

Original Research

Zero-Valent Iron-Reactive Recirculation Wells for Remediation of Benzene and Toluene Contaminated Groundwater in Homogeneous and Nonhomogeneous Aquifers

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Abstract

Benzene and toluene contamination of groundwater can pose a serious threat to human health. Although extraction-treatment and other *ex-situ* remediation technologies can be used to rapidly reduce the concentration of pollutants at the initial stage of remediation, the inevitable tailing and rebound effects make it a research hotspot to explore more efficient *in-situ* remediation technologies. Groundwater circulating well is a kind of *in-situ* remediation technology for groundwater that is more and more widely used. This paper improves the removal efficiency of benzene and toluene by adding zero-valent iron reaction materials to the well structure, through the comparative experiment of homogeneous and heterogeneous aquifers, it is concluded that the remediation efficiency of pollutants in homogeneous aquifers is higher than that in heterogeneous aquifers. This paper provides a theoretical basis for the engineering practice of zero-valent iron reactive groundwater circulation well.

Keywords: benzene, toluene, groundwater circulation well

Introduction

Organic pollution of groundwater is a prominent problem, especially benzene and toluene as the representative of the benzene hydrocarbons pollution is very serious. [1-3]. Benzene and toluene, as organic solvents commonly used in industry, are widely used in industrial production, and at the same time, these substances are often used in the process of pesticide

production, so these pollutants are widely present in pesticide chemical contaminated sites [4-6]. The damage caused by benzene and toluene is enormous. Specifically, benzene can cause leukemia in adults and congenital defects in infants, toluene can harm the urinary system and retard bone growth, and even cause mutations and deformities in severe cases, which can affect muscle and bone growth and can also lead to deformities [7-9].

A number of domestic and international experts have proposed solutions for benzene contamination of groundwater. Kao et al. [10] monitored benzene at the gasoline leak site and obtained a daily natural attenuation

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rate of 0.036% for benzene. Mulligan et al. [11] quantified the rate of natural attenuation of benzene, and it took about 250 years for benzene contamination with an initial concentration of 900 mg/L to decay naturally. In terms of remediation materials, Sheikholeslami et al. [12] found that magnetic hematite nanoparticles have higher performance in removing benzene homologues, but they need to be activated under UV and visible light for benzene homologues wastewater treatment. Zahedniya et al. [13] used ZnO single-walled carbon nanotubes to remove benzene homologues from water by adsorption and found the most suitable conditions. Permeable reactive barrier are widely used for benzene contamination remediation, Bianchi-Mosquera et al. [14] used MgO_2 as oxygen releasing compound and Permeable reactive barrier technique to remove benzene and toluene from groundwater, and the concentration of both contaminants decreased significantly after 18 h of reaction.

The prototype of the recirculation well technology emerged from Dr. Raymond's experiments on aeration and aeration in wells in Germany [15], and Gvirtzman et al. [16] used gas lift technology in groundwater recirculation wells to treat VOCs, ultimately achieving good remediation results. The German company IEG created the vacuum gasification well technology around 1980, making it the first commercial application of the technology in Europe. Research institutions and universities in the United States innovated the technology several times around 1990 and conducted demonstration applications and technology evaluations on the technology in the Keesler, Massachu, and Edward Air Force Base projects in the U.S. Meanwhile, the recirculation well technology was greatly improved in structure and function [17-18]. Montgomery T. [19] used the recirculation well technology combined with biological remediation technology to treat benzene-contaminated groundwater, the recirculation well blow-off treated a portion of the volatile benzenes and also enhanced the activity of microorganisms in the subsurface environment, which enhanced the remediation effect.

The application of recirculation well technology in low permeability formations has been shown to be effective and feasible. Tatti et al. [20] conducted experimental and numerical evaluation of recirculation well technology as a remediation technology for source areas of persistent low permeability contaminants and concluded that recirculation well technology is more suitable than pump-and-treat technology for remediation of contamination in low permeability aquifers. Ciampi et al. [21] showed that recirculation wells enable pumping from very low permeable formations to pump lower groundwater to the upper part, which can circulate contaminants and more effectively facilitate the capture or adsorption of contaminants in low permeability formations. However, relatively few studies have been conducted to investigate the application of recirculation well technology in non-homogeneous formations.

In this study, zero-valent iron-reactive materials and recirculation well technology were organically combined to simulate zero-valent iron-reactive recirculation wells to treat benzene homologues contaminated groundwater in homogeneous and non-homogeneous aquifers. Experiments were conducted to determine the differences in remediation effectiveness between zero-valent iron-reactive recirculation wells in homogeneous and non-homogeneous aquifers, and to provide data to support future applications of recirculation wells in actual sites.

Material and Methods

Materials

The VOC standard (1000 mg/L) was purchased from Amperex Co. The VOC mixed internal standard (2000 mg/L) and the VOC substitute (2000 mg/L) were purchased from Tanmo Co. The 0 # gasoline is purchased from Sinopec.

