

PERFORMANCE PREDICTION OF A PERMEABLE REACTIVE BARRIER FOR REMEDIATION OF GROUNDWATER CONTAMINATED WITH ZINC

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Abstract : Discharge of waste water from the industries has resulted in contaminated groundwater. Heavy metals have been found in contaminated groundwater in the Industrial estate areas. Treatment of the heavy-metal contaminated groundwater using pump-and-treat technique is costly. Alternatively, a permeable reactive barrier (PRB) can be used. An objective of this study is to study the performance of the PRB for remediation of zinc-contaminated groundwater using groundwater flow and contaminant transport modeling. In this study, the adsorption of zinc ions was simulated based on adsorption parameters obtained from batch adsorption tests. Three simulation cases were conducted to evaluate the performance of the PRB: effect of reactive media, effect of PRB thickness and effect of velocity of groundwater flow. Simulation results show that, for zinc-contaminated groundwater having initial concentration of 100 mg/L, all reactive media; namely, iron filling, activated sludge and mixture of iron filling and activated sludge, showed good treating performance since the zinc concentrations of treated groundwater were lower than that of groundwater standard. The velocity of groundwater flow didn't significantly affect the performance of the PRB. Thicker PRB showed better performance than the thinner ones.

Keywords : Permeable Reactive Barrier, Zinc Contamination, Groundwater Remediation, Iron Filling, Activated Sludge

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1. INTRODUCTION

Discharge of waste water from the industries and leachate from landfills has resulted in contaminated groundwater which impact consumers and valuable groundwater resources. Currently, heavy metals have been found in contaminated groundwater in the Industrial estate areas around Thailand. The heavy-metal contaminated groundwater can be treated by pump-and-treat technique, but it is costly. Alternatively, a permeable reactive barrier (PRB) can be used. Permeable reactive barrier or PRB is one of many techniques that are preferred for treatment of contaminated groundwater in the USA, Canada and Europe because PRB is effective with many kind of contaminant [1].

Map Ta Put Eastern Industrial Estate is one of the biggest industrial estate in Thailand. There are many reports on groundwater contamination in Map Ta Put Eastern Industrial Estate. Wangkiat (2007) [2] studied water in shallow wells in Map Ta Put area. Results show that, heavy metal concentration of the groundwater samples were higher than groundwater standard including; iron, manganese, magnesium and zinc. The groundwater quality reported by Pollution control department (2008) [3] indicates that groundwater in Map Ta Put Eastern Industrial Estate was contaminated with zinc.

An objective of this study is to study the performance of the PRB for treatment of zinc-contaminated groundwater via groundwater flow and contaminant transport simulation using Visual MODFLOW software. The simulate results in term of concentration versus time were used for evaluating the adsorption performance of the PRB.

2. BACKGROUND

2.1 Permeable Reactive Barrier

Permeable reactive barrier (PRB) is one of the most famous alternative processes, among passive decontamination method. Typically PRB consist of a trench filled with reactive material placed in the path of a contaminant plume as show in Figure 1. As groundwater passes through the PRB, contaminants are removed by chemical and/or biological reaction and/or sorption to the PRB material. Regardless of the removal mechanism, PRB performance depends on the placement of the barrier to capture the targeted contaminant plume and residence time within the PRB to accomplish the remediation [4].

East Helena, Montana operated for more than 100 years as smelting operations at the site deposited lead, arsenic copper, zinc, cadmium, and 15 other hazardous into groundwater. A pilot-scale zero valent iron (ZVI) permeable reactive barrier was installed at the site to treat arsenic contaminated groundwater. Preliminary evaluation of system indicates that, arsenic concentration as high as 20 mg/L are reduced to below 0.010 mg/L within the barrier [5].

Permeable reactive barrier was installed at the U.S Coast Guard Support Center in North Carolina, to treat groundwater contaminated with chromium and TCE discharging from an old chrome plating shop on the base. The initial maximum concentration entering PRB were more than 4,320 microgram per liter for TCE and over 3,430 microgram per liter for chromium ions, respectively. The complete removal of the chromium and reduction of TCE to below treatment goal; 0.05 mg/L for chromium ions and 5 ug/L for TCE [6].

