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Original Article

Performance of iron filings and activated sludge as media for permeable reactive barriers to treat zinc contaminated groundwater

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Abstract

Zinc is one of the important contaminants in groundwater. Removal of zinc by iron filings, activated sludge and lateritic soil was studied with batch test. The lowest optimum pH for removal of zinc by iron filings, activated sludge and lateritic soil was 6. From isotherm studies iron filings and activated sludge were chosen as media for permeable reactive barrier (PRB). The PRB of 0.5-m thick was simulated in the unconfined aquifer with the distance of 21.5 m downgradient of the zinc contaminated site having constant concentration of 100 mg/l. The groundwater flow in the site was induced by the hydraulic gradient of 0.02. Simulation results indicated that the concentration of zinc of treated groundwater was less than 5 mg/l, which met Thai Groundwater Quality Standard for Drinking Purposes. The continuous PRBs using iron filings and activated sludge could treat zinc for 2,170 and 2,248 days, respectively.

Keywords: permeable reactive barrier, zinc, iron filings, activated sludge, lateritic soil

1. Introduction

Map Ta Put Eastern Industrial Estate (MTPIE) is one of the biggest industrial estates in Thailand. A study on 80 samples of rainwater and shallow well water from Map Ta Put area, during 2006-2007, found varying levels of heavy metal contamination (Saetang, 2010). An analysis of 77 water samples from shallow well ponds and artesian wells from 25 communities in Map Ta Put, with sampling during November 26-27, 2005, and during February 4-5, 2006, shows concentrations of heavy metals higher than groundwater standard levels for cadmium, iron, manganese, lead, and zinc (Thai Health Promotion Foundation, 2008). Zinc is one of the most important pollutants for surface and ground water because of its acute toxicity (Coruh, 2008).

Heavy metal contaminated groundwater can be conventionally treated by a pump-and-treat technique, but this would be costly compared to a permeable reactive barrier (PRB). USEPA (1989) defined PRB as '*an emplacement of reactive media in the sub-surface designed to intercept a contaminated plume, provide a flow path through the reactive media and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier*'. A PRB applies the natural hydraulic gradient of the groundwater plume to move the contaminants through the reactive permeable wall. It acts on the contaminants by adsorption, microbial fixation, and electrokinetic remediation (Hashim *et al.*, 2011). The advantages over traditional pump-and-treat technology include cost effectiveness and low maintenance in the long term (Phillips, 2009). Therefore, PRB has been considered as the most practical all-round solution for remediation of contaminated groundwater.

Many materials, including zero valent iron (ZVI), zeo-

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lite, peat moss, granular activated carbon, and lime mud (Wirojanagud *et al.*, 2004) have been successful individually or in combinations, in the remediation of heavy metal contaminated groundwater. ZVI, typically in the form of scrap iron filings, is the most commonly used reactive material in PRBs. The removal of heavy metals by ZVI is based on transformation from toxic to non-toxic forms, precipitation (Naftz *et al.*, 2002), adsorption, and surface complexation (Junyapoon, 2005). It is difficult to indicate a dominant mechanism even at a specific remediation site, given the multiple reaction pathways. Variations in the physical and chemical characteristics of ZVI affect the complicated redox chemistry of the solution. Alternatively, the removal of heavy metals (Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+}) is possible with activated sludge based on sorption (Hammaini *et al.*, 2007). Biosorption of heavy metals on particle surfaces in activated sludge depends on the complexes formed by the heavy metal with functional groups such as carboxyl, hydroxyl, and phenolic groups in extracellular polymeric substances (Yuncu *et al.*, 2006). It has been suggested that the mechanism of sorption is based on exchange reactions, complexation with negatively charged groups, adsorption, and precipitation (Ong *et al.*, 2010). Lateritic soils (red soils) are common in areas with a hot and humid climate, and are rich in iron and aluminum (Townsend, 1985). Both ligand and ion exchanges may be the mechanisms with which lateritic soil treats arsenic (Nemade *et al.*, 2009).

To design a PRB, batch experiments can be used to select the best performing reactive materials, and column tests to model an in situ PRB (Carey *et al.*, 2002). Alternatively, a three-dimensional groundwater model using Modflow can be used to evaluate the effectiveness of PRB. This study had three parts. The first was to investigate physical and chemical properties of the three reactive materials, namely iron filings, activated sludge, and lateritic soil. Batch experiments were carried out in the second part to study the removal of zinc from an aqueous solution and the effects of contact time and initial solution pH on it. Finally, the parameters obtained from isotherm studies in the batch experiments were used in a three-dimensional groundwater simulation model, to predict PRB performance.

