Table 2 and they are calculated by using non-linear regression fitting in Excel (2016) utilizing the "Solver" option. It is clear from this figure in combination with coefficient of determination (R^2) mentioned in the Table 2 that the two model is able to represent of sorption data for case under consideration. The maximum adsorption capacity of CKD is equal to 84.1 mg/g with affinity constant of 0.04360 L/mg.

Fig. 5 : Langmuir isotherm model for sorption of cadmium ions onto CKD.

Table 2 : Constants of isotherm model for description the sorption of cadmium ions onto CKD.

Model	Parameter	Value
Langmuir	q_{max} (mg/g)	84.1
	b (L/mg)	0.04360
	R^2	0.97471

Cadmium transport in the 2D bed consisted of sand and CKD

Application of COMSOL Multiphysics was achieved to simulate the 2D steady flow of water and transient contaminant transport through a sand aquifer with the presence of CKD barrier. The geometry of the bed is described previously in Figure 2. It seems that the model has dimensions of 0.8 m length and 0.4 m width for bed height of 5 cm; also, the alignment of barrier has dimensions of 0.1 × 0.3 m as well as the contaminant can be injected from continuous line source of 0.10 m. Tables 3 and 4 listed all required information for modeling of the present problem by COMSOL Multiphysics 3.5a. The solution procedure is needed to find the values velocity vector from solving the groundwater flow equation; then, the outputs can be used as the input data for solving solute transport equation to plot the distribution of contaminant concentration within the flow domain.

Table 3 : Constants utilized for modeling of 2D transport of contaminant in the LPB and aquifer.

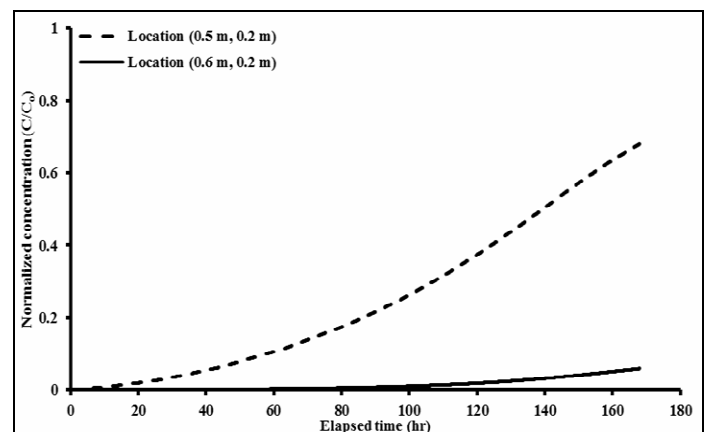| Bed	Variable	Value
Sand aquifer	n	0.31
	K	4.1×10^{-4}
	ρ_b	1733.5
LPB	n	0.62
	K	9.7×10^{-15}
	ρ_b	1170

n= Porosity; K= Hydraulic conductivity (m/s); ρ_b= Bulk density (kg/m^3)

Table 4 : Conditions adopted in the modeling of cadmium ions transport for the 2D laboratory scale tank.

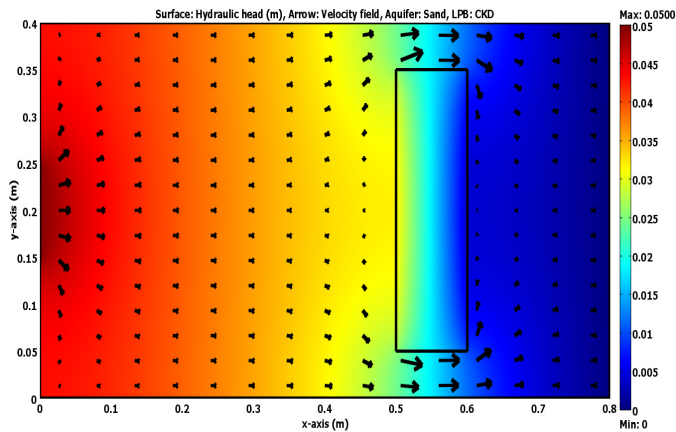| Item	Location	Type	Value
Boundary conditions for fluid flow	Line source	Hydraulic head (cm)	5
	Outlet side	Hydraulic head (cm)	zero
	All other sides	Zero flux/symmetry	------
Boundary conditions for solute transport	Line source	Concentration (mg/L)	50
	Outlet side	Advective flux	------
	All other sides	No flux/symmetry	------
Initial condition for solute transport	------	Concentration (x,y) at t=0	zero

The COMSOL package can be utilized to predict the spatially and temporally normalized concentrations of cadmium ions within the hypothetical problem adopted in this study. Accordingly, Figure 6 is introduced the comparison between the predictions of breakthrough curves for locations just before the CKD barrier (0.5 m, 0.2 m) and just beyond this barrier (0.5 m, 0.2 m). It is clear that this barrier plays a significant role in the protection of location beyond the barrier. This means that the concentrations of contaminant have the lowest values in the locations adjacent to the barrier from down gradient side.

