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Effects of operational parameters on methyl tert-butyl ether removal by permeable reactive barrier from polluted waters

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Abstract

Background: Recalcitrant organics remediation from water resources continues to be a significant environmental problem and there is a continued effort to demonstrate practicable and economical treatment options for pollution removal.

Methods: In this study, the efficiency of the permeable reactive barrier (PRB) in a column reactor using zero-valent iron (ZVI) particles and sand mixture in the removal of methyl tert-butyl ether (MTBE) from aquatic phases was investigated. The system performance was MTBE removal while initial pH, reaction time, pollutant content, catalyst load, hydraulic loading rate (HLR), and the reaction rate constant were independent variables.

Results: The results showed that the process efficiency decreased by increasing pH, HLR, and pollutant concentration. In this case, the optimal conditions were obtained at pH = 7, HLR = 0.23 $m^3/m^2 \cdot d$, and $C_0 = 1$ mg/L, which achieved a remarkable removal efficiency up to 90.32%. The high nitrate concentrations and hardness as intervening factors reduced process efficiency to less than 44.61 and 51.4%, respectively. The lack of interfering factors had a considerable effect on the reaction rate of MTBE reduction, which is approximately 2.65 and 4.11 times higher than that in the presence of calcium hardness and nitrate, respectively.

Conclusion: The PRB technology can be suggested as a reliable and robust system to remediate groundwater containing hydrocarbons based on filling media and hydraulic conditions.

Keywords: Groundwater, Hardness, Iron, Methyl tertiary butyl ether, Nitrates, Sand

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Introduction

Increasing use of transportations in human societies and exploration of fossil fuels is causing various kinds of pollutants to the environment (1). Among the existing chemical compounds in use fuels of most countries could be noted to methyl tert-butyl ether (MTBE) (2). Despite the bans in some countries, it has become the second most common organics detected contamination in municipal groundwaters (3-5). The United States Environmental Protection Agency (EPA) has represented the recommended allowable limit of 20 to 40 μg/L for drinking water on the basis of threshold limits of smell and taste and has placed this substance among compounds that are probable carcinogen for humans (6).

In the last years, several studies have been implemented on the removal of MTBE (2,3,7). The major disadvantages of physical and chemical methods have produced potential of by-products with higher toxicity of the main pollutants (8,9). Permeable reactive barriers (PRBs) are efficient methods for in situ remediation of contaminated groundwater, the effectiveness of which more depends on the reactive filling media (10-13). The main benefits of PRB system are its affordable maintenance and operation cost, but the drawbacks of technology are the precipitate created around the media. Thus, monitoring is needed for PRB system to decrease operational costs (14,15). A PRB is conventionally installed in an aquifer, perpendicularly to the direction of groundwater flow. Previous studies have proved that ZVI is the most common media that has a high capability for removal of a widespread range of organic pollutions and heavy metals through oxidation-reduction reactions, and adsorption. Other materials that have been successfully used in PRBs for groundwater remediation include activated carbon, ion-exchange resins, phosphates and some natural materials such as chitin, zeolite, limestone, and organic clays with different costs (16,17).

Zero-valent iron (ZVI) has shown promising results for several types of water contaminants. Limitation for PRB having ZVI as its reactive material was incomplete removal of some halogenated hydrocarbons as there is no change in their aromatic structures (18). The main reason for suitability of using ZVI in PRB media is its reusability in removing pollutant and its easy recovery after using. Low values of ZVI are also capable to remove high volumes of pollutants (19-22).