Characterization

The determination of benzene and toluene was performed by water quality determination of volatile organic compounds by purge trap/gas chromatography-mass spectrometry (TELEDYNE, ATOMXxyz). purge flow rate: 40 ml/min; purge time: 11 min; dry purge time: 1 min. Gas chromatograph model 7890B/5977B (Agilent), inlet temperature: 220°C, injection method: split injection (split ratio 30:1). The detection limits for both benzene and toluene were 0.1 $\mu\text{g/L}$. The concentrations of benzene and toluene were determined for each frontal sampling port at each time, and the kriging interpolation in Sufer was used to derive benzene and toluene concentration plots.

Zero-Valent Iron-Reactive Circulation Wells

Zero-valent iron reactive circulation wells are obtained by upgrading the circulation wells. The application in the simulation tank was considered, a suitable size and structure of zero-valent iron reactive circulation well was made by using acrylic material. The zero-valent iron reactive circulation well mainly consists of inner well pipe, outer well pipe, flange, well cover, upper and lower flower holes, packer, tail gas pipe, aeration head and aeration pipe, and other structural components, as shown in Fig. 1. The total length of the outer well of the circulating well is 63 cm, the length of the outer well pipe below the flange well cover is 60 cm, the diameter of the outer well pipe is 12 cm, the length of the upper flower hole of the outer well pipe is 10 cm, the length of the lower flower hole of the outer well pipe is 6 cm, the length of the inner well pipe is 49 cm, the inner diameter of the inner well pipe is 5 cm, the zero-valent

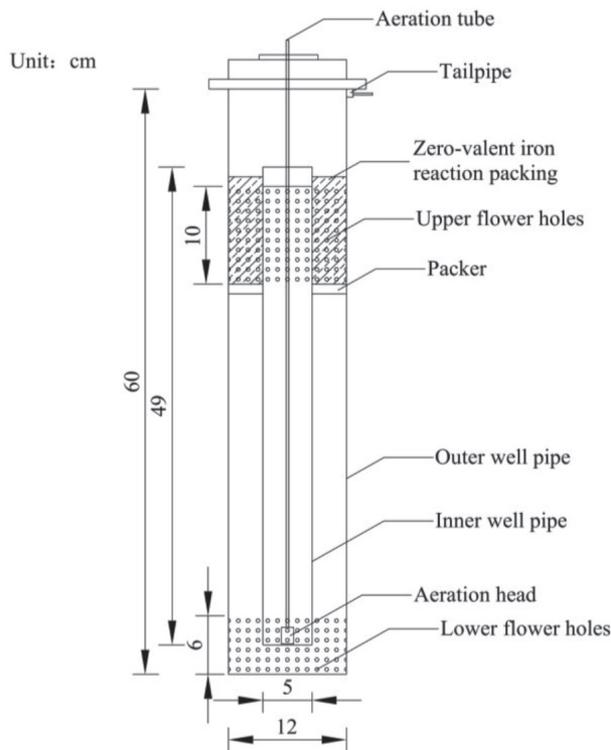


Fig. 1. The zero-valent iron reactive circulation well structure.

iron is filled in the circular area between the inner well and the outer well pipe above the packer, the single filling amount is 2.5 kg of common iron powder, the filling height should not exceed the height of the inner well. The filling height should not exceed the upper edge of the inner well.

The contaminated groundwater enters via the lower flower hole of the outer well pipe of the zero-valent iron reaction type circulation well, and after aeration by the

aeration pipe, transported upward to the reaction bin by the inner well pipe of the zero-valent iron reaction type circulation well, and then the contaminated groundwater flows through the reaction of the zero-valent iron powder package and flows out of the circulation well by the upper flower hole of the outer well pipe, and the cycle is repeated. The volatile gas is discharged to the VOCs treatment unit through the upper tail gas pipe.

The Homogeneous Simulation Tank Structure

The experiments were carried out in a two-dimensional acrylic simulation tank with the dimensions of 130 cm×30 cm×80 cm (length×width×height), and the water distribution area and the water discharge area with a width of 10 cm on the left and right sides of the simulation tank. The distance between two adjacent rows of sampling ports is 10 cm, the distance between two adjacent columns of sampling ports is 20 cm, the distance between the outermost sampling port and the partition is 15 cm, and the zero-valent iron-reactive circulation well is wrapped with filter cloth and placed in the middle position between the third and fourth columns of sampling ports, and the simulation tank is filled with medium sand with a thickness of 56 cm, which is used as medium for water content, and is filled in layers and continuously compacted. The whole simulation tank is covered with a layer of clay with a thickness of 1 cm, and the leakage source is located in the middle of the sampling port between column 1 and column 2, and is located between the sand layer and the clay layer, which effectively inhibits the volatilization of VOCs. As the specific structure is shown in Fig. 2.