2. Materials and Methods

2.1 Metal solutions and chemicals

A stock solution was prepared by dissolving 1.00 g/l of zinc chloride ($ZnCl_2$) in deionized water (DI-water). Then test solutions were prepared by further dilution to desired concentration. All pH adjustments were by nitric acid (HNO_3) or sodium hydroxide (NaOH).

2.2 Reactive materials

The three reactive materials were iron filings, activated sludge and lateritic soil. Iron filings were obtained from Five Tigers Engineering Co., Ltd., which is an automotive and industrial workshop in Hat Yai, Thailand. The activated sludge was from the wastewater treatment plant of Nissui (Thailand) Co., Ltd., a company producing and exporting frozen salmon. Lateritic soil was collected from depths between 50 and 100 mm below the ground surface, from KhoHong, Hat Yai. All materials were dried at 60°C in an oven for 72 hours. Then they were crushed and sieved to retain sizes of 1.00-1.76 mm, and stored in a desiccator at about 30°C room temperature. The specific surface areas were evaluated by a Brunauer–Emmett–Teller (BET) surface area analyzer (Quantachrome Autosorb-1, U.S.A.). The morphology and surface characteristics were investigated using a scanning electron microscope (SEM, JEOL JSM-5800LV, Japan), and the chemical elemental compositions were determined with energy dispersive X-Ray (EDX) spectrometer (Oxford Instruments, UK). Cation exchange capacities (CEC) were determined by the Na-method (Chapman, 1965).

2.3 Batch experiments

To study the effects of contact time on the zinc removal efficiency, the solution was adjusted to have pH=6. The effects of pH were separately determined in the range from 4 to 10. The reactive media were added to centrifuge tubes containing 50 ml of zinc solution, and the tubes were shaken continuously at 170 rpm and at controlled 30°C temperature. For determine isotherms 10–100 mg/l zinc solutions were treated with a reactive medium dosage of 8 g/l at solution pH 6 (operating parameters were from pre-tests). The pH of the solution was adjusted to each desired value with HNO_3 or NaOH. Samples after treatment were filtered through a syringe filter. The cake was washed with DI water and the filtrates were analyzed for remaining zinc ions in the solution. Ion concentrations were determined by atomic absorption spectrophotometer (AAS, Perkin Elmer, AAanalyst 100). Each determination was repeated three times and the results given are averages. The removal efficiency, % Removal, was calculated as:

$$\%\,\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of zinc ions in the solution.

2.4 Site description and groundwater model set up

A sandy unconfined aquifer of the MTPIE is 6 m thick and underlain by an aquitard, which consists mainly of clay and silty clay. A three dimensional groundwater model for this aquifer was set up using Visual Modflow software. The length and width of the simulation PRBs were 100 m with two layers. The top layer was 6 m aquifer of sandy soil with hydraulic conductivity of $1\text{x}10^{-3}$ cm/s. The bottom layer was the aquitard with hydraulic conductivity of $1\text{x}10^{-7}$ cm/s. Hydraulic conductivity values applied in this study were

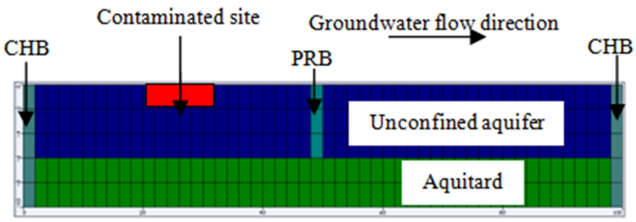


Figure 1. Aquifer system and contaminated site.

covered the values observed in MTPIE (Malem *et al.*, 2012). Grid sizes used in the model varied from 0.05 to 5 m for x- and y- direction whereas grid size of 2 m was used for z-direction. Groundwater flow from upgradient on the left (North) to down gradient on the right (South) of the model (shown in Figure 1) was simulated using two different constant head boundaries (CHB). Head on the left was 2.0 m and head on the right was 0 m, equivalent to a hydraulic gradient of 0.02 calculated using Equation 2.