The recent uses of ZVI processes in treatment of polluted water can be widely separated into two classes, according to the chemistry engaged in the removal process: Systems which use ZVI as an adsorbent, separable or immobilizing factor as absorbency/stabilization systems; and those which use ZVI as an electron donor to cleavage or to transform pollutants into a less toxic or moving form consider to reductive systems (23). To date, only a limited number of laboratory experiments and a few field trials have been undertaken to study the MTBE removal from groundwater using PRB of ZVI/sand mixture as a simple and economical method (7,8,12,24). Recently, removal of MTBE in columns filled with modified natural zeolites has been performed and close to 90% removal of this chemical has reported (25). The results of another research for treatment of MTBE-contaminated groundwater using a biological permeable barrier with a lab-scale column have shown only 50% of MTBE removal (8). Limitations in the application of PBR for removal of MTBE in water involve retaining ZVI reactivity and sustaining the PRB permeability. These problems can be resolved by retaining suitable particle size distribution. Reactivity, toxicity, decrease in permeability and complexity to apply the method to contaminated water with multiple contaminants are the major operational challenges. Other limitations and contaminants removal by PRB system have been extensively explained in previous studies (12,18).

Despite extensive works, robust and feasible treatment of the MTBE has still to be implemented, and, there is a continued effort to generate effective technologies for MTBE removal. Moreover, the combination of ZVI/sand mixture is simple and cost-effective. Consequently, the aim of this study was to evaluate and discuss the efficacy of PRB system for MTBE remediation based on the filling media and hydraulic conditions using laboratory testing as one of the applicable technologies for physical and chemical removal of MTBE from polluted water.

Materials and Methods

Materials

The ZVI was prepared from Merck Company with purity ≥ 99%, with particle size ≥65% of <10 μm and ≤35% of >45 μm. The MTBE purchased from Merck Company also had purity ≥99.5%. The sands were prepared from the Zanjan water treatment plant, the effective size and uniformity coefficient of which were 0.67 mm and 1.68, respectively. These sands with using 12 N hydrochloric acid have been retained for 48 hours for wiping any mineral until its EC reached less than 1 μS/cm (26). At the next step, the sands were passed from a 0.75 mm sieve in order to separate the fine particles.

Batch experiments

The purpose of batch experiments was to achieve the optimum time and pH for removing MTBE from the media. This section includes a four glasses-covered container with a volume of 50 mL containing 5 mg/L MTBE solutions and a certain amount of ZVI with the blank sample container without ZVI. The dose of ZVI equal to 2, 10, 20 and 40 g/L were weighted and poured into containers. Then, the container around was covered by foil and shaken in the dark with a speed of 150 rpm. Shaking time was 2, 5, 10, 15, 30, and 60 minutes. After completing every step, the solution passed through the syringe filter. The above steps were done at pH = 7. After obtaining the optimum time, the effects of pH in the range of 5-9 were investigated in the presence of 10 and 20 g/L ZVI (27).

Column of PRB

In order to study the PRB system, a cylindrical Plexiglas column with a height of 46.5 cm, the inner diameter of 4 cm, and total volume of 0.57 L, was used. The reactive material in the presented column was ZVI that was mixed with silica sand for providing the necessary porosity. For steady distribution of flow, the sand was put in 5 cm from the above and 5 cm from the bottom of the column while the direction of inflow to the column was upwardly. Based on batch runs, the weight percentage of iron powder and silica sand in the media were selected 10 and 90%, respectively.

Iron mass within the total column has been 210 g. In order to investigate the required iron mass and proper thickness of PRB media, sampling was done in six different heights of column that each of them represented definite mass of iron. The height of the sampling port of the column was equal to 7.5, 12.5, 22.5, 28, 42, and 46.5 cm, and the amount of mass iron into these heights were equal to 14.8, 23.5, 34.3, 44.7, and 93.6 g, respectively. The time of sampling (the necessary time for sampling after crossing flow into the column) was determined based on the media porosity and flow rate. Therefore, the water entrance time to each height (or port) were determined 3.45, 6.2, 11, 13.35, 19.3, and 22.4 hour at flow rate of 0.2 mL/min. The porosity of iron and sand mixed layers was 0.45. The porosity of the sand column as a blank reactor was 0.56. Also, peristaltic pump was used for lifting flow to the upward, a check valve at the lowest point of the column was considered as input. Different hydraulic loading rates (HLRs) of 0.23, 0.57, and 1.14 $m^3/m^2 \cdot d$ (equal to flow rate of 0.2, 0.5, and 1 mL/min) were used in the column. Flow rates in the present work were higher than the actual conditions in most regions and groundwater to keep the operational issues in the lab. In order to evaluate the roles of interfere agents on MTBE removal by PRB, the nitrate ions and hardness were selected in the range of 30-180 and 100-200 mg/L, respectively. The bench-scale PRB system built and used in the experiments is shown schematically in Figure 1.