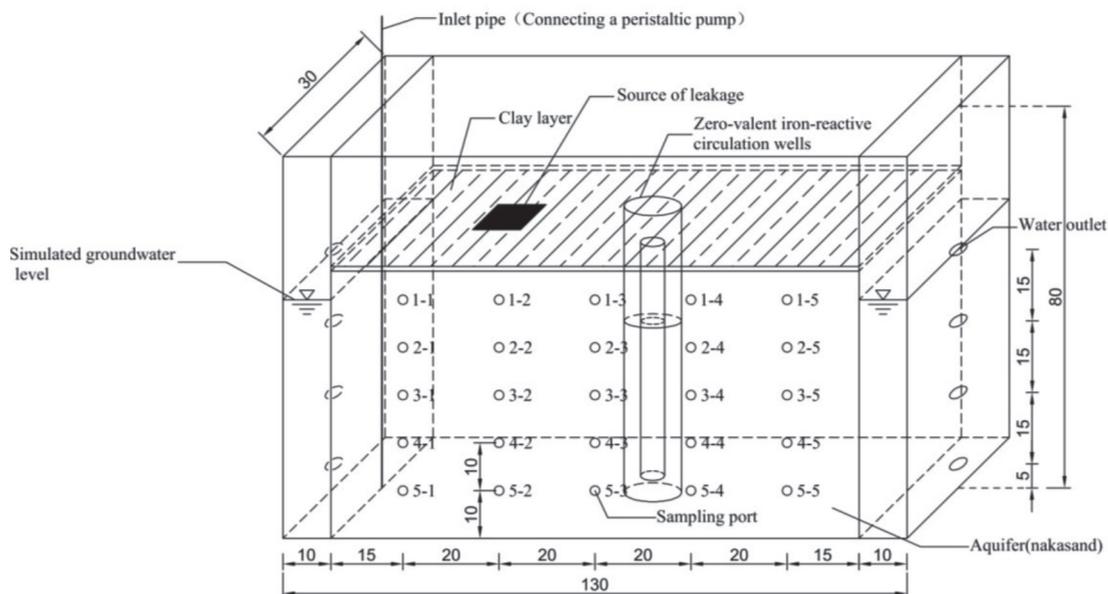


Fig. 2. The non-homogeneous simulation tank structure (Unit:cm).

The Non-Homogeneous Simulation Tank Structure

The distance of adjacent two rows of sampling ports is 10 cm, the lowermost sampling port is 5 cm from the bottom plate of the simulation tank, the distance of adjacent two columns of sampling ports is 20 cm, the distance of the outermost sampling port from the partition is 15 cm, the zero-valent iron reactive circulation well wrapped with filter cloth is placed in the middle position between the third and fourth columns of sampling ports, the simulation tank is filled with medium sand of 56 cm thickness, which is used as medium sand as water-bearing medium, loaded in layers and continuously compacted, the filling density, permeability coefficient and porosity are consistent with the homogeneous water-bearing sand tank. In contrast to the homogeneous water-bearing sand trough, two lenses composed of clay are filled between 2-1 and 3-2, and between 3-4 and 4-5. Finally, the whole simulation tank is covered with a layer of clay with a thickness of 1 cm, and the leakage source is located in the middle of the sampling port between column 1 and column 2, and between the sand layer and the clay layer, which effectively inhibits the volatilization of VOCs. The specific structure is shown in Fig. 3.

Experimental Method

Contaminant dosing and transport experiments were completed, the concentration of pollutants at the zero-valent iron-reactive circulation wells in the simulation tank was not too high at this time, and in order to achieve the effect of the remediation experiments, the pump flow rate was adjusted and the experimental device was set to simulate a groundwater flow rate of 2.89×10^{-7} m/s with a one-time injection of 50 ml of 0 #

diesel fuel at the leak source. Samples were taken once every 24 h. After determining that the contamination halo had been distributed throughout the simulated tank, the zero-valent iron-reactive groundwater circulation well was turned on and the aeration rate was set to 0.0002 m³/s. Frontal sampling ports were sampled at 1 h, 3 h, 5 h, 8 h, 12 h and 24 h, respectively, and laboratory tests were performed at the specified time after sampling to analyze the changes in petroleum hydrocarbon concentrations.

Results and Discussion

Remediation Data Analysis of Contaminants in Homogeneous Simulation Tanks

After the contaminants were restocked in the homogeneous simulation tank, the contamination halo of contaminants was distributed throughout the simulation tank after showing a higher concentration around the zero-valent iron-reactive groundwater circulation wells, as shown in Fig. 4 the highest concentration of benzene in the simulation tank was 198.36 mg/L. Toluene was 390.25 mg/L, which was mainly due to the fact that the groundwater around the well body before the well body was started. The phenomenon of bypass flow occurs, so that the groundwater in the well body and the external water quality exchange rate is less than the surrounding groundwater medium. Upon clarification of the aquifer media characteristics, groundwater flow direction and velocity, contaminant type, concentration and contamination range and other prerequisites, the petroleum hydrocarbon contaminated aquifer was remediated using zero-valent iron-reactive groundwater circulation well technology.