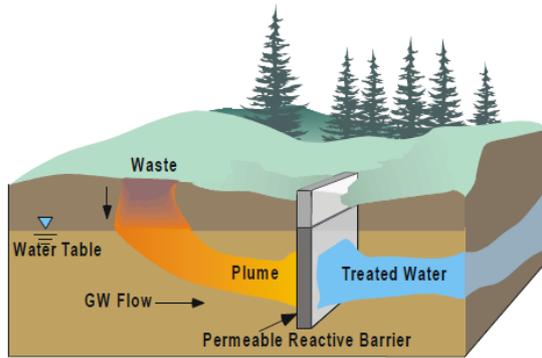


Figure. 1 Contaminated groundwater treated by PRB [7]

2.2 Reactive Media

There are many reactive media used for treating groundwater contaminated with heavy metal. Iron fillings or zero-valent iron was the first material used in PRB and it continues to be the main material used in the construction of PRB. There are many reports on high potential removal of various heavy metals by zero-valent iron [8]. However, the exact mechanism of degradation of contaminants in the presence of iron is not fully understood. The degradation mechanism comprises of heterogeneous reactions. The reactions occur when the reactant molecules reach the iron solid surface and then associate with the surface at sites that may be either reactive or non-reactive. For removal of heavy metals the degradation mechanisms were reported to be transformation from toxic to non-toxic forms or adsorption on the iron surface depending on the type of heavy metals [9].

2.3 Biomass as reactive media

An innovative multibarrier concept was recently introduced. Biomaterial or biomass, such as activated sludge was put into the ground to stimulate the growth of microbes that facilitate groundwater remediation. Interactions between metals and biomass lead to the binding of both depending on the functional groups contained in the cell walls or

the biopolymers of dead microorganisms. Many variables, such as pH, redox potential, metal concentration, presence of certain anions of complexing character or not, ionic strength, etc., play an important role in the process [10].

3. METHODOLOGY

In this study, the remediation of groundwater contaminated with zinc ions on PRB was simulated by Visual MODFLOW based on adsorption parameters obtained from batch adsorption study Yaead et al. (2008) [11]. Three adsorbent materials: iron fillings, activated sludge and mixture of iron fillings and activated sludge were used as PRB media to simulate the performance of the PRBs.

Three simulation cases were conducted to evaluate the absorption performance of the PRB: 1) effect of reactive media, 2) effect of PRB thickness and 3) effect of velocity of groundwater flow. Effect of PRB thickness was simulated by varying the thickness from 0.2 to 1.0 meter. Effect velocity of groundwater flow was achieved by varying up-gradient groundwater head.

In modeling, Visual MODFLOW software equipped with MODFLOW and MT3DMS was used for simulation of groundwater flow and mass transport.

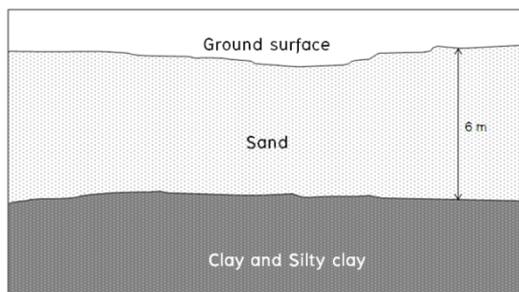
4. SITE DESCRIPTION

An unconfined aquifer located at Map Ta Put Eastern Industrial Estate was used for assessing the performance of the PRB on treating zinc-contaminated groundwater. Location of the site is shown in Figure 2a. The unconfined aquifer of the site consists mainly of sand with 6 meters in depth. Clay and silty clay layer is an aquitard underneath the aquifer as shown in Figure 2b [12]. Zinc was assumed to be the main contaminant in the local

groundwater. Contaminated groundwater was assumed to have concentration of 100 mg/L.



(a)



(b)

Figure 2. Study area of Map Ta Put, Rayong; (a) Site map, (b) Soil profile

5. REACTIVE MEDIA PROPERTIES

Yaeed et al. (2008) [11] studied a performance of six reactive media: iron filing; laterite; activated sludge; 50:50 w/w iron filing and activated sludge; 50:50 w/w laterite and activated sludge; and 33:33:34 w/w/w iron filing, activated sludge and laterite for removal of zinc and lead ions from aqueous solutions by batch experiments. The result indicated that 50:50 iron filing and activated sludge gave the greatest removal of 5,263 mg zinc/g media and 7,692 mg lead/g media by Langmuir isotherm fixation.

The Langmuir isotherm relates the adsorption of molecules on a solid surface to concentration of a medium above the solid surface at a fixed

temperature. The Langmuir equation is presented in Equation 1.

$$\frac{C_e}{q} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (1)$$

where q_m is the amount of adsorbate adsorbed at equilibrium (mg/g), K_L is the Langmuir adsorption equilibrium constant (L/mg), q is mass sorbed per mass of adsorbent, C_e is equilibrium concentration.

In this study, three adsorbent materials: iron filings, activated sludge and mixture of iron filings and activated sludge were used as PRB media. The properties of adsorbent materials such as hydraulic conductivity (K), Langmuir isotherm constants (K_L) and maximum sorption capacity (C_e) were tabulated in Table 1.