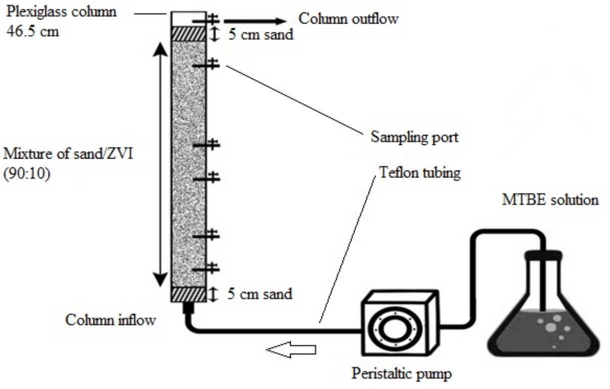

Figure 1. Schematic diagram of the experimental set-up.

Analyses

MTBE samples were taken from different heights of the column. All samples were collected, covered with an airtight cap, and kept in the refrigerator at temperature of 4°C before analysis. The MTBE concentration was measured using Gas Chromatography (GC) device made by the Agilent company equipped with the Flame Ionization Detector (FID) according to the U.S EPA502.2 test method for analysis of MTBE in the liquid phase through GC with the purge and trap device (28). The absorption column of HP-5 with a length of 30 m and inner diameter of 0.32 mm was used. The temperature program of the column was as follows: Initial temperature of the column was 35°C and after 4 minutes, at the rate of 10°C per minute up to the 150°C and with reaching to this temperature, the method was finished. The FID temperature, hydrogen flow, and air flow were selected to be 300°C, 25 mL/min, and 250 mL/min, respectively. The three-step purge and trap, purge, desorb, and bake were performed. The time to purge was 11 minutes, the flow rate was 40 mL/min, temperature was 25°C, and dry purge flow was 200 mL/min. The time of desorb and bake were 2 minutes, flow rate was 300 mL/min, and temperature was 250°C. Temperature of the bake was 270°C and flow rate was 400 mL/min. To determine the accuracy and precision of MTBE measurement, known concentration samples were analyzed triplicate in identical condition, the relative standard deviation in this method did not exceed more than 1%. The limit of detection was 0.01 mg/L.

Results

Control column

Before conducting main reactor runs, several blank experiments were conducted in order to determine the reduction route of MTBE through the mechanisms with the exception of ZVI chemical reactions. The control runs were performed with sand column in the absence of ZVI with a constant concentration of MTBE at neutral pH. The data in Figure 2 present that there is little adsorption of MTBE at different HLR of 0.23, 0.57, and 1.14 $m^3/m^2 \cdot d$ (equal to flow rate of 0.2, 0.5, and 1 mL/min) in the column led to 16.97%, 8.12%, and 3.83% removal, respectively.

Batch experiments

Figure 3 shows the effect of retention time on MBTE removal in a batch system. The amount of MBTE removal in time periods of up to 60 minutes by weight values of ZVI in the range of 2 to 40 g/L was investigated. At retention time of 30 minutes, the maximum removal of 58% was obtained. Also, by increasing retention time to 60 minutes, MTBE removal found a constant trend. As shown in Figure 4, the highest rate of MTBE degradation occurs within 30 minutes under acidic pH values (degree of conversion obtained 66.34% for pH = 5 but 27.29% for pH = 9). However, a little decrease was observed at neutral pH value. The results suggest that with increasing pH, the removal percent decreases dramatically.