$$i = \frac{\Delta h}{L} = \frac{(2-0)\,m}{100\,m} = 0.02 \qquad (2)$$

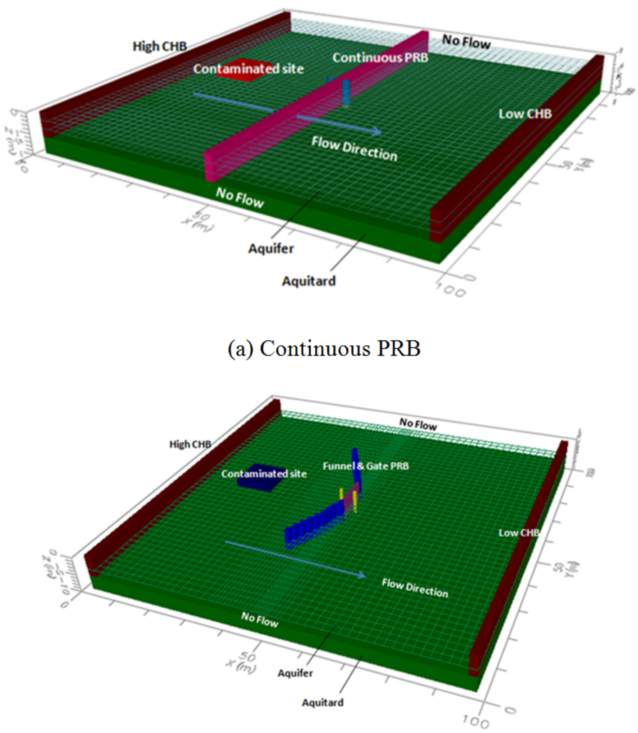
where i is hydraulic gradient, Dh is hydraulic head difference, and L is horizontal distance between two different constant head boundaries. Zinc contaminated ground water was simulated at a constant 100 ppm concentration. The concentrations were logged during simulation at “monitoring wells” that were placed in front of, within, and behind the PRB at 5 cm spacing.

There are two main types of PRB, namely “continuous” and “funnel and gate” types (Figure 2). The funnel and gate PRB applies impermeable walls (sheet pilings, slurry walls, etc.) as a “funnel” to direct the contaminant plume to a “gate(s)” containing the reactive media, whereas the continuous PRB completely transects the plume flow path with reactive materials (USEPA, 1998). In our continuous PRB the reactive medium was placed in the middle of the simulated volume, as a barrier with 0.5 m thickness in the flow direction. For our funnel and gate type PRB, the gate part was 10 m long while each funnel was 20 m long. From constant head permeability test (ASTM D2434-28, 2006) the hydraulic conductivities of the reactive materials in the PRBs were 0.1 cm/s. In the field the hydraulic conductivities may be modified with other materials. However, these values are still much higher than hydraulic conductivity of sand, which is 10^{-3} cm/s. The hydraulic conductivity of the impervious zone or the funnel parts was set at 1×10^{-6} cm/s.

3. Results and Discussion

3.1 Characterization of reactive materials

Physical properties and chemical compositions as lists of main elements, of the reactive materials, are shown in Table 1. According to the criteria for selection of materials for the permeable reactive barrier (United States Environmental Protection Agency, 1998) it is important that the reactive material is not a source of contamination itself. Zinc was not found in any of the investigated materials. EDX spectrometer analysis indicated that the iron filings had iron, carbon, silica, and manganese. The lateritic soil contained iron, silica and



(b) Funnel and gate PRB

Figure 2. Simulation of two types of PRBs (a) continuous PRB and (b) funnel and gate PRB.

Table 1. Properties of reactive materials.

Adsorbent material	BET surface area (m^2/g)	Chemical elements	Cation exchange capacity, CEC (meq/100 g)
Iron filings	13.73	C, Si, Mn, Fe	343
Activated sludge	2.11	C, O, Na, Al, Si, P, S, Cl, K, Ca, Fe	1,645
Lateritic soil	3.67	O, Al, Si, K, Ti, Fe	415

aluminum with other elements. The activated sludge consisted of iron, carbon, silica, aluminum, and other elements, with more elements than in the lateritic soil and the iron filings. Therefore, the activated sludge might act with the most complex mechanisms. Iron, silica, aluminum, manganese and copper are elements commonly found in the materials used for remediation of heavy metals (Benaïssa *et al.*, 2011).

The BET surface area of iron filings was 13.73 m^2/g, which was larger than those observed for activated sludge (2.11 m^2/g) or lateritic soil (3.67 m^2/g). The specific surface is an important factor affecting adsorption efficiency with high specific surface giving an advantage.The surface morphology and fundamental physical properties of the reactive materials were assessed by SEM imaging. The SEM pictures of iron filings, activated sludge and lateritic soil, both before and after treatment, are shown in Figure 3. It can be seen from Figure 3(a)-(c) that the pore sizes in all materials are very small (<1 µm). It is reported that fine nano-sized zero valent iron (NZVI) particles are much more reactive than granular ZVI, and have the potential to quickly remove high concentrations of chlorinated volatile organic compounds. In addition, fine particles are easier to inject into soil than coarse particles, so a small particle size of NZVI helps its delivery (Gavaskar *et al.*, 2005). Lateritic soil was more porous than iron filings or activated sludge. The adsorbed Zn(II) ions were either engulfed or coated on the surfaces of the reactive materials, as seen in Figure 3(d)-(f).