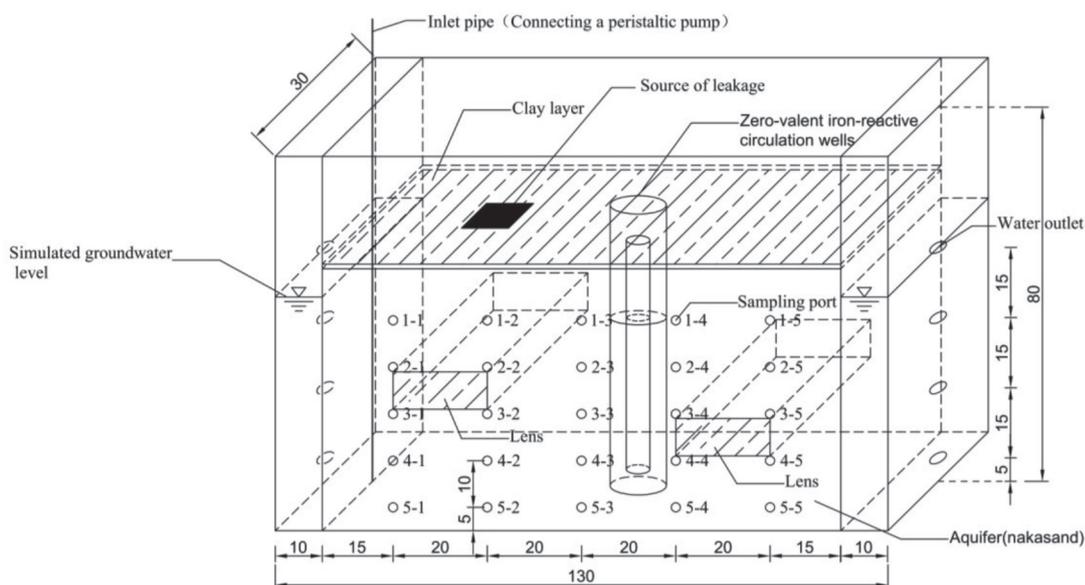


Fig. 3. The Non-homogeneous simulation tank structure (Unit:cm).

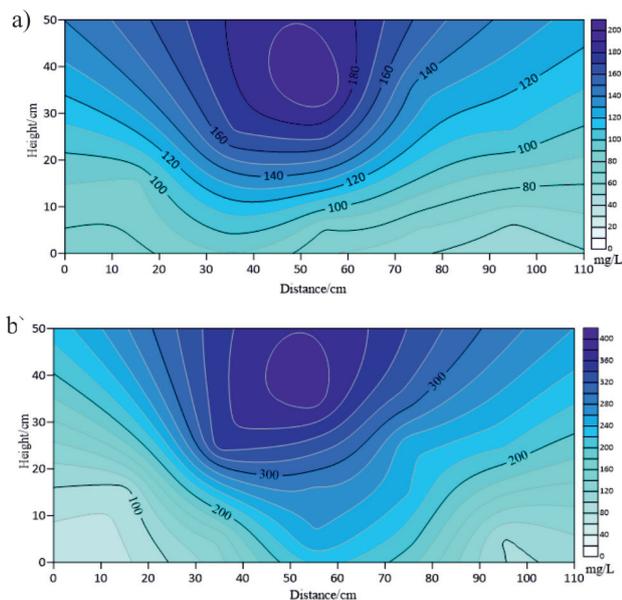


Fig. 4. Initial pollutant concentration (Unit:mg/L). a) Initial benzene concentration in the homogeneous simulation tank; b) Initial toluene concentration in the homogeneous simulation tank.

As can be seen from Figs 5 and 6, after the zero-valent iron-reactive circulation well was launched, the concentrations of benzene and toluene in the simulated tank decreased rapidly, and at 1 h of reaction, the maximum concentration of benzene had decreased to 29.41 mg/L with an average concentration of 16.72 mg/L, and the maximum concentration of toluene had decreased to 151.31 mg/L with an average concentration of 98.03 mg/L. At 3 h of reaction, the maximum

