Removal of MTBE From Groundwater Using A PRB of ZVI/Sand Mixtures: Role of Nitrate And Hardness

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Abstract

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 main operating parameters influence reactor performance such as pH, reaction time, pollutant content, catalyst load, hydraulic loading rate, and the reaction rate constant was evaluated. The results showed that the efficiency of process decreased with increasing pH, inflow, and pollutant concentration. In this case, the optimal conditions were obtained at pH=7, flow rate=0.23 m³/m².d and C₀=1 mg/L, which achieved a remarkable removal efficiency up to 90.32%. The being of high nitrate and hardness concentrations as intervening factors were led to reduce process efficiency to less than 44.61% and 51.4%, respectively. Lack of interfering factors had a considerable effect on the reaction rate of MTBE reduction that is approximately 2.65 and 4.11 times higher than in the presence of calcium hardness and nitrate, respectively. The PRB can be operated to remediate groundwater containing hydrocarbons based on filling media and hydraulic conditions.

Highlights

- PRB can effectively be used in the treatment of groundwater containing MTBE.
- MTBE removal decreased with increasing hardness and nitrate ions in the feed.
- Reduction of flow rate from 1.14 to 0.23 m³/m².d does have an effect in MTBE removal.
- MTBE was mainly removed at the beginning of the reactor.

Introduction

Increasing use of transportations in human societies and exploration of fossil fuels is causing various kinds of pollutants to the environment and finally to water resources. Among the existing chemical compounds in use fuels of most countries could be noted to MTBE(Zhang et al. 2019). Despite the bans in some countries, it has become the second most common organics detected contamination in municipal groundwaters (Levchuk et al. 2014, Purswani et al. 2014, Abbasi et al. 2020). The American environmental protection agency has been representing 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 been placed this substance among compounds that is probable carcinogen for humans (Hu et al. 2008).

In last years, several works have been implemented on the removal of MTBE (Levchuk et al. 2014, Thiruvengkatachari et al. 2008, Zhang et al. 2019). The major disadvantages of physical and chemical methods have produce potential of by-products with higher toxicity of the main pollutants (Liu et al. 2006). PRBs are efficient methods for in situ remediation of contaminated groundwater, the effectiveness of which more depends on the reactive filling media (Liu et al. 2015, Obiri-Nyarko et al. 2014, Kumarasinghe et al. 2018, Gibert et al. 2010, Beiyuan et al. 2017, Zhang et al. 2018). 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 and the substitution of reactive media from the PRB. Thus, monitoring is needed for PRB system to decrease operational costs (Thakur et al. 2020, Li et al. 2019).

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. The main reason for suitability of using ZVI in PRB media is its reusability in pollutant removing and its easy recovery after using. Low concentrations of ZVI is also capable to remove high volumes of pollutants (Noubactep 2008, Dominguez et al. 2018, Lee et al. 2009, Toli et al. 2021).

Present uses of ZVI processes in treatment of polluted water can be widely separated into two classes, according to the chemistry be engaged in the removal process: systems which use ZVI as a 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 (Cundy et al. 2008). Recently, removal of MTBE in columns filled with modified natural zeolites has performed and close to 90 percent removal of this chemical has reported (Russo et al. 2015). The results of another research for treatment of MTBE-contaminated groundwater using a biological permeable barrier with lab-scale column have shown only 50 percent of MTBE removal (Liu et al. 2006). 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 works (Obiri-Nyarko et al. 2014, Thakur and Kumar 2021).

Despite extensive work, robust and economical treatment of the MTBE has still to be implemented, and, there is a continued required to generate effective technologies. The aim of this work was to evaluate the effectiveness of PRB using ZVI as one of the applicable technologies for physical and chemical removal of MTBE from polluted water.