Table 1. The properties of adsorbent materials [11]

Parameter	Iron filing	Activated sludge	Mixture*
Conductivity (m/s)	0.821	1.050	0.934
K_L (L/g)	0.66	0.81	0.44
C_e (mg/g)	3.26	3.52	3.34

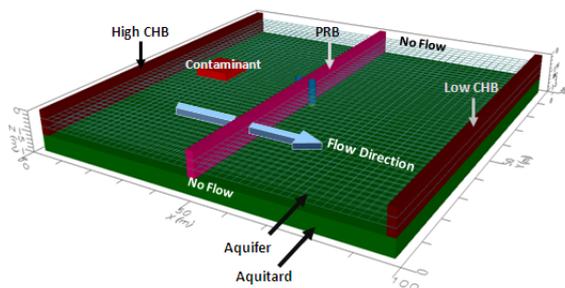
* Mixture of iron filings and activated sludge 50:50 w/w

6. GROUNDWATER FLOW AND MASS TRANSPORT MODELING

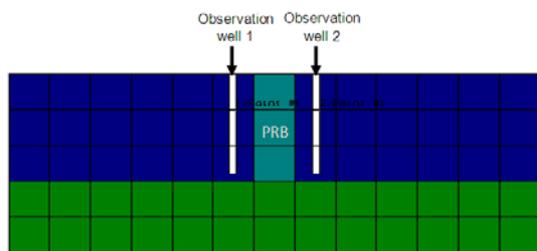
A groundwater flow and mass transport model of an unconfined aquifer with a PRB installed is shown in Figure 3a. The model was 100 m long, 100 m wide and 10 m deep. As mentioned previously, the thicknesses of aquifer and aquitard were 6 and 4 m, respectively. The PRB thickness varied from 0.2 to 1.0 m. The grid size varied from 0.1 to 5 m for x- and y- directions, whereas grid size in z-direction was 2 m. Boundary conditions of model were no

flow and constant head (CHB) for the direction parallel and perpendicular to the flow direction, respectively. High (up-gradient) and low (down-gradient) constant head boundaries were used to initiate flow. Up-gradient constant head boundary was varied from 1 to 6 m; whereas, down-gradient constant head boundary was fixed at 0.00 m for all simulations.

A zinc-contaminated source was modeled using a contaminated area on the top layer with the size of 10-m long and 10-m wide as shown in Figure 3a. It was located on the up-gradient side with distance of 20 m away from the PRB. Two observation wells located adjacent to the PRB were used to monitor zinc concentration transported into and out off the PRB (Figure 3b).



(a)



(b)

Figure 3. A Groundwater simulation model; (a) A groundwater flow and contaminant transport model
 (b) location of observation wells

7. RESULTS AND DISCUSSIONS

7.1 Effect of Reactive Media

To determine the effect of types of reactive media on zinc treatment performance of the 0.5-m thick PRB, the constant head boundary of was set as 5 m on the up-gradient side. Simulation results in term of relationships between concentrations of zinc of the treated groundwater observed via monitoring well 2 with time are shown in Figure 4. Note that standard zinc concentration in groundwater is 5 mg/L. The simulation results show that, all reactive media used show good performance on treating zinc-contaminated groundwater. Zinc concentrations of the treated groundwater were lower than 0.22 mg/L comparing to initial concentration of 100 mg/L. The types of reactive media used indicate the insignificant difference of zinc-treating performance of the PRB. Similar performance of all reactive media was due to their similar adsorption parameters as shown in Table 1. Additionally, time required for all reactive media to treat zinc using the PRB was approximately 322 days.

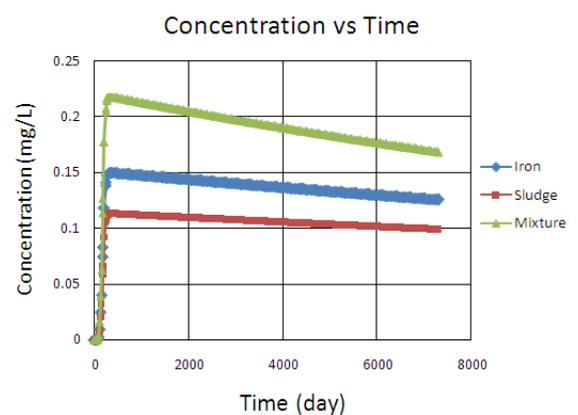


Figure 4. Calculated zinc concentration in monitoring well 2 after treating by PRB. Note that the initial concentration of zinc was 100 mg/L.