The activated sludge had the highest capacity to exchange cations (1,645 meq/100 g), followed by the lateritic soil (415 meq/100 g), and the iron filings (343 meq/100 g). Clinoptilolite has an excellent cation exchange capacity (150 meq/100 g) and has been studied in laboratory scale for PRB treatment of groundwater contaminated by ammonium, lead, and copper (Park *et al.*, 2002). All the materials in this study have a higher cation exchange capacity than clinoptilolite. The zinc removal ability of each material will be discussed in the following sections.

3.2 Effects of contact time

Figure 4 shows the effects of contact time on the removal of zinc. The removal efficiencies increased with time, and an initial rapid removal was due to the presence of a large number of vacant sites in the materials. As time proceeds, the removal rate was reduced due to the accumulation of zinc in the vacant sites. The iron filings were the most effective material with a 100% removal reached in 12 hours. The effectiveness of activated sludge was closely similar to lateritic soil, with equilibrium reached in about 16 hours. This is because the iron filings had the largest surface area and adsorption kinetics dominated the initial removal rates. All three materials had reached equilibrium at 16 hours, so that no further removal of zinc took place. The equilibration time depends on both adsorption capacity and initial metal concentration. To ensure that equilibrium was reached, the batch experiments were continued up to 24 hours.

3.3 Effects of initial solution pH

One of the most important factors affecting the removal of metal ions is the pH of the solution. Zinc in an aqueous solution can form various ionic species depending on the solution pH. The predominant ionic species is Zn^{2+} for pH < 7, and zinc is present mainly as Zn^{2+} and $Zn(OH)_2$, and in lesser quantities as $Zn(OH)^+$ for pH between 8 and 9 (Leyva Ramos *et al.*, 2002). In addition, the pH can modify the surface charge of the sorbent, thereby enhancing or decreasing the quantity of metal sorption (Sandesh *et al.*, 2013). At pH < 6, the removal of zinc was low for all three materials (Figure 5). This is because at pH < 6, the H_3O^+ ions

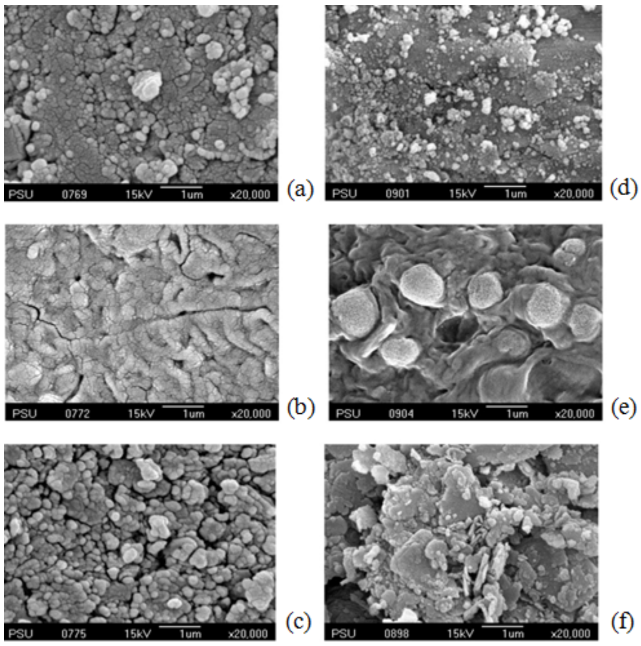


Figure 3. SEM photographs (a) iron filings before treatment (b) activated sludge before treatment (c) lateritic soil before treatment (d) iron filings after treatment (e) activated sludge after treatment and (f) lateritic soil after treatment.

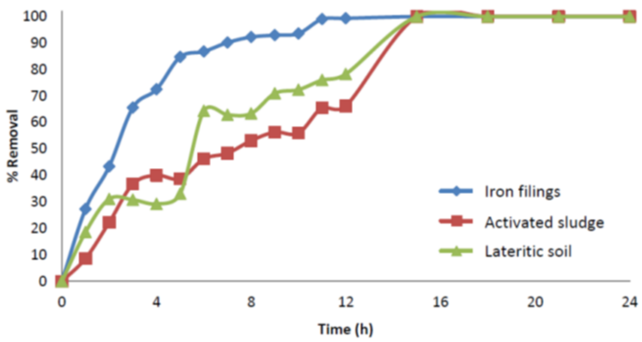


Figure 4. Effect of contact time on removal efficiency (initial concentration of Zn(II) 50 mg/l, material dosage 8 g/l and initial solution pH 6).

