

Using Zeolite and Granule Activated Carbon Combination for Remediating Landfill Leachate-contaminated Groundwater in Permeable Reactive Barriers

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Abstract

Over the last decade, there has been an explosion in activities directed to development and implementation of PRBs. Considering the high concentrations of ammonium, heavy metals and organic contaminants in landfill leachate-contaminated groundwater, single-reactor-PRB may not be effective; for that reason a sequenced PRB has been developed. The major objective of this study is to investigate and compare the adsorption performances of Granular Activated Carbon (GAC) which is a form of carbon processed to have small, low volume pores that increase the surface area, and Natural Zeolite (NZ) which is the aluminosilicate, on one hand and combination of them in remediating landfill leachate-contaminated groundwater on the other. To come close to this goal, a novel PRB in pilot scale was designed in Plexiglas column. Three parts of 5 cm height were considered to put the reactive media in the middle of the column. The simulated groundwater contaminated with a COD concentration of 600 mg/l was supplied to the end of the column in upflow direction with a flow rate of 10 ml/min. by a small pump. Results showed that GAC has predominated NZ for COD removal. However, no significant removal of COD could be observed by using only NZ as a reactive medium. In addition, using NZ and GAC layers simultaneously had no significant effect on COD removal. Therefore, due to NZ acting as a good adsorbent for ammonium and heavy metals, it is recommended that the NZ and GAC compartments should rather be considered as up-gradient and down-gradient barriers, respectively.

Key words: PRB, Landfill Leachate, Groundwater, Zeolite, GAC, COD Removal.

Introduction:

Permeable Reactive Barriers (PRBs) have shown a great promise as an alternative to pump and treatment for remediating groundwater containing a wide array of contaminants including organics, metals (Hashim *et al.*, 2011), and radionuclides (Henderson & Demond, 2007). Over the last decade, there has been an explosion in activities directed to the development and implementation of PRBs (Thiruvengkatachari *et al.*, 2008). This technology is defined as an emplacement of reactive media in the subsurface which has been designed to intercept a contaminated plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms aiming to

attain remediation concentration goals down-gradient of the barrier (Fig 1). PRB has become popular because of its efficient removal of pollutants and low operation and maintenance costs. An important step towards PRB construction is to choose effective fillings (Jun *et al.*, 2009).

This study classified the reactive barrier materials according to target pollutant and removal mechanism.

Activated carbons and zeolites are widely considered as a suitable adsorbent for on-site or off-site treatment of contaminated groundwater. Activated carbon presents a high adsorption capacity for many organic and inorganic contaminants for its high surface area, due to the micro-porous structure, and a high degree of surface reactivity caused by surface oxide groups and inorganic impurities (Arora *et al.*, 2011a). During the last decade a lot of the research has been done on landfill leachate treatment via activated carbon adsorption process. In most cases, activated carbon adsorption has revealed the importance of removing considerable amount of organic compounds and ammonium nitrogen from leachate sample (Foo and Hameed, 2009). In granular form, activated carbon appears to be highly suitable for using in permeable barriers (Han *et al.*, 2000). Zeolite is tectosilicates with three-dimensional aluminosilicates structure containing water molecules, alkali and alkaline earth metals in their structural framework. These minerals have very high capacity for ion-exchange, adsorption, catalytic, molecular sieving and make them potentially useful as treatment mineral for applying in PRBs (Lee *et al.*, 2010).