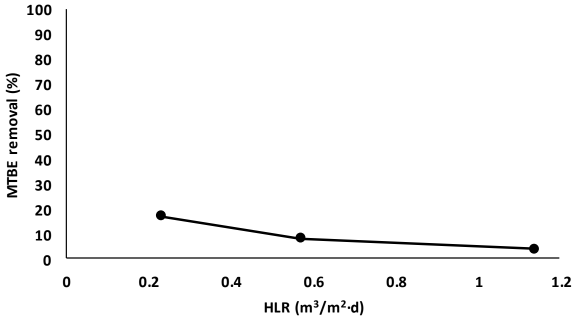

Figure 2. The role of blank column in MTBE removal at different inflow rates (C_0 = 5 mg/L, pH = 7).

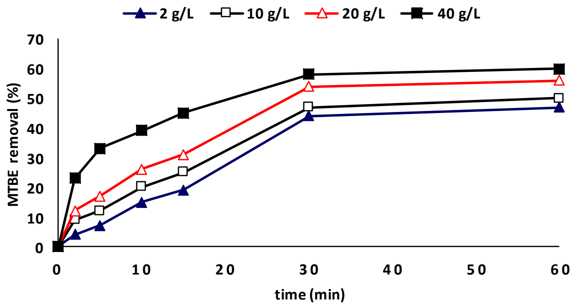

Figure 3. Effect of different initial ZVI concentrations in Batch experiments (C_0 = 5 mg/L, pH = 7, rpm = 150).

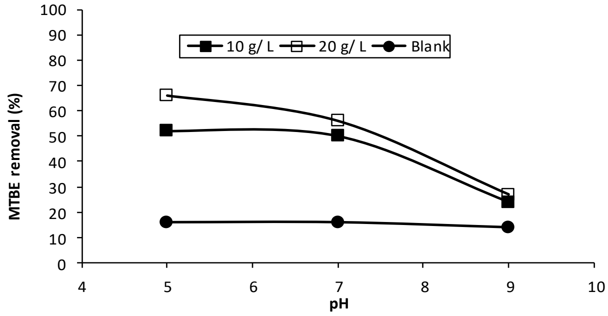

Figure 4. Effect of pH at different ZVI concentrations in the batch experiments (C_0 = 5 mg/L, rpm = 150).

Column experiments

Effect of initial MTBE concentrations

The disappearance of MTBE at different initial concentrations in the range of 0.5 to 5 mg/L and neutral pH are compared in Figure 5. The best results were obtained at low initial concentrations, where 80.76% of MTBE removed at reaction time less than 22.4 hour. The removal of MTBE decreased by increasing C_0 under the conditions studied; however, the total amount of MTBE degraded actually increased in the PRB system.

Effect of HLR

As clearly shown in Figure 6, the performance of PRB system is dependent on HLR and a significant effect was observed at this operating condition. The MTBE removal rates in HLR of 0.23, 0.57, and 1.14 m^3/m^2·d were 90.32%, 77.31%, and 69.47%, respectively.

Effect of pH

The effect of initial pH in PRB system for MTBE removal at special conditions (pH = 5, 7, 9, C_0 = 1 mg/L, HLR = 0.23 m^3/m^2·d, t = 22.4 hours) are depicted in Figure 7. The findings showed that the highest removal rates of MTBE was obtained under different pH values (removal rate of 93.4% for pH 5 but 90.32% for pH 7, and 61.35% for pH 9). In general, the results illustrated that as pH increased, the MTBE removal efficiency decreased.

Effect of Nitrate in the durability of PRB system

As shown in Figure 8, more than 90% MTBE removal could be obtained at 22.4 hours in the absence of nitrate. The initial MTBE concentration was kept constant at 1 mg/L, while the HLR was 0.23 m^3/m^2·d. The high nitrate concentrations had a substantial effect on the removal rate. The MTBE removal in nitrate concentrations of 30, 60, and 180 mg/L were 64.15%, 52.75%, and 44.61%, respectively. These results proved that the presence of nitrate as a disturbing factor, decreases MTBE removal.