For present simulations described by COMSOL package, the hydraulic head and velocity values was plotted in the flow field under the effect of LPB as shown in Figure 7. The barrier has ability to create two stagnant points in the up- and down-gradient sides of this wall with significant change in the advection front in the locations nearby the barrier. This figure elucidates that the velocity of the flow is decreased significantly inside the barrier, while a smaller region of reduced speed can be observed outside the barrier. Figure 8 plots the contours of cadmium normalized concentration across the bed model as predicted by the COMSOL software for various times. The barrier situated beyond the line source of contamination is caused a significant reduction in the rate of advective transport with lateral deviation of the contaminant plume as the streamlines spread to pass the barrier.
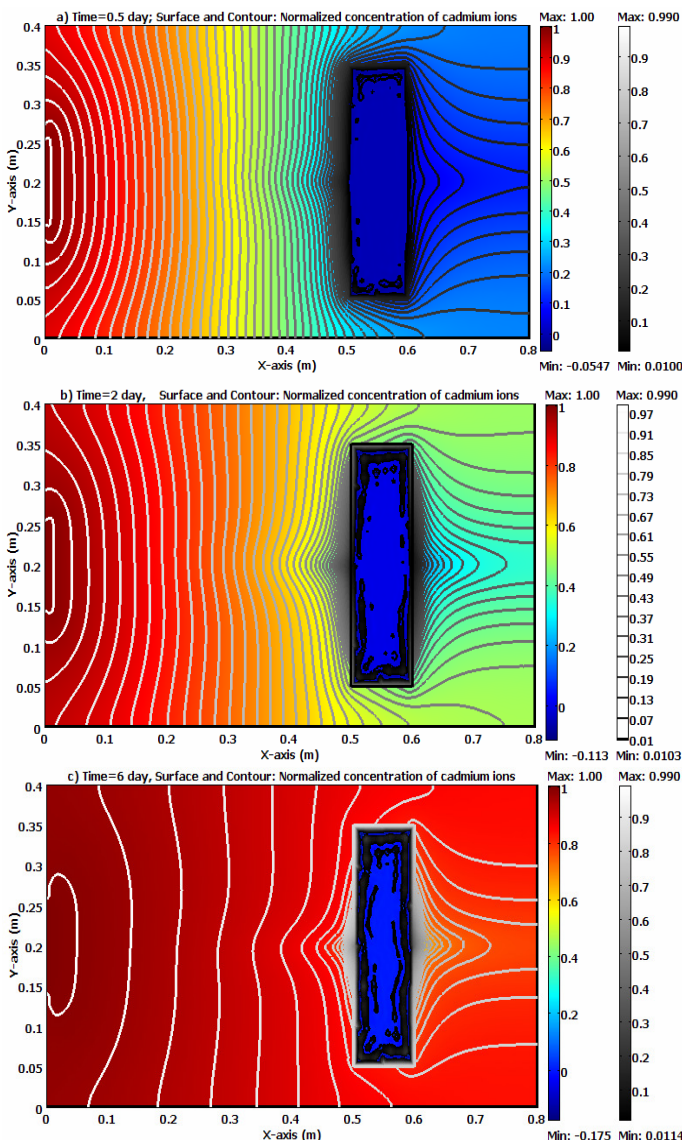

Fig. 6 : Predictions of COMSOL for cadmium normalized concentrations in the selected points for sand aquifer with presence of CKD barrier.

Fig. 7 : Velocity field and hydraulic head distribution across the bed model as calculated from COMSOL software for steady state.

Fig. 8 : Contours of cadmium normalized concentration across the 2D bed model as calculated by the COMSOL software for (a) 0.5, (b) 2 and (c) 6 day.

Conclusions

- For restriction the migration of cadmium ions towards the water resources, the results proved that the cement kiln dust byproduct can be used in the low permeable barrier technique.

- The conditions of time=1 hr, dosage=0.7 g/100 mL, and speed=250 rpm for initial concentration of 50 mg/L are suitable to achieve the maximum removal efficiency of 97.6%.

- Results revealed that the average hydraulic conductivity of CKD was equal to 9.7×10^{-15} m/s which is achieved the requirements of low permeable barrier.

- The maximum sorption capacity of CKD was equal to 84.1 mg/g as calculated from Langmuir model. This model in combination with mathematical model was able to represent the migration of cadmium ions for hypothetical problem. The groundwater flow equation and advection-dispersion-sorption equation solved by applying COMSOL Multiphysics 3.5a (2008) software.

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