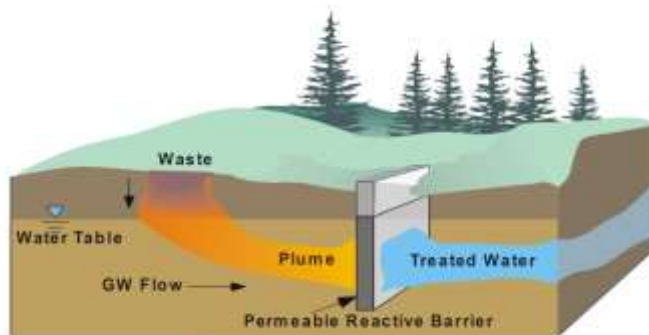


Figure 1. Example of plume being treated by a permeable reactive barrier wall (USEPA, 1998)

In the recent years, risk of groundwater pollution; due to leachate seepage has become a major global environmental concern (Kurniawan *et al.*, 2006). Landfill leachates have been generally characterized as a complex recalcitrant wastewater (Bu *et al.*, 2010), containing pollutants that can be divided into four main categories: dissolved organic matter; inorganic compounds; heavy metals; and xenobiotic organic substances (Iaconi *et al.*, 2006). The leachate of municipal solid waste landfill is often disposed of without any treatment (Gupta and Singh, 2007), and can be seeped into the ground, moving into the nearby underground water supplies of a community with all the negative consequences implicated in the process (Rivas *et al.*, 2006). Considering the high concentrations of ammonium, heavy metals and organic contaminants in landfill leachate-contaminated groundwater, single-reactor-PRB may not be effective, so sequenced PRB has been developed (Jun, *et al.*, 2009). Performances of different adsorbents were not compared systematically in the literature reports for PRB remediation of landfill leachate-contaminated groundwater. Therefore, the major objective of this study is to investigate and

compare the adsorption performances of GAC and NZ for PRB remediation of landfill leachate-contaminated groundwater.

Materials and methods:

Materials and analytical methods:

Using a polyethylene bottle the stock leachate sample was from the municipal sanitary landfill where is located in Tehran, Iran, in July 2014 and preserved in refrigerator at 4°C according to the Standard Methods. The main characteristics of the leachate are shown in Table 1. COD has been measured with Hach spectrophotometer (HACH, DR4000, USA) using hach vials (range 20-1500 mg/l) according to the Standard Methods. BOD₅ was measured according to the Standard Methods 5210B. pH has been controlled using a pH meter (340i, WTW, Germany) Metals were analyzed with an inductively coupled plasma emission spectroscopy with an Optima 3000 ICP-OES system from Perkin-Elmer, Norwalk, CT, USA.

Table 1. The main characteristics of the leachate

Parameter	Value	Parameter	Value	Parameter	Value
pH	6.84	K (ppm)	2100	Zn (ppm)	1.1
COD (mg/l)	52000	Sr (ppm)	15	As (ppm)	0.5>
BOD ₅ (mg/l)	12000	V (ppm)	0.6	Mn (ppm)	0.1>
Alkalinity (mg/l as CaCO ₃)	18400	La (ppm)	0.1>	Cu (ppm)	0.1>
TDS (mg/l)	29500	Be (ppm)	0.02>	Co (ppm)	0.1>
EC (mS/cm)	34.7	Al (ppm)	1>	Cd (ppm)	0.02>
Fe (ppm)	26	Cr (ppm)	1	Ni (ppm)	1>
Ca (ppm)	3200	Ba (ppm)	0.65	Pb (ppm)	0.5>
Na (ppm)	3100	Li (ppm)	0.9	Cs (ppm)	0.02>
Mg (ppm)	510	Ag (ppm)	0.5>	Ti (ppm)	0.5>

GAC was made out of coconut husk and natural zeolite, with a grain-size distribution of 0.6-2.36 mm and 0.425-0.85 mm, respectively. The X-ray diffraction (XRD) of natural zeolite sample has been analysed using a “Siemens D 500/D 501” diffract meter (CuK_α radiation, 2θ=2-60°). The major mineralogical component is clinoptilolite with feldspar, calcite and quartz as main impurities, and montmorillonite, illite, and halite as low content components. The chemical composition of the tested zeolite samples was as follows (wt %): SiO₂_68; Al₂O₃_11.5; CaO_2.5; K₂O_1.9; Na₂O_1.8; Fe₂O₃_1.5; loss of ignition_12.2.