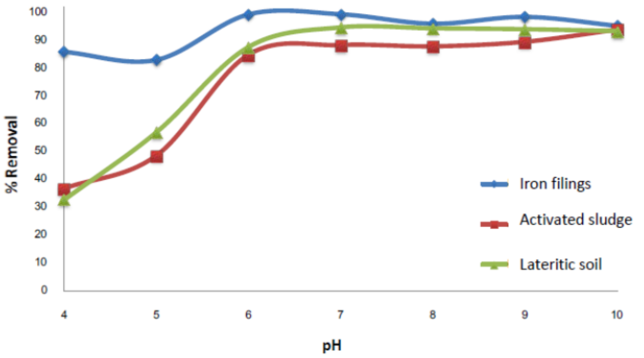


Figure 5. Effect of initial solution pH on removal efficiency (initial concentration of Zn(II) 50 mg/l, material dosage 8 g/l and contact time 24 hrs).

compete with the Zn^{2+} for the exchange sites in the adsorbent. Similar results hold for the removal of zinc by peanut hulls (Oliveira *et al.*, 2010). The removal efficiency of iron filings was less affected by the pH than those of activated sludge or lateritic soil. ZVI has been found effective for removal heavy metals at a low pH, for example in groundwater impacted by acid mine drainage (Wilkin and McNeil, 2003). In the case of activated sludge, the interaction between sorbate and biosorbent is affected by the solution pH in two ways. Firstly, the metal ions can have various speciation forms depending on the pH, and secondly, the surface of the biosorbent consists of biopolymers with many functional groups, so the net charge on biosorbent is also pH dependent. In addition, at a low pH, the surface charge of the biosorbent is positive, which is not good for sorption of cations. Concurrently, the hydrogen ions compete strongly with metal ions for the active sites, resulting in less biosorption (Benaïssa *et al.*, 2011). When the pH was increased from 4 to 6 in the current experiments, electrostatic repulsions between zinc ions and surface sites of activated sludge as well as the competition by hydrogen ions decreased, so that the biosorption increased.

3.4 Adsorption kinetics

The kinetic data of zinc treatment by the three candidate materials under various experimental conditions were analyzed by two common equations, the pseudo first order model (Lagergren, 1898) and the pseudo second order model (Ho and Mckay, 1999). These are shown as Equation 3 and 4.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{t}{q_e} \tag{4}$$

where q_e and q_t are the amounts of zinc removal (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the pseudo first-order rate constant of sorption (min^{-1}) while k_2 is the pseudo second-order rate constant of sorption (g/mg-min). The pseudo first order and second order parameters fit to experimental data are given in Table 2.

The pseudo first order model describes adsorption in a solid-liquid system based on the sorption capacity of solid (Ho, 2004). It is assumed that each sorption site on the solid surface can bind exactly one zinc ion. The pseudo second order model fit well the sorption of zinc by iron filings, as well as by activated sludge. The pseudo second order model describes chemisorption involving valency forces through the sharing or exchange of electrons as covalent forces and ion exchange (Ho, 2006). The rate limiting step in this adsorption could be ascribed to chemical interactions. It is assumed that one zinc ion is sorbed onto two sorption sites on the solid surface. Both pseudo first order and pseudo second order models fit well the sorption of zinc by lateritic soil.

3.5 Adsorption isotherms

The effects of initial zinc concentration in the range

Table 2. Pseudo first order and pseudo second order kinetic parameters.

Adsorbents	Pseudo first order parameters			
	R^2	k_1 (min^{-1})	q_e exp (mg/g)	q_e cal (mg/g)
Iron filings	0.92	0.0062	6.25	6.37
Activated sludge	0.83	0.0014	6.25	5.78
Lateritic soil	0.94	0.0021	6.25	6.18
Adsorbents	**Pseudo second order parameters**			
	R^2	k_2 (g/mg-min)	q_e exp (mg/g)	q_e cal (mg/g)
Iron filings	0.99	0.0011	6.25	6.29
Activated sludge	0.96	0.0009	6.25	6.27
Lateritic soil	0.94	0.0001	6.25	6.63

10–100 mg/l were studied experimentally. The zinc removal efficiency decreased with initial concentration. The experimental data were then analyzed for adsorption isotherms. Among the various equations for adsorption isotherms, the most common are Langmuir, the theoretical equilibrium isotherm, and Freundlich, the empirical equilibrium isotherm. The Langmuir isotherm is derived assuming a saturated monolayer of solute molecules on the adsorbent surface at maximum adsorption, constant adsorption energy, and no transmigration of the adsorbate along the surface. The linear form of a Langmuir isotherm is (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad (5)$$

where q_e is the amount of zinc sorbed at equilibrium per g of sorbent (mg/g), q_m is the maximal metal sorption capacity of sorbent material (mg/g), C_e is the equilibrium zinc concentration in the solution (mg/l) and K_L is the Langmuir constant of equilibrium (l/mg). The Freundlich isotherm is an empirical equation successfully used with heterogenous systems. The linear form of Freundlich isotherm is (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_F is the Freundlich constant of equilibrium and n is a constant.