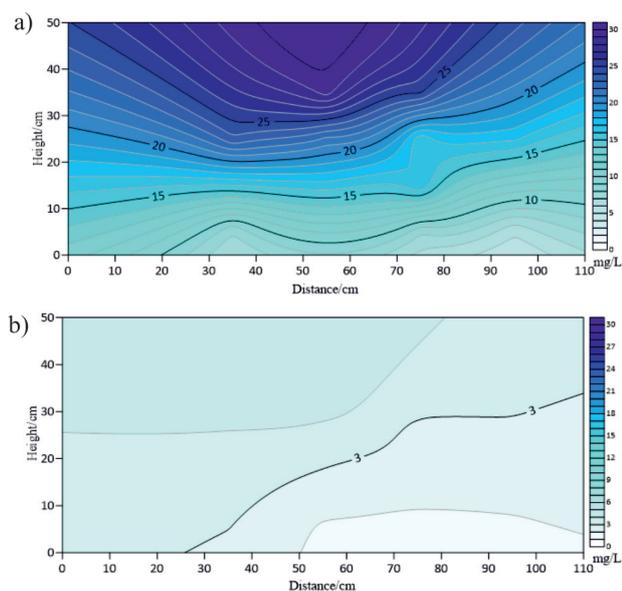


Fig. 5. Variation of benzene concentration in homogeneous simulation tank (Unit:mg/L); a) Plot of benzene concentration at 1 h, b) Plot of benzene concentration at 3 h.

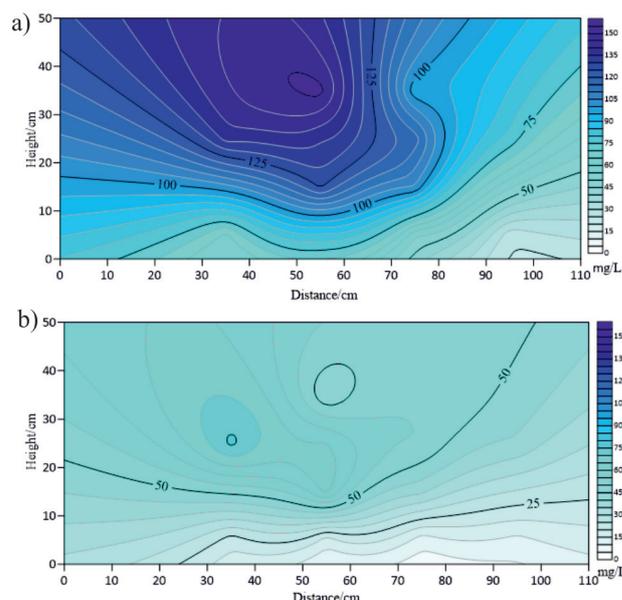


Fig. 6. Variation of toluene concentration in homogeneous simulation tank (Unit:mg/L); a) Plot of toluene concentration at 1 h, b) Plot of toluene concentration at 3 h.

concentration of benzene had decreased to 4.95 mg/L with an average concentration of 2.89 mg/L, and the maximum concentration of toluene had decreased to 76.16 mg/L with an average concentration of 41.64 mg/L. The maximum concentration of benzene dropped to 4.95 mg/L with an average concentration of 2.89 mg/L and the maximum concentration of toluene dropped to 76.16 mg/L with an average concentration of 41.64 mg/L. As the reaction proceeded, the

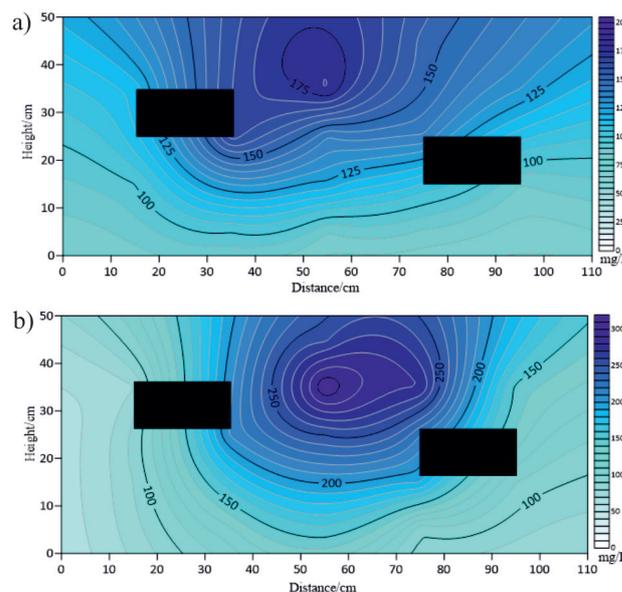


Fig. 7. Initial pollutant concentration (Unit:mg/L); a) Initial benzene concentration in the non-homogeneous simulation tank, b) Initial toluene concentration in the non-homogeneous simulation tank.