7.2 Effect of Groundwater Flow Velocity

To study the effect of groundwater flow velocity on PRB performance, the up-gradient constant heads used were 1, 2, 3, 4, 5, and 6 m which corresponded to groundwater velocity of $9.39e-3$, $1.88e-2$, $2.82e-2$, $3.76e-2$, $4.70e-2$, $5.63e-2$ m/d, respectively. Because of the fact that all three reactive media used do yield fairly the same PRB performance as mentioned previously, thus, iron filling was used in this set of simulations for demonstration purpose. Simulation results in term of relationships between concentrations of zinc in the observation well 2 and time are shown Figure 5. It can be seen that groundwater flow velocity does not affect the adsorption performance of PRB, since, for every flow velocity used the zinc concentration was reduced from 100 mg/L to 0.15 mg/L. On the other hand, zinc treating time is affected by the groundwater flow velocity because zinc was transported faster from the source to the PRB with greater groundwater flow velocity. As shown in Figure 5, time required for transport and treatment processes as observed in observation well 2 for hydraulic head of 1, 2, 3, 4, 5, and 6 m are 1647, 845, 573, 429, 322, and 284 days, respectively.

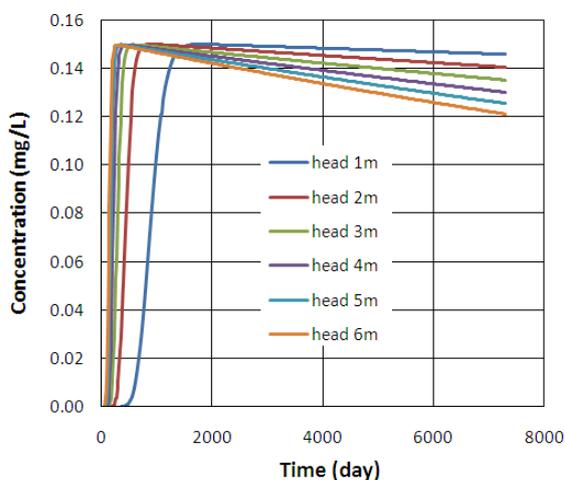


Figure 5. Relationships between zinc concentration and time in observation well 2.

7.3 Effect of PRB Thickness

Effect of PRB thickness on zinc treatment is illustrated in Figure 6. The PRB thickness varied from 0.2 to 1.0 m. Generally, for all thickness values used, the PRB can treated zinc contamination fairly well since it can reduced zinc concentration from 100 mg/L to the values not greater than 0.4 mg/L. However, considering each thickness, the simulation results indicate that, thicker PRB is showing better zinc treatment than the thinner ones (Figure 6). The thicker PRB provides better zinc treatment performance because the zinc solution is having greater retention time that allows better adsorption process in the PRB.

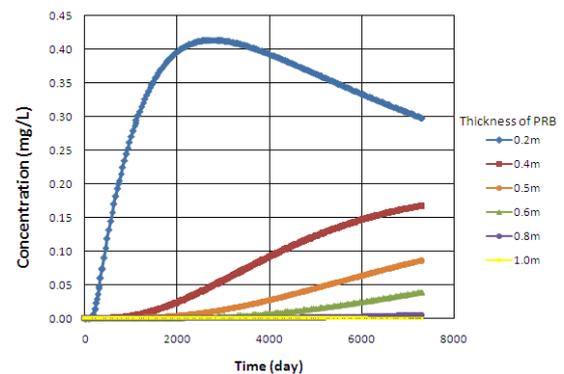


Figure 6. Concentration versus time of various PRB thickness.

8. CONCLUSION

Performance of remediating zinc-contaminated groundwater in Map Ta Put unconfined aquifer using Permeable Reactive Barrier (PRB) was assessed by mathematical modeling of groundwater flow and contaminant transport. Effects of reactive media, groundwater flow velocity, and PRB thickness on PRB performance were studied. The following conclusion can be drawn.

1. Three reactive media used were iron filling, activated sludge, and mixture of iron filling and activated sludge. In general, all reactive media showed good and fairly similar results of zinc remediation of the contaminated groundwater. The concentrations of zinc in treated groundwater were lower than standard groundwater concentration of 5 mg/L.

2. Groundwater flow velocity is found to have no effect on the adsorption performance of PRB, but it does have affect on treating time because zinc is transported faster from its source to the PRB with greater groundwater flow velocity.

3. Generally, for PRB thickness ranged from 0.2 to 1.0 m, the PRB can treated zinc-contaminated groundwater fairly well with zinc concentration reduction of more than 99%. In additions, the simulation results indicate that, thicker PRB is showing better zinc treatment than the thinner ones

9. ACKNOWLEDGEMENT

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