Materials And Methods

2.1 Materials

The ZVI was prepared from the Merck Company with purity of $\geq 99\%$, with particle size $\geq 65\%$ of $\leq 10 \mu\text{m}$ and $\leq 35\%$ of $\leq 45 \mu\text{m}$. The MTBE also had purity of $\geq 99.5\%$ that was purchased from Merck Company. The sands were prepared from the Zanjan water treatment plant that the effective size and uniformity coefficient were 0.67 mm and 1.68, respectively. These sands with using 12 N hydrochloric acid have been retained for 48 h for wiping any mineral until it's EC reaches less than $1 \mu\text{S/cm}$ (Sadeghi et al. 2011). At the next step, the sands were passed from 0.75 mm sieve in order to separate the fine particles.

2.2 Batch Experiments

The purpose of batch experiments was to achieve optimum time and pH for removing MTBE from the media. This section includes 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 weighted and poured into containers. Then, using foil covered the container around and shaking in the dark with a speed of 150 rpm. Shaking time was 2, 5, 10, 15, 30 and 60 min. After completing every step, the solution passed through the syringe filter. The above steps done with pH = 7. After obtaining the optimum time, the effects of pH in the range of 5–9 were investigated in the present of 10 and 20 g/L ZVI.

2.3 Column of PRB

In order to study the PRB system, cylindrical plexiglass column with a height of 46.5 cm, the inner diameter of 4 cm and total volume of 0.57 L has been used. The reactive material in the presented column is 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 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 has been done in six different heights of column that every one 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 that amount of mass iron into these heights were equal to 14.8, 23.5, 34.3, 44.7 and 93.6 g, respectively. For calculating time of sampling (the necessary time for sampling after crossing flow into the column), was determined based on 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 22.4h at flow rate of 0.2 ml/min. Porosity mixed layers of iron and sand have been 0.45. The porosity of the sand alone 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 rate (HLR) of 0.23, 0.57 and 1.14 m³/m².d (equal to flow rate of 0.2, 0.5 and 1 ml/min) were used in the column. Flow rates in present work were higher than the actual conditions in most regions and groundwaters to keep the operational issues in the lab. The bench-scale PRB system built and used in the experiments is shown schematically in Fig. 1.

2.4 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 4°C temperature before analyzed. 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 (Mehran et al. 1990). The absorption column of HP-5 with a length of 30 m and inner diameter of 0.32 mm was used A 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 300°C, 25 mL/min and 250 mL/min, respectively. The three-step purge and trap, purge, desorb and bake have performed. The time to purge was 11 minutes, the flow was 40 mL/min, temperature was 25°C and dry purge flow was 200 mL/min. The time of desorb and bake were 2 min, flow was 300 mL/min and temperature was 250°C. Temperature bake was 270°C and flow 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 (RSD) in this method did not exceed more than 1%. The limit of detection (LOD) was 0.01 mg/L.

Results And Discussion

3.1 Control Column

Before conducting main reactor runs, several blank experiments were conducted in order to determine the reduction route of MTBE through the mechanisms other than ZVI chemical reactions. The control runs were performed with sand alone column in the absence of ZVI with a constant concentration of MTBE at neutral pH. The data in Fig. 2 presents that there is little adsorption of MTBE at different HLR of 0.23, 0.57 and 1.14 m³/m².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 percent, respectively.

3.2 Batch Experiments

Figure 3 shows the effect of retention time in MBTE removal in a batch system. The amount of MBTE removal in time periods of up to 60 min by weight values of ZVI in the range of 2 to 40 g/L was investigated. At retention time of 30 min the maximum removal of 58% was obtained. Also, with increasing retention time to 60 min, MTBE removal found a constant trend. While, the findings of other study have presented that with increasing of retention time, removal percent of halogenated aliphatic hydrocarbons are increasing. Hence, at a retention time of about 100 h with ZVI powder in the batch system, the residual concentration of organic matter fell nearly to zero (Gillham and O'Hannesin 1994). Another study by using ZVI powder showed that 45% of MTBE removed within 24 h in a batch system (Russo et al. 2015). The batch experiments demonstrate that the removal of MTBE is affected significantly by pH. As shown in Fig. 4, the fastest rate of MTBE degraded occurs within 30 min under acidic pH values (degree of conversion obtained 66.34% for pH = 5 but 27.29% for pH = 9). Although little decreasing was observed in neutral pH value. The results suggest that with increasing pH, the removal percent decreases dramatically. This provides further support to earlier work that MTBE in the presence of ZVI can be significantly removed in the acidic pH in columns filled with modified natural zeolites (Russo et al. 2015).