The adsorption isotherms for zinc removal by the three materials are parametrically summarized in Table 3. Both isotherms fit well the experimental data with R^2 values better than 0.8. The lateritic soil removed the least zinc from an aqueous solution. Therefore, only iron filings and activated sludge were chosen as the reactive materials, for the PRB simulations with Modflow software.

3.6 PRB simulations

The simulations show the transport of zinc by advection and diffusion, with dispersion in the porous medium, from high hydraulic head and high concentration on the left-hand side to lower respective values on the right-hand side. Zinc contaminated groundwater is transported from the contaminated site to the PRB within 275 days. Both continuous and funnel and gate PRBs can be used to successfully treat zinc contaminated groundwater and the outflow concentration exceeded the limit of Thai Groundwater Quality Standard for Drinking Purposes (zinc concentration <5 mg/l). Performance characteristics of the PRBs with iron filings and activated sludge are summarized in Table 4. For both PRB types and both reactive materials simulated, the 0.5 m thickness was adequate for reducing the zinc concentration from 100 mg/l to less than 5 mg/l, in contaminated groundwater

Table 3. Adsorption isotherms parametrically.

Reactive materials	Langmuir			Freundlich		
	K_L (l/g)	q_m (mg/g)	R^2	K_F	n	R^2
Iron filings	0.66	3.26	0.90	1.16	2.03	0.94
Activated sludge	0.81	3.52	0.96	1.45	1.72	0.96
Lateritic soil	0.11	2.42	0.82	1.04	0.08	0.93

Table 4. Comparison of the maximum zinc adsorption capacities from the current study with literature curated values.

Materials	Maximum adsorption Capacity (mg/g)	Reference
Formaldehyde modified bean husk	2.18	Adediran *et al.*, 2007
Pyridine modified bean husk	2.48	Adediran *et al.*, 2007
Kaolinite	4.95	Shahmohammadi-Kalalagh *et al.*, 2011
Bentonite	3.24	Tito *et al.*, 2008
Cork	3.4	Chubar *et al.*, 2004
Activated carbons derived from oil palm empty fruit bunches	1.63	Zahangir Alam *et al.*, 2008
Sawdust	2.58	Agoubordea and Navia, 2009
Waste-reclaimed adsorbent	0.60	Jo *et al.*, 2010
Streptomyces noursei	1.6	Green-Ruiz *et al.*, 2008
Brachystegia spiciformis leaf powder	1.85	Chigondo *et al.*, 2013
Iron filings	3.26	This study
Activated sludge	3.52	This study

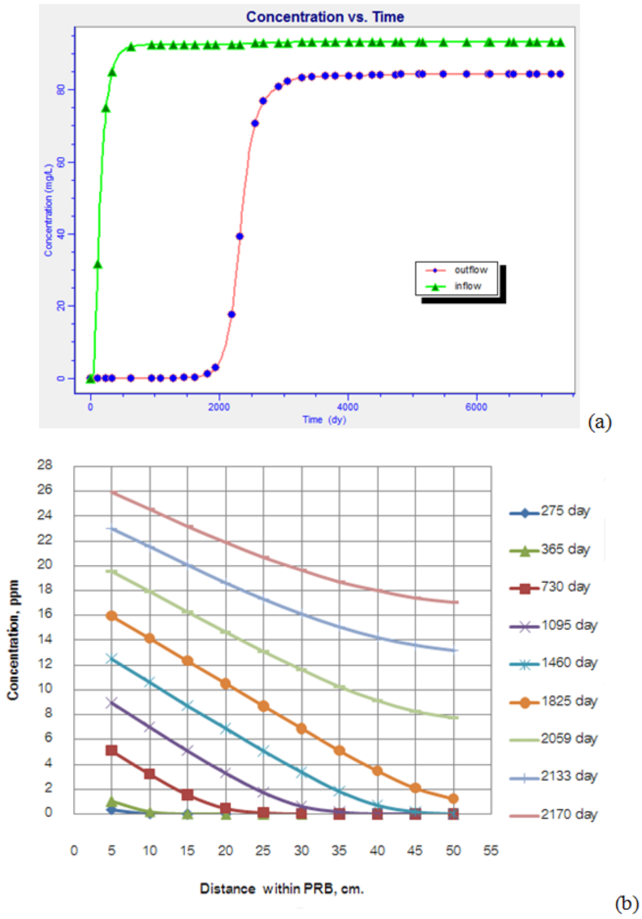


Figure 6. Zinc treated with continuous PRB (a) concentration and time using iron filings, (b) concentration and distance using iron filings, (c) concentration and time using activated sludge and (d) concentration and distance using activated sludge.