Effect of Hardness in the durability of PRB system

Figure 9 exhibits the efficiency of the PRB column in MTBE removal in the presence of calcium hardness as a nuisance factor. All of operating conditions were the same as nitrate. The MTBE removal with hardness concentrations of 100, 120, and 200 mg/L were 66.66%, 57.75%, and 51.4%, respectively. The results show that hardness as an interfering factor reduces MTBE removal.

Reaction Kinetics

The reduction of MTBE as a function of residence time in the PRB system is presented in Figure 10. In order to evaluate MTBE removal from the PRB system in the presence and absence of interfering factors (i.e. nitrate and calcium hardness), the reaction rate constants (k)

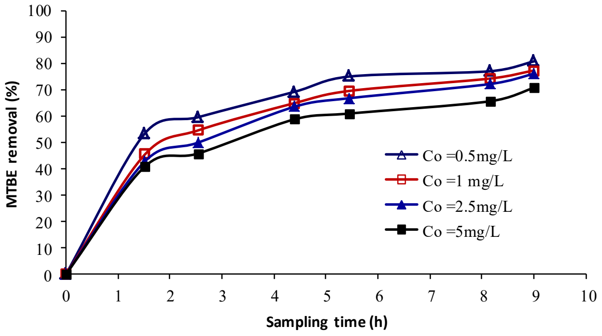

Figure 5. Effect of initial concentrations of MTBE in PRB system (pH = 7, HLR = 0.57 m^3/m^2·d).

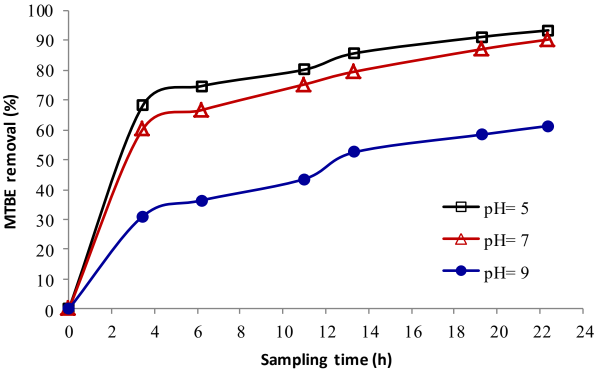

Figure 7. Effect of feed pH in PRB system for MTBE removal (pH = 5, 7, 9, C_0 = 1 mg/L, HLR = 0.23 m^3/m^2·d).

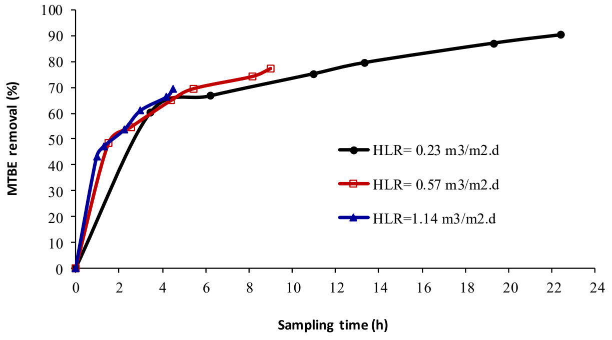

Figure 6. Effect of flow rates in PRB system for MTBE removal (C_0 = 1 mg/L, pH = 7).

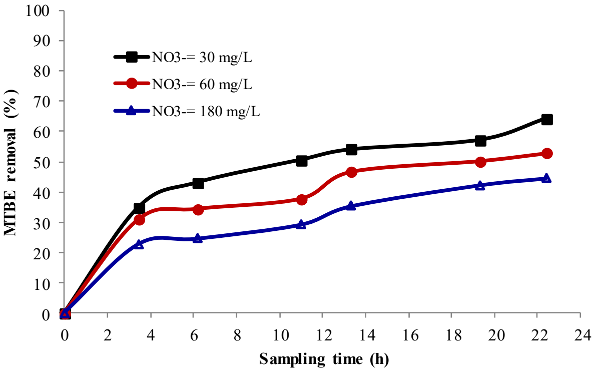

Figure 8. Effect of nitrate in PRB system for MTBE removal (pH = 7, C_0 = 1 mg/L, HLR = 0.23 m^3/m^2·d).