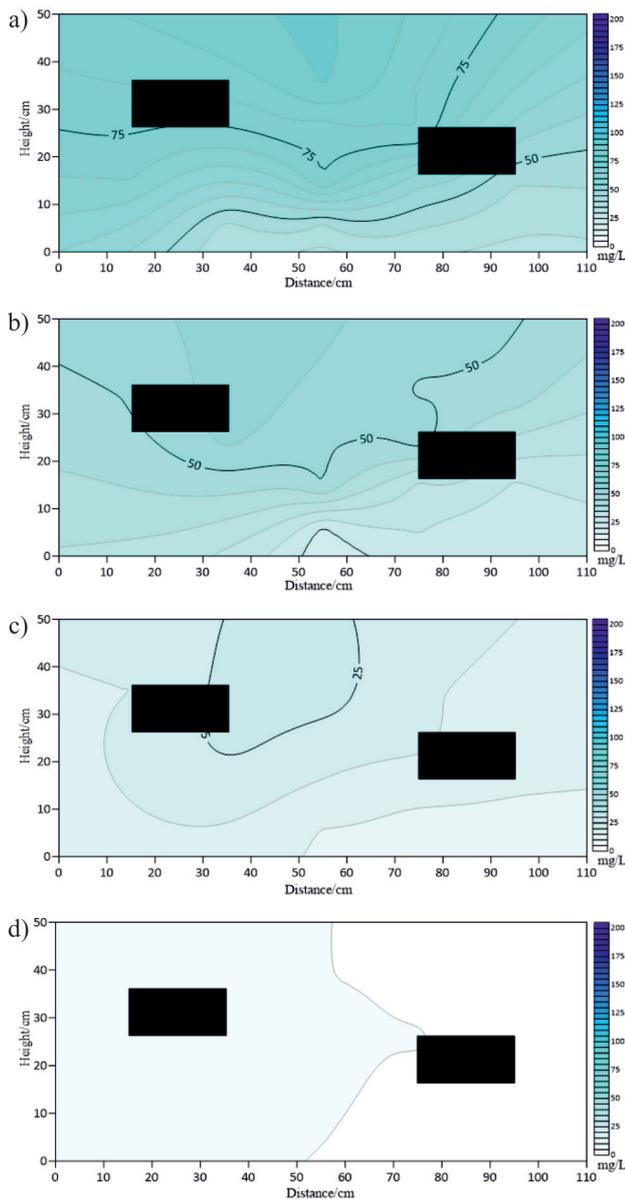


Fig. 8. Variation of benzene concentration in a non-homogeneous simulation tank (Unit:mg/L); a) Plot of benzene concentration at 1 h, b) Plot of benzene concentration at 3 h, c) Plot of benzene concentration at 5 h, d) Plot of benzene concentration at 8 h.

concentrations of benzene and toluene in the simulated tank were lower than the detection limit at 5 h, and the simulated tank was completely clean of benzene and toluene at this time.

Remediation Data analysis of Contaminants in Non-Homogeneous Simulation Tanks

After the re-addition of pollutants in the non-homogeneous simulation tank, the pollutants were concentrated between the upper and lower lenses, as shown in Figs 7, the highest concentration of benzene in the simulation tank was 180.46 mg/L and toluene was 309.45 mg/L. This was mainly due to the different adsorption of benzene and toluene by the lenses, which

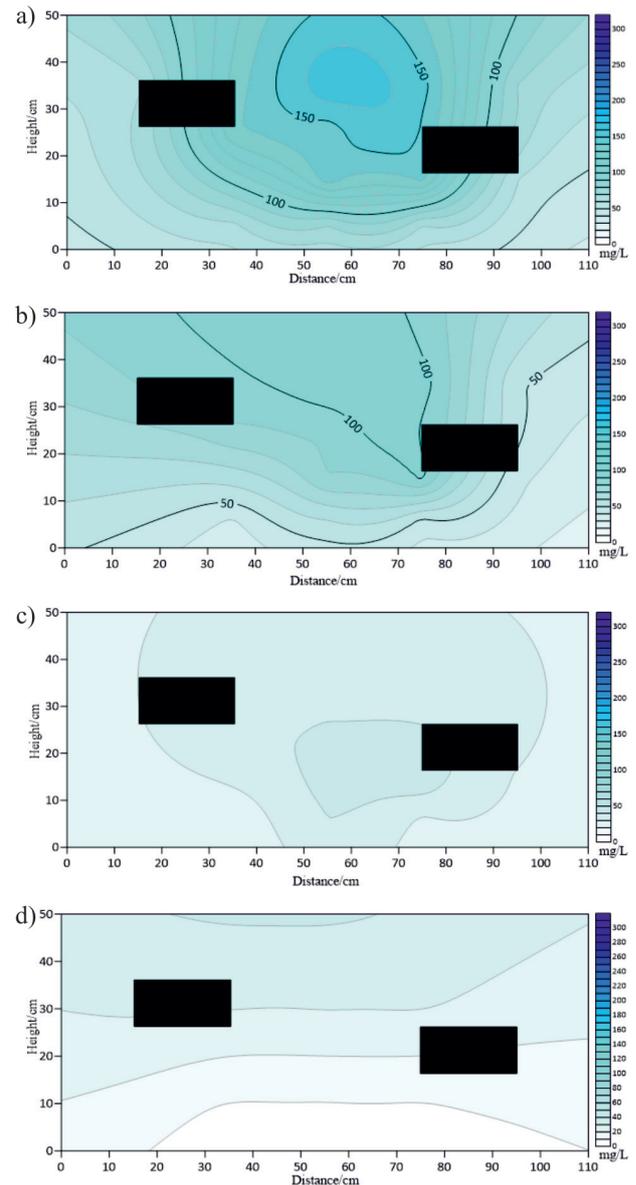


Fig. 9. Variation of toluene concentration in a non-homogeneous simulation tank (Unit:mg/L); a) Plot of toluene concentration at 1 h, b) Plot of toluene concentration at 3 h, c) Plot of toluene concentration at 5 h, d) Plot of toluene concentration at 8 h.