Experimental set-up:

An experimental reactor was performed in Plexiglas column (Gavaskar, 1999) with total height of the column 45 cm and inner diameter 5 cm (Fig 2) (Bartzas *et al.*, 2006). The column was packed with washed sand of non-uniform size (Hosseini *et al.*, 2011), NZ (Woinarski *et al.*, 2006), and GAC (Arora *et al.*, 2011b) as reactive media according to Table 2. Three parts of 5 cm height (A, B, and C) were considered for packing the reactive media in the middle of the column. At variable speed, a peristaltic pump was used to pump the influent throughout the column with at a flow rate of 10 ml/min.

Table 2. The main characteristics of column media

Material	Washed Sand	Natural Zeolite	Granular Activated Carbon
	• D ₅₀ = 0.76±2 mm	• D ₅₀ = 0.70±2 mm	• D ₅₀ = 1.85±2 mm

Characteristics	<ul style="list-style-type: none"> • $\rho = 2.64 \text{ (gr/cm}^3\text{)}$ • Porosity $n = 0.4$ 	<ul style="list-style-type: none"> • $\rho = 2.16 \text{ (gr/cm}^3\text{)}$ • Porosity $n = 0.4$ 	<ul style="list-style-type: none"> • $\rho = 1.43 \text{ (gr/cm}^3\text{)}$ in water • Porosity $n = 0.4$
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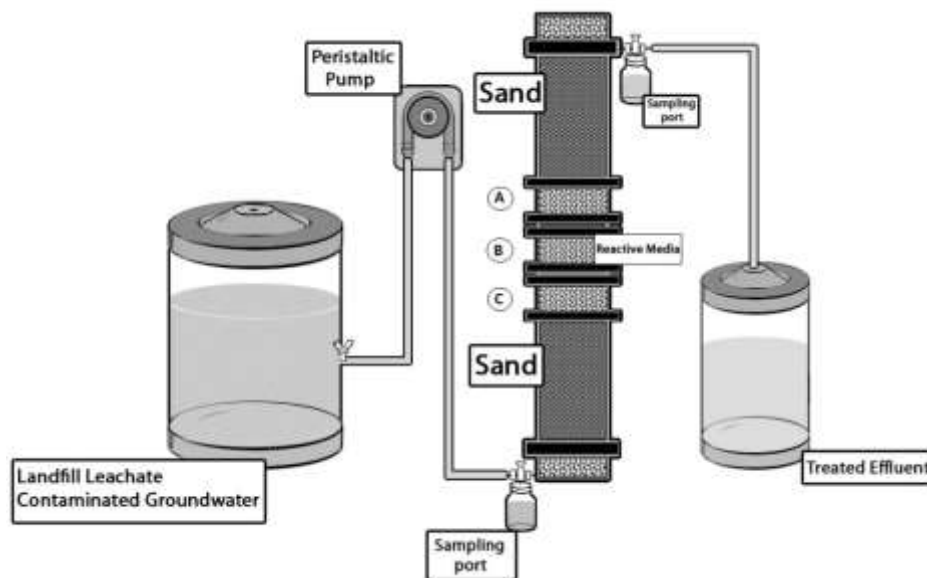


Figure 2. Experimental column set-up to evaluate NZ and GAC as PRB media

Experimental procedure

Leachate samples were removed from the refrigerator and placed for about 2h at about 22°C for conditioning. Samples were thoroughly agitated for re-suspension of possible settling solids before conducting any test (Aziz *et al.*, 2007). The simulated contaminated groundwater was prepared from the stock solution using deionised water with at a COD concentration of 600 mg/l (Yang *et al.*, 2010) and has been supplied to the end of the column in upflow direction (Arora *et al.*, 2011b) at flow rate of 1.5 pore volume per hour (PV/h) equivalent to superficial feed velocity of 8.492E-03 cm/s, by a peristaltic pump in order to eliminate channeling and gas entrainment (Bartzas *et al.*, 2006). In addition, two coarse sand parts with sand diameter of 2.36mm at the top and end of the column and two porous glasses at the top and end of the column with porous diameter of 2mm allowed the formation of well-distributed flow in the reactor. The effluent samples were collected at exit column at appropriate interval and analysed for COD concentration.