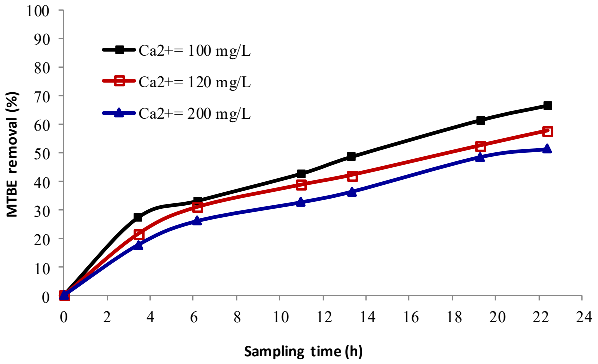

Figure 9. Effect of hardness in PRB system for MTBE removal (pH = 7, C_0 = 1 mg/L, HLR = 0.23 m^3/m^2.d).

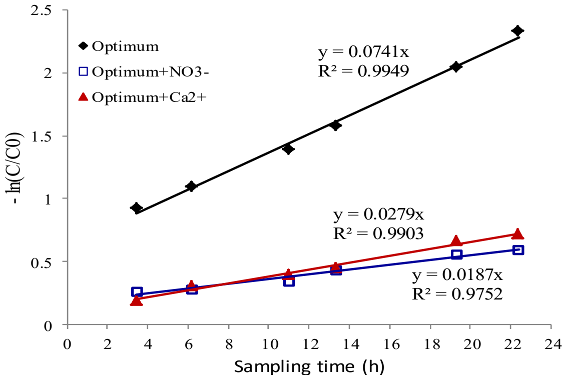

Figure 10. Variations of kinetic reaction rates in the presence of nitrate and hardness at optimum condition (pH = 7, C_0 = 1 mg/L, HLR = 0.23 m^3/m^2·d, NO_3^- = 180 mg/L, Ca^{2+} = 200 mg/L).

were compared. As can be seen in Figure 10, the results revealed that both disturbing factors have a negative effect on MTBE removal rates. As predicted, lack of interfering factors had a considerable effect on the rate of MTBE degradation with rate constant equal to 0.0741 1/min that is approximately 2.65 and 4.11 times higher than that in the presence of calcium hardness and nitrate, respectively.

Discussion

Batch experiment

According to the results of this part, the removal efficiency of MTBE increased by increasing the contact time. The increasing of the removal efficiency with time is due to the availability of a large number of active surface sites. The reaction time reached equilibrium in 30 minutes and by increasing retention time to 60 minutes, MTBE removal found a constant trend. Also, by increasing the pH of reactor, the removal percent decreases significantly. While, the findings of another study have presented that by increasing retention time, removal percent of halogenated aliphatic hydrocarbons are increasing. Hence, at a retention time of about 100 hours with ZVI powder in the batch system, the residual concentration of organic matter fell nearly to zero (27). Another study conducted using ZVI powder showed that 45% of MTBE removed within 24 hours in a batch system (25). The batch experiments demonstrated that the removal of MTBE is affected significantly by pH. This provides further support to earlier work that showed MTBE in the presence of ZVI can be significantly removed in the acidic pH in columns filled with modified natural zeolites (25). According to recent studies, the main mechanisms for organic pollutants removal by ZVI in batch and column experiments were oxidation-reduction reactions and adsorption (14,16).