hindered the migration of pollutants and caused the pollutants to collect in the two lenses between the two lenses. After clarifying the prerequisites of aquifer media characteristics, groundwater flow direction and velocity, pollutant types, concentrations and pollution ranges, the zero-valent iron-reactive groundwater recycling well technology was used to remediate the petroleum hydrocarbon-contaminated aquifer.

As shown in Figs 8 and 9, the concentrations of benzene and toluene in the simulated tank decreased rapidly immediately after the start of the zero-valent iron-reactive circulation well, but the restoration effect was still different compared to that in the homogeneous reaction tank. In the non-homogeneous reaction tank, the maximum concentration of benzene decreased

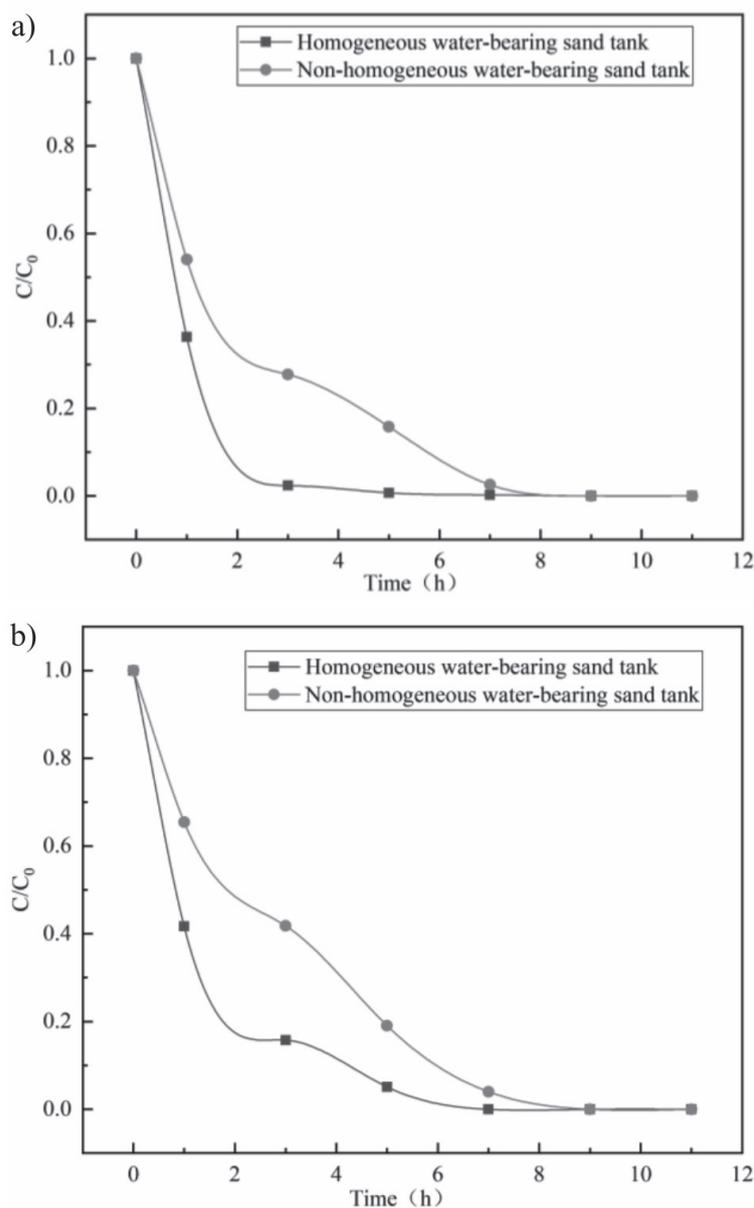


Fig. 10. 3-2 C/C_0 plots of benzene and toluene at the sampling port: a) Plot of benzene C/C_0 variation at 3-2 sampling port, b) Plot of toluene C/C_0 variation at 3-2 sampling port.

to 90.15 mg/L and the average concentration was 65.55 mg/L at 1 h. The maximum concentration of toluene decreased to 167.26 mg/L and the average concentration was 112.38 mg/L. At this time, the pollutants were still enriched between the two lenses; at 5 h, the maximum concentration of benzene decreased to 27.45 mg/L and the average concentration was 35.70 mg/L. At 5 h of reaction, the maximum concentration of benzene dropped to 27.45 mg/L and the average concentration was 35.70 mg/L, and the maximum concentration of toluene dropped to 47.35 mg/L and the average concentration was 35.77 mg/L; at 8 h of reaction, the maximum concentration of benzene had dropped to 7.12 mg/L and the average concentration was 4.90 mg/L, and the maximum concentration of toluene dropped

to 15.67 mg/L and the average concentration was 12.22 mg/L. As the reaction proceeded, the concentrations of benzene and toluene in the simulation tank were lower than the detection limit at 12 h, and the benzene and toluene in the simulation tank had been completely treated.