A control experiment in the absence of NZ and GAC has been done and COD concentrations were quantified during this period of time. Similar experiments were conducted by using NZ without any GAC (B1), GAC without any NZ (B2), and with NZ and GAC simultaneously (AB & BA) as a reactive media under the same conditions. The experiments have been performed three times to check the reproductibility of results and the match (with $\pm 3\%$) between successive experiments was excellent. Temperature during the operation was $20 \pm 2^\circ\text{C}$.

Results and discussion:

In order to compare the performances of removing COD from NZ (B1), GAC (B2) and their conjunctive use (AB & BA), column experiments were performed. Variation of COD in term of relative effluent concentration for control experiment is depicted in Fig 3 (C_C/C_0 , where C_0 influent concentration and C_C effluent concentration). Figure 3 indicates that COD concentration in effluent samples of control column decreased drastically within three pore volumes at the beginning of the experiment to achieve an equilibrium in the system and remove residuals when polluted water flowed through the column, then declined slowly for the remainder of the experiment period.

COD removal in the control experiment was considered to be zero and all removal rates in other experiments have been based upon control experiment COD values ($E = C_C/C_0 - C_0/C_0$) (Kargi and Pamukoglu, 2004). The columns, which consist of GAC, are more effective for COD removal but no significant removal of COD was observed using only NZ as a reactive medium. In addition, Fig 4 indicates the conjunctive use of these materials had little positive impacts on COD removal. This is due to differences in reactive media. GAC has predominated NZ for COD removal. Therefore, according to Fig. 4 the application of NZ and GAC respectively as up-gradient and down-gradient barriers had the best performance for COD removal. In these Figures, pore volume number (PVN) represents the ratio of accumulated water volume over time to the pore volume of the column media (Jun *et al.*, 2009).

Fig. 5 presents variations of pH measurements in effluent samples. Measurements of pH in the control column effluents varied from 7.8 to 7.2 throughout the experiment. The observed pH in the effluent of the column with GAC as a reactive media was around 8.2 during the early operation period and then slowly dropped to 7.9 before the end of experiment. The observed pH values in the effluent of the column with NZ as a reactive media were around 8.1 after two PVN operations and then dropped to 7.2 at the end of experiment. Variation of pH values in the columns effluent samples, which consist of both GAC and NZ, were resulted from simultaneous effect of these materials according to Fig 5. Therefore, the increase in pH values of this system would become one of the controlling factors for COD removal, especially during early operation. But for field application, pH would not be a concern because of the natural soil/groundwater buffer and dilution capacity (Kao *et al.*, 2001).