Column experiments

Effect of initial MTBE concentrations

Based on the results, by increasing the MTBE initial concentration to 5 mg/L, the removal rate decreased; however, the total amount of MTBE degraded actually increased in the PRB system. In general, the ZVI can remove the MTBE by reduction via iron or electron relocation at the superficial of corrosion intermediates, adsorption, or precipitation (12,29). Similarly, the results of another study for MTBE removal by using zeolite granule in batch and column systems showed that at less initial concentrations, the removal percent of MTBE increases, because at high concentrations larger pore is needed for obtaining more removal efficiency (30). This result is consistent with those reported by other studies (2,3,5). The application of a PRB system filled with natural pyrite to treat a Cr (VI)-contaminated groundwater have shown the same results as other studies (19). Similar results were presented with heavy metals removal in ZVI/pumice PRBs. Increasing initial concentration of Ni and Cu led to a decrease in the efficiency of PRB system. In addition, increasing the ratio ZVI/Pumice, increased removal of Ni and Cu (31). Also, ZSM-5 zeolite has been evaluated for MTBE removal in fixed-bed column tests. It was observed that both the breakthrough time and saturation time decreased, and the slope of breakthrough curves between the breakthrough and saturate points, i.e. mass transfer zone, became slightly steeper by increasing the influent MTBE concentration (2).

Effect of HLR

The results presented that by increasing the HLR, the removal efficiency of MTBE decreased. This is due to the fact that the motion of MTBE is speed up with an increase in the flow rate, which could cause inadequate retention time of MTBE in the PRB column (2). The obtained result showed that by increasing the amount of inflow, system efficiency decreases. This provides further support to earlier work that perchlorate ethylene (PCE) removal from water by PRB with ZVI media can be obtained by reducing the amount of inflow to the column, and with a flow of 2 mL/min, PCE removal of 93% has achieved (32). Similarly, the findings of other study for MTBE removal using zeolite in batch and column systems concluded that removal amount of MTBE increases in low flow rates.

By considering the flow rate of 5.2 mL/min, removal of 95% has been obtained (30). This phenomenon obtained in the present study would be described that the higher HLR could induce the higher mass transfer driving force and the shorter retention time between adsorbents and contaminant, which is consistent with the results of recent studies (33-35).

Effect of pH

The surface properties of the pollutants and filling media including the surface charge and functional groups of the material and the ionization degree of the contaminants were affected by the pH values in the water (36). The pH of the solution prevails the degradation process due to the strongly pH-dependent properties such as ZVI surface charge condition and dissociation of the solution. The removal rate increase in lower pH values due to ZVI stability is less disturbed. The main reason to explain this behavior may be that the surface reaction led to the corrosion of ZVI, which generates hydrogen gas and hydroxyl ion according to the following equations:

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (2)$$

These equations recommend that iron corrosion could have a destructive effect on the removal of MTBE as water competes with MTBE for the electrons from ZVI. At higher pH values, the ferrous and hydroxyl ions form ferrous hydroxide and precipitate. The deposition of Fe(III) on ZVI could impede the movement of the MTBE and clog the reactive spots on ZVI, and hence, reduce the overall performance. As the solubility of Fe(III) is strongly dependent on pH, content of Fe(III) on the surface of ZVI is controlled by pH. Therefore, pH could affect the rate of iron corrosion and the amount of precipitation on ZVI exterior (34). Similarly, the results of a study on the effects of pH in the range of 1.7 to 10 on dechlorination of trichloroethylene (TCE) by ZVI declared that pH 4.9 had the most efficiency. No removal was observed at pH 9 and 10 and with increasing pH, the removal efficiency had dramatic reduction (37). This result is consistent with those reported by other studies (3,19,38). Also, long-term efficiency of ZVI barriers during clean-up of copper containing solutions has illustrated that increasing pH values resulted to a decrease in copper solution removal efficiency (39). This confirms the amended efficiency of ZVI/sand integrations.