3.3 Column Experiments

3.3.1 Effect of Initial MTBE Concentrations

The disappearance of MTBE at different initial concentrations ($C_0 = 0.5\text{--}5\text{ mg/L}$) and neutral pH are compared in Fig. 5. The best results were obtained at low initial concentration, where that 80.76% of MTBE removed in less than 22.4 h reaction time. The removal of MTBE decreased with increasing C_0 under the conditions studied; 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 (Obiri-Nyarko et al. 2014, Liu et al. 2015).

Similarly, the results of other study for MTBE removal with using zeolite granule in batch and column systems showed that in less initial concentration, the removal percent of MTBE increases, because in high concentrations larger pore is needed for obtaining more removal efficiency (Abu-Lail et al. 2010). This result is in agreement with those reported by other researchers (Levchuk et al. 2014). The application of a PRB system filled with natural pyrite to treat a Cr (VI)-contaminated groundwater have shown the same results as other researchers (Noubactep 2008). Similar results presented with heavy metals removal in ZVI/pumice permeable reactive barriers. Increasing initial concentration of Ni and Cu led to decrease efficiency of PRB system. As well as increasing of ratio ZVI/Pumice, increased removal of Ni and Cu (Chen et al. 2010).

3.3.2 Effect of HLR

It is clearly shown in Fig. 6 that the performance of PRB system is dependent of HLR and significant effect was observed at this operating condition. The MTBE removals in HLR of 0.23, 0.57 and $1.14\text{ m}^3/\text{m}^2\cdot\text{d}$ were 90.32%, 77.31% and 69.47%, respectively. 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 (Zhang et al. 2019). The obtained result showed that with 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 (Eslami et al. 2015). Similarly, the findings of other study for MTBE removal using of zeolite in batch and column systems concluded that removal amount of MTBE increases in low flow rates. With considering the flow rate of 5.2 ml/min, removal of 95% has been obtained (Abu-Lail et al. 2010).

3.3.3 Effect of pH

The pH of the solution prevails the degradation process due to the strongly pH dependent of the properties such as ZVI surface charge condition and dissociation of the solution. As shown in Fig. 7, the most rate of MTBE vanished take places within 22.4 h under different pH values (degree of removal obtains 93.4% for pH 5 but 90.32% for pH 7 and 61.35% for pH 9). The removal rate increase in lower pH value due to ZVI stability is less disturbed. The main reason to explain this behavior may be the surface reaction led to the corrosion of ZVI, which generates hydrogen gas and hydroxyl ion according to following equations:

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, 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 the pH. Therefore, pH could affect the rate of iron corrosion and the amount of precipitation on ZVI exterior. Similarly, the results of a study on the effects of pH in the range of 1.7 to 10 on dechlorination of TCE by ZVI declared that pH 4.9 had the most efficiency. No observed any removal at pH 9 and 10 and with increasing pH, the removal efficiency had dramatic reduction (Chen et al. 2001). This result is in agreement with those reported by other works (Noubactep 2008, Levchuk et al. 2014). Also, long-term efficiency of ZVI barriers during clean-up of copper containing solutions has illustrated that increasing of pH values resulted to decrease in copper solution removal efficiency (Komnitsas et al. 2007). This gives verification of the amended efficiency of ZVI/sand integrations.

3.3.4 Effect of Nitrate in the Durability of PRB System

As shown in Fig. 8, more than 90% MTBE removal could be obtained at 22.4 h in the absence of nitrate. The initial MTBE concentration was kept constant at 1 mg/L, while the HLR was 0.23 m³/m².d. The being of high nitrate concentrations had a substantial effect on the removal rate. The MTBE removal in nitrate concentration 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 disturbing factor, decreases MTBE removal. 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 that caused ZVI reaction with non-target materials (disturbing ions) and consequently caused to reduce efficiency of target pollutant removal in water (Elliott and Zhang 2001). 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 with in overlaying these surface active sites, resulting in a drop in removal efficiency (Khalil et al. 2018).