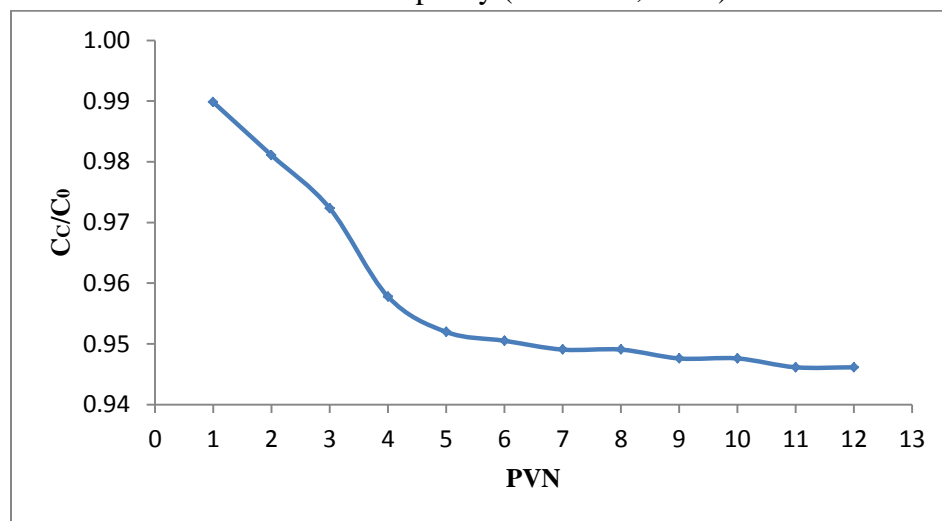


Figure 3. Variation of effluent COD for control experiment

Conclusion

Various physical, chemical and biological methods have been described aiming to remove COD from wastewaters but many of those are expressed non-economical when applied at field-scale operation. Therefore, it was decided to remove COD by sorption on reactive media in PRB system. Accordingly, the performance of two different adsorbents: GAC and NZ, and their combination were compared in PRB system for remediating landfill leachate-contaminated groundwater. The results show that GAC performance versus NZ has been enhanced comparing to NZ for COD removal, where and also no significant removal of COD could be observed by using only NZ as a reactive medium. In addition, using

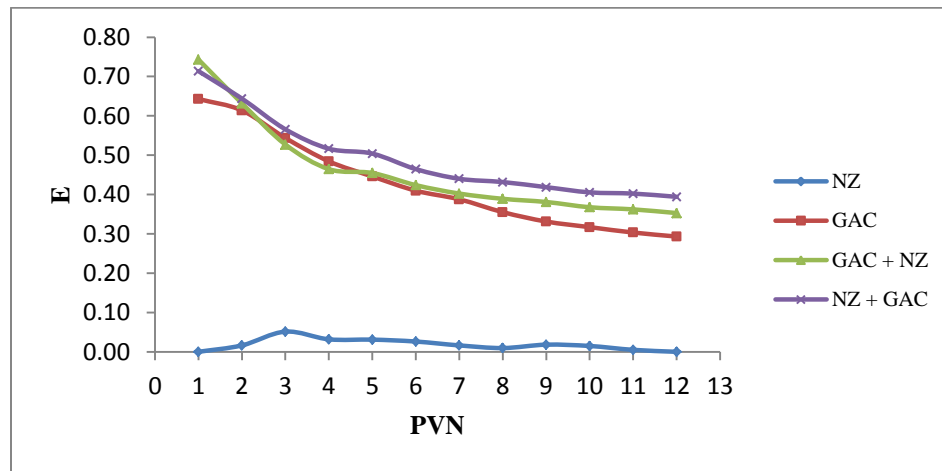


Figure 4. COD removal by various reactive media

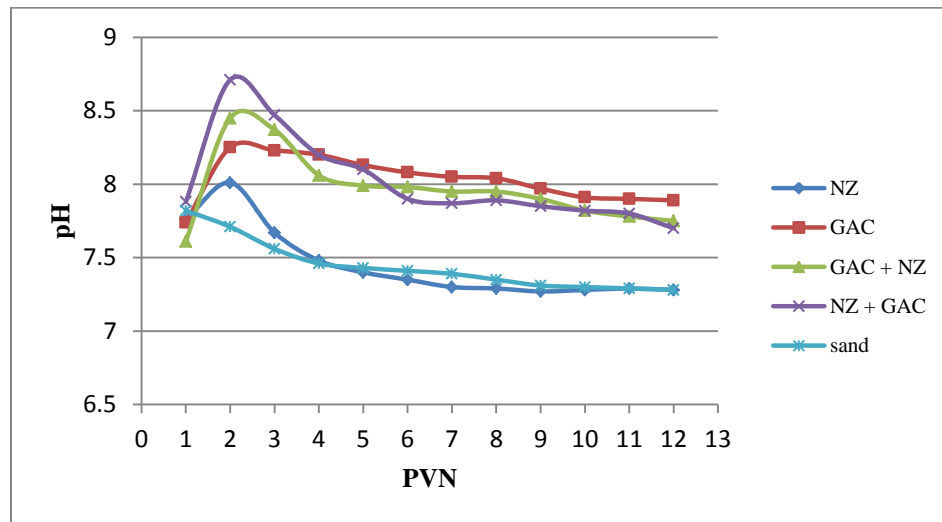


Figure 5. pH variations by various reactive media

NZ and GAC layers simultaneously had no noticeable effect on COD removal. Consequently, since NZ acts as a good adsorbent for ammonium and heavy metals (Jun *et al.*, 2009), it is recommended that the NZ and GAC compartments should rather be considered as up-gradient and down-gradient barriers, respectively.