flow. For continuous PRBs, satisfactory operation ranged from 2,170 days (PRB using iron filings) to 2,248 days (PRB using activated sludge), whereas for funnel and gate PRBs, the maintenance free operation times ranged from 1,675 days (PRB using iron filing) to 1,803 days (PRB using activated sludge). The comparatively short operation times of the funnel and gate PRBs are reasonable, because the continuous PRBs use more of the reactive material. Better operation times of funnel and gate PRBs can be achieved by redesign the PRBs to have thicker barrier than 0.5 m but this would be beyond the scope of this paper. To the end, types of PRBs have chosen depending on suitable technical and economic issues. A funnel and gate configuration is preferred when the reactive material is expensive (Thiruvenkatachari *et al.*, 2008). A continuous wall is chosen because it minimizes the potential for bypass around (Vogan *et al.*, 1999).

The zinc absorption performance of the continuous PRB across its 0.5 m thickness is depicted in Figure 6. The performance of PRBs using activated sludge was comparable to those using iron filings. The use of activated sludge appears promising for the treatment of zinc contaminated groundwater. While PRBs composed of zero valent iron have been applied widely, activated sludge is less mature in these applications and information on it is still very limited according to more complex mechanism might be involved.

4. Conclusions

The three media differed in their characteristics in such manner that their ranking in zinc remediation could not be predicted from these basic facts. The iron filings had the greatest specific surface, the activated sludge had the highest cation exchange capacity and the lateritic soil was the most porous material. The lowest optimum pH for removal of zinc by the three materials was 6. From experimentally determined zinc adsorption isotherms, the iron filings and the activated sludge have a potential as a media for a permeable reactive barrier. In numerical simulations of groundwater flow at a specific application target, the continuous PRBs with iron filings or activated sludge could reduce zinc from 100 mg/l to less than 5 mg/l, for a duration of about 2,200 days. Activated sludge is considered as an efficient and promising PRB material for remediating zinc contaminated groundwater, with the specific advantage of comparatively low cost.

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Table 5. Performance summary of the simulated PRBs.

Type of PRB and reactive media	Heavy metal	Applicability of using 0.5-m thick PRB	Operation time (days)
Continuous PRB using iron filings	Zinc	Yes	2,170
Continuous PRB using activated sludge	Zinc	Yes	2,248
Funnel and gate PRB using iron filings	Zinc	Yes	1,675
Funnel and gate PRB using activated sludge	Zinc	Yes	1,803

References

ASTM D2434-28. 2006. Standard test method for permeability of granular soils (Constant head).

Benaïssa H. and Elouchdi M.A. 2011. Biosorption of copper (II) ions from synthetic aqueous solutions by drying bed activated sludge. Journal of Hazardous Materials. 194, 69–78.

Carey, M.A., Fretwell, B.A., Mosley N.G. and Smith, J.W.N. 2002. Guidance on the use of permeable reactive barriers for remediating contaminated groundwater. National Groundwater and Contaminated Land Centre Report NOC/01/51, Environment Agency, Solihull, UK.

Chapman, H.D. 1965. Cation exchange capacity. In Method of Soil Analysis, Black, J.A., editor. Vol. 9. American Society of Agronomy, Winconsin, U.S.A., pp 891–901.

Coruh, S. 2008. The removal of zinc ions by natural and conditioned clinoptilolites. Desalination. 225, 41-57.

Freundlich, H.M.F. 1906. Over the adsorption in solution, The Journal of Physical Chemistry. 57, 385–470.

Gavaskar, A., Tatar, L. and Condit, W. 2005. Cost and performance report nanoscale zero-valent iron technologies for source remediation. Contract Report CR-05-007-ENV.

Hammaini, A., Gonzalez, F., Ballester, A., Blazquez, M.L. and Munoz, J.A. 2007. Biosorption of heavy metals by activated sludge and their desorption characteristics. Journal of Environmental Management. 84, 419-426.

Hashim, M.A., Mukhopadhyay, S., Sahu, J.N. and Sengupta, B. 2011. Remediation technologies for heavy metal contaminated groundwater. Journal of Environmental Management. 92, 2355-2388.

Ho, Y.S. and Mckay, G. 1999. Pseudo-second order model for sorption processes. Process Biochemistry. 34, 451–465.

Ho, Y.S. 2004. Citation review of Lagergren kinetic rate equation on adsorption reactions. Scientometrics. 59, 171–177.

Ho, Y.S. 2006. Review of second-order models for adsorption systems. Journal of Hazardous Materials. B136, 681–689.

Junyapoon, S. 2005. Use of zero-valent iron for wastewater treatment. King Mongkut's Institute of Technology Ladkrabang, KMITL Science and Technology Journal. 5, 587-595.