3.3.5 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 the 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. Similarly, the findings of another study illustrated that the presence of hardness ions caused reduction of Cr removal from water to 33% by ZVI filled column. They have proven that the existence of calcium, magnesium and carbonate

ions in groundwater have vast impact on the ZVI by development of inactive deposits, such as CaCO_3 and $\text{Mg}(\text{OH})_2$, on the ZVI surface resulting in a decreased durability of the ZVI by preventing electron conduction (Lo et al. 2006). This result is in agreement with those reported by other works (Khalil et al. 2018). 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 is presumably to strongly change the capability of ZVI to reduce TCE (Cundy et al. 2008).

3.3.6 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) (Obiri-Nyarko et al. 2014).

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

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

As can be seen in Fig. 10, the results revealed that the both of 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 in the presence of calcium hardness and nitrate, respectively. This is consistent with the findings of other studies (Zhang et al. 2010, Zhang et al. 2017). Reduction of nitrate by ZVI has fitted well the pseudo-first order rate constant depending on nitrate concentration (Wang et al. 2018). 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 in 6.7 (Zhang et al. 2010). Denitrification by ZVI is primarily depends on pH, nitrate concentration and, surface-mediated process (Zhang et al. 2017).

Conclusion

The results 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 $\text{m}^3/\text{m}^2\cdot\text{d}$, $C_0 = 1 \text{ mg/l}$) was obtained 90.32%. The amount of MTBE removal was relying on pH, inflow and initial concentration. Therefore, with increasing each of these variables, removal amount of MTBE decreased. Existence of interference factors such as nitrate and hardness in the PRB system was impressive as these factors caused the reduction of system efficiency down to 44.46% and 51.4%,

respectively. Further investigation is necessary into the effect of multiple organic pollutants and ionic strength of water on the efficiency of MTBE removal in PRB system.

Declarations

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Data Availability

The authors declare that data supporting the findings of this study are available and were cited within the article.

Conflicts of Interest/Competing Interests

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

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Authors' Contributions

Ali Assadi instructed to the study's conception, design, supervision, data curation, funding acquisition and wrote the first draft of the paper. Sevda Naseri performed material preparation, data collection, experiments, analysis and wrote pre-draft. Mehran Mohammadian conducted methodology, validation, formal analysis. All authors reviewed and approved the final manuscript.

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Figures

Figure 1

Schematic of the experimental set-up

Figure 2

The role of blank column in MTBE removal at different inflow ($C_0 = 5 \text{ mg/L}$, $\text{pH}=7$)

Figure 3

Effect of retention time in Batch experiments ($C_0 = 5 \text{ mg/L}$, $\text{pH}=7$, $\text{rpm}=150$)

Figure 4

Effect of pH in the batch experiments ($C_0 = 5\text{mg/L}$, $\text{rpm} = 150$)

Figure 5

Effect of initial concentrations of MTBE in PRB system ($\text{pH} = 7$, $\text{HLR} = 0.57 \text{ m}^3/\text{m}^2\cdot\text{d}$)

Figure 6

Effect of flow rates in PRB system for MTBE removal ($C_0 = 1 \text{ mg/L}$, $\text{pH}=7$)

Figure 7

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

Figure 8

Effect of nitrate in PRB system for MTBE removal (pH= 7, C₀ =1mg/L, HLR= 0.23 m³/m².d)

Figure 9

Effect of hardness in PRB system for MTBE removal (pH= 7, C₀ =1mg/L, HLR= 0.23 m³/m².d)

Figure 10

Variations of kinetic reaction rates in the presence of nitrate and hardness at optimum condition (pH= 7, C₀ =1 mg/L, HLR= 0.23 m³/m².d, NO₃⁻= 180 mg/L, Ca²⁺= 200 mg/L