Effect of nitrate in the durability of PRB system

According to the results, the addition of nitrate as disturbing factor and common groundwater pollution in various concentrations, decreases MTBE removal efficiency in the PRB column. This provides further backing to the earlier supposition that one of the problems associated with ZVI particles is the enhancement of reactivity of these particles with reduction of selectivity of pollutant removal from water, which caused ZVI reaction with non-target materials (disturbing ions), and consequently, reduced the efficiency of target pollutant removal in water (35,40). To elucidate this decline in target pollutant removal, it was described that the active sites of nZVI surface have a positive charge state originally; thus, a contest between various negatively charged anions such as nitrate, phosphate, and sulfate ions involves in overlaying these surface active sites, resulting in a drop in removal efficiency (41).

Effect of hardness in the durability of PRB system

The efficiency of the PRB column in MTBE removal in the presence of calcium hardness as a nuisance factor at different concentrations was reduced. All of operating conditions were the same as nitrate. Similarly, the findings of another study illustrated that the presence of hardness ions caused a reduction in Cr removal from water to 33% by the ZVI-filled column. They have proven that the existence of calcium, magnesium, and carbonate ions in groundwater have a vast impact on the ZVI by development of inactive deposits, such as $CaCO_3$ and $Mg(OH)_2$, on the ZVI surface, resulting in a decreased durability of the ZVI by preventing electron conduction (42). This result is consistent with those reported by other studies (41). Similarly, the other study has investigated the dechlorination of TCE under different quality of groundwater and anaerobic environments. For the two water types tested, dechlorination of TCE was a little superior for the soft and low alkalinity groundwater than for the hard and high alkalinity groundwater. The results recommend that the mixture of groundwater presumably to strongly changes the capability of ZVI in reducing TCE (23).

Reaction kinetics

The main factor in the column kinetic study is the retention time defined as the time needed for water and the filling media inside the PRB to be in contiguity to get treatment aims. The retention time t_R, of the pseudo-first-order reaction, can be calculated using Eq. (3).

$$t_R = [-\ln(C_t/C_0)/k] \quad (3)$$

where C_t is the MTBE concentration down-gradient of the PRB, C_0 is the concentration of the MTBE entering the PRB, and k is the rate of reaction (12). Hence, since the flow rate and the initial porosity of the reactive material are known, the distances through the column can be easily converted to retention times. The results presented that the nitrate and calcium hardness as disturbing factors have a negative effect on the MTBE removal rates. This is consistent with the findings of other studies (43, 44).

Reduction of nitrate by ZVI has fitted well the pseudo-first order rate constant depending on the nitrate concentration (45). The *k* of reductive denitrification of nitrate was reported to be 0.086 1/min with nanoscale iron dosage of 1.0 g/L and pH 6.7 (43). Denitrification by ZVI is primarily dependent on pH, nitrate concentration, and surface-mediated process (44).

Conclusion

The results of the present study clearly prove that ZVI/sand mixtures are a potentially suitable reactive medium for PRBs used for remediation of MTBE-contaminated water. The best MTBE removal in the optimal conditions (pH = 7, HLR = 0.23 $m^3/m^2 \cdot d$, $C_0 = 1$ mg/L) was obtained 90.32%. The amount of MTBE removal was dependent on pH, inflow rate, and initial concentration. Therefore, with increasing each of these variables, removal amount of MTBE decreased. The existence of interference factors such as nitrate and hardness in the PRB system was impressive as these factors reduced the system efficiency down to 44.46% and 51.4%, respectively. Further investigation is necessary on the effect of multiple organic pollutants and ionic strength of water on the removal efficiency of MTBE in PRB system. Hence, the role of the interconnection between the reactive material filling the PRB and the influence exerted by the density of the reagent need to be evaluated.

Acknowledgments

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Ethical issues

The authors hereby certify that all the data collected during the research are as expressed in the manuscript, and no data from the study has been or will be published elsewhere separately.

Competing interests

Authors declare that they have no conflict of interest or finance.

Authors' contributions

AA contributed to the study's conception, design, supervision, data curation, funding acquisition, and wrote the first draft of the paper. FG performed material preparation, data collection, experiments, analysis, and wrote pre-draft. MRM conducted methodology, validation, formal analysis. All authors reviewed and approved the final manuscript.

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