Lagergren, S. 1898. Zur Theorie der sogenannten adsorption gelöster Stoffe, Kungliga Srenska Vetenskapsakademiens. Handlingar. 24, 1–39.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids, Journal of the American Chemical Society. 38, 2221–2295.

Leyva Ramos, S., Bernal Jacome, L.A., Mendoza Barron, J., Fuentes Rubio, L. and Guerrero Coronado, R.M. 2002. Adsorption of zinc(II) from aqueous solution onto activated carbon. Journal of Hazardous Materials. B90, 27-38.

Malem, F., Soonthorndecha, P. and Saenton, S. 2012. Assessing soil and groundwater contamination of volatile organic compounds in an industrial estate in eastern Thailand. Proceeding of The International Association of Hydrogeologists (IAH) Congress, Niagara Falls, Canada. September, 16-21, 2012.

Naftz, D.L., Morrison, S.J., Davis J.A. and Fuller, A.C. 2002. Handbook of Groundwater Remediation Using Permeable Reactive Barriers. Academic Press, California, U.S.A.

Nemade, P.D., Kadam, A.M. and Shankar, H.S. 2009. Adsorption of arsenic from aqueous solution on naturally available red soil. Journal of Environmental Biology. 30, 499-504.

Oliveira, F.D., Soares, A.C., Freitas, O.M. and Figueiredo, S.A. 2010. Copper, nickel and zinc removal by peanut hulls: Batch and column studies in mono, tri-component systems and with real effluent. Global Nest Journal. 12, 206-214.

Ong, S.A., Toorisaka, E., Hirata, M. and Hano, T. 2010. Adsorption and toxicity of heavy metals on activated sludge. ScienceAsia. 36, 204-209.

Park, J.B., Lee, S.H., Lee, J.W. and Lee, C.Y. 2002. Lab scale experiments for permeable reactive barriers against contaminated groundwater with ammonium and heavy metal using clinoptilolite (01-29B). Journal of Hazardous Materials. B95, 65-79.

Phillips, D.H. 2009. Permeable reactive barriers: A sustainable technology for cleaning contaminated groundwater in developing countries. Desalination. 251, 352-359.

Saetang, P. 2010. Ecological alert and recovery-Thailand (Earth), Mekong Watch Annual Meeting, Tokyo, Japan.

Sandesh, K., Suresh Kumar, R. and JagadeeshBabu, P.E. 2013. Rapid removal of cobalt (II) from aqueous solution using cuttlefish bones; equilibrium, kinetics, and thermodynamic study. Asia-Pacific Journal of Chemical Engineering. 8, 144–153.

Thai Health Promotion Foundation. 2008. Thai Health 2008: Global warming-A real threat from humans, Institute for Population and Social Research, Mahidol University, Thailand.

Thiruvenkatachari, R., Vigneswaran, S. and Naidu, R. 2008. Permeable reactive barrier for groundwater remediation. Journal of Industrial and Engineering Chemistry. 14, 145-156.

Tito, G.A., Chaves, L.H.G. and de Souza, R.S. 2008. Zinc adsorption in bentonite clay: particle size and pH influence. Revista Caatinga. 21, 1-4.

Townsend, F.C. 1985. Geotechnical characteristics of residual soils. Journal of the Geotechnical Engineering Division, ASCE 111, 77–94.

United States Environmental Protection Agency. Permeable reactive barrier, Technology for contaminant remediation, EPA/600/R-98/125 (1998) 8.

USEPA, 1989. Evaluation of Groundwater Extraction Remedies. EPA Office of Emergency and Remedial Responses, Washington, DC., U.S.A.

USEPA, 1998. Permeable Reactive Barrier Technologies for Contaminant Remediation, EPA 600/R-98/125, Washington, DC 20460, 94-95.

Vogan, J.L., Focht, R.M., Clark, D.K. and Graham, S.L. 1999. Performance evaluation of a permeable reactive barrier for remediation of dissolved chlorinated solvents in groundwater. Journal of Hazardous Materials. 68, 97–108.

Wilkin, R.T. and McNeil, M.S. 2003. Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage. Chemosphere. 53, 715-725.

Wirojanagud, W., Tantemsapya, N. and Tantriratna, P. 2004. Precipitation of heavy metals by lime mud waste of pulp and paper mill. Songklanakarin Journal of Science and Technology. 35, 563-568.

Yuncu, B., Sanin, D.F. and Yetis, U. 2006. An investigation of heavy metal biosorption in relation to C/N ratio of activated sludge. Journal of Hazardous Materials. 137, 990-997.

Zahangir Alam, Md., Muyibi, S.A. and Kamaldin, N. 2008. Production of activated carbon from oil palm empty fruit bunches for removal of zinc. In Proceedings of Twelfth International Water Technology Conference, IWTC12 2008 Alexandria, Egypt, 1-11.