Acknowledgements

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References

- Arora, M.; I. Snape; and G. Stevens (2011a). The effect of temperature on toluene sorption by granular activated carbon and its use in permeable reactive barriers in cold regions. *Cold Regions Science and Technology*. 66(1): 12-16.
- Arora, M.; I. Snape; and G. Stevens (2011b). Toluene sorption by granular activated carbon and its use in cold regions permeable reactive barrier: Fixed bed studies. *Cold Regions Science and Technology*. 69(1): 59-63.
- Aziz, H.; S. Alias; M. Adlan; a. Faridah Asaari; and M. Zahari (2007). Colour removal from landfill leachate by coagulation and flocculation processes. *Bioresource technology*. 98(1): 218-20.
- Bartzas, G., K. Komnitsas; and I. Paspaliaris (2006). Laboratory evaluation of Fe₀ barriers to treat acidic leachates. *Minerals Engineering*. 19: 505–514.
- Bu, L., K. Wang; , Q. L. Zhao; L. L. Wei; J. Zhang; and J. C. Yang (2010). Characterization of dissolved organic matter during landfill leachate treatment by sequencing batch reactor, aeration corrosive cell-Fenton, and granular activated carbon in series. *Journal of Hazardous Materials*, 1096–1105.
- Foo, K.; and B. Hameed (2009). An overview of landfill leachate treatment via activated carbon adsorption process, Review. *Journal of Hazardous Materials*. 171(1-3): 54–60.
- Gavaskar, A (1999). Design and construction techniques for permeable reactive barriers. *Journal of Hazardous Materials*. 68: 41-71.
- Gupta, S., and G. Singh (2007). Assessment of the efficiency and economic viability of various methods of treatment of sanitary landfill leachate. *Environ Monit Assess*. 107-117.
- Han, I., M. Schlautman; and B. Batchelor (2000). Removal of Hexavalent Chromium from Groundwater by Granular Activated Carbon. *Water Environment Research*. 72(1): 29-39.
- Hashim, M.; S. Mukhopadhyay; J. Narayan Sahu; and B. Sengupta (2011). Remediation technologies for heavy metal contaminated groundwater. *Journal of Environmental Management*. 92: 2355-2388.
- Henderson, A.; and A. Demond (2007). Long-Term Performance of Zero-Valent Iron Permeable Reactive Barriers: A Critical Review. *Environ. Eng. Sci*. 401-423.
- Hosseini, S.; B. Ataie-Ashtiani; and M. Kholghi (2011). Bench-Scaled Nano-Fe₀ Permeable Reactive Barrier for Nitrate Removal. *Ground Water Monitoring & Remediation*. 1-13.
- Iaconi, C., R. Ramadori; and A. Lopez (2006). Combined biological and chemical degradation for treating a mature municipal landfill leachate. *Biochemical Engineering Journal*. 118–124.
- Jun, D.; Z. Yongsheng; Z. Weihong; and H. Mei (2009). Laboratory study on sequenced permeable reactive barrier remediation for landfill leachate-contaminated groundwater. *Journal of Hazardous Materials*, 224-230.
- Kao, C., S. Chen; and M. Su (2001). Laboratory column studies for evaluating a barrier system for providing oxygen and substrate for TCE biodegradation. *Chemosphere*, 44: 925-934.
- Kargi, F.; and M. Pamukoglu (2004). Adsorbent supplemented biological treatment of pre-treated landfill leachate by fed-batch operation. *Bioresource technology*. 94(3): 285-91.

- Kurniawan, T.; W. H. Lo; and G. Chan (2006). Degradation of recalcitrant compounds from stabilized landfill leachate using a combination of ozone-GAC adsorption treatment. *Journal of Hazardous Materials*, 443-455.
- Lee, S. h.; H. Jo; S. t. Yun; and Y. Lee (2010). Evaluation of factors affecting performance of a zeolitic rock barrier to remove zinc from water. *Journal of Hazardous Materials*, 175: 224-234.
- Rivas, F.; F. Beltran; O. J. GimenoFrades; & F. Carvalho (2006). Adsorption of landfill leachates onto activated carbon Equilibrium and kinetics. *Journal of Hazardous Materials*, 170–178.
- Thiruvengkatahari, R.; S. Vigneswaran; and R. Naidu (2008). Permeable reactive barrier for groundwater remediation: Review. *Journal of Industrial and Engineering Chemistry*, 145-156.
- USEPA. (1998). *Permeable reactive barrier technology for contaminant remediation*. Washington, DC: Report number EPA/600/R-98/125.
- Woinarski, A., G. Stevens; and I. Snape (2006). a natural zeolite permeable reactive barrier to treat heavy-metal contaminated. *Process Safety and Environmental Protection*. 84(B2): 109–116.
- Yang, J.; L. Cao; R. Guo; and J. Jia (2010). Permeable reactive barrier of surface hydrophobic granular activated carbon coupled with elemental iron for the removal of 2, 4-dichlorophenol in water. *Journal of Hazardous Materials*. 184(1-3): 782-787.

استخدام مركب من الزيوليت والكربون الفعّال الحبيبي في معالجة المياه الجوفية الملوثة برشاحات مجمع النفايات في الحواجز الفعّالة

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الملخص

في العقود الأخيرة كان هناك نشاطات كبيرة قادت إلى تطور في تطبيق الحواجز الفعّالة النفوذة (PRBs). إذا ما أخذنا بعين الاعتبار التراكيز الكبيرة للألمونيوم والمعادن الثقيلة والملوثات العضوية في المياه الجوفية الملوثة برشاحات مجمع النفايات فإن (PRB) المؤلف من مادة واحدة غير فعّال ولهذا السبب تم تطوير (PRB) المؤلف من عدة مواد متتابعة. و الهدف الأساسي من هذا البحث هو إجراء تحقيق و مقارنة قدرة امتصاص كل من الكربون الفعّال (GAC) و هو فحم مصنّع بأسلوب مسامي بحيث يصبح ذو مساحة سطح عالية جداً، والزيوليت الطبيعي (NZ) و هي نوع من أحجار سيليكات الألمنيوم، و تركيبهم مع بعضهم البعض في معالجة المياه الجوفية الملوثة برشاحات مجمع النفايات. لذلك تم تصميم بابلوت بشكل عمودي من مادة البليكسي كلاس وهو مؤلف من ثلاث حجرات ارتفاع كل واحدة منها 5 سم في وسط العمود وتم تهيئة مياه جوفية ملوثة بتركيز (COD = 600 mg/l) والتي رُوّدت من نهاية عمود البابلوت وتمّ ضخّها نحو الأعلى بمعدل جريان (10 ml/min) بواسطة مضخة صغيرة. بينت النتائج أن الكربون الفعّال أكثر فعالية في حذف (COD) من الزيوليت ومن جهة أخرى لم يكن هناك حذف واضح لـ (COD) باستخدام الزيوليت كمادة جاذبة لوحدها، لذلك يُنصح باستخدام الكربون الفعّال مع الزيوليت بشكل يكون (NZ) من الأعلى و (GAC) من الأسفل على اعتبار (NZ) فعّال في حذف الألمونيوم والمعادن الثقيلة.

الكلمات المفتاحية: PRB، رشاحات مجمع النفايات، المياه الجوفية، الزيوليت، GAC، إزالة COD.