To further illustrate the effect of non-homogeneous conditions on the remediation effect of zero-valent iron-reactive recirculating wells, sampling ports 3-2 and 4-4 were selected, and the contaminant concentration at the sampling port at the beginning of remediation was C_0 , and the contaminant concentration at the sampling port at each moment was C . With C/C_0 as the vertical coordinate and the remediation time as the vertical coordinate, Figs 10 and 11 were plotted, and when C/C_0 in the figure was zero, it indicates that the pollutant

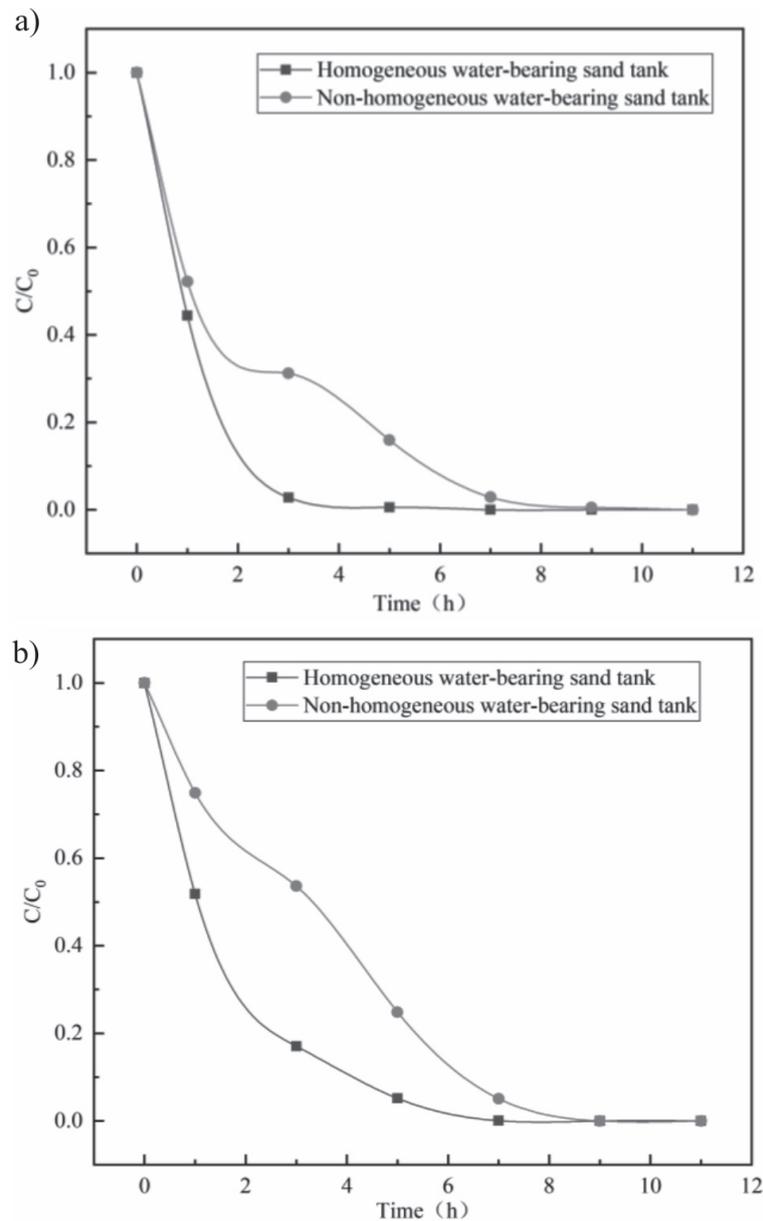


Fig. 11. 4-4 C/C_0 plots of benzene and toluene at the sampling port: a) Plot of benzene C/C_0 variation at 4-4 sampling port, b) Plot of toluene C/C_0 variation at 4-4 sampling port.

is no longer detectable at this sampling port. It can be seen from the graphs that the remediation effect in the non-homogeneous simulation tank is significantly reduced compared to the homogeneous simulation tank. The benzene was completely removed in the homogeneous simulation tank in about 5 h, but it took about 8 h to be completely removed in the non-homogeneous simulation tank. Similarly, toluene was completely removed in the homogeneous simulation tank in about 7 h, but it took 9 h to be removed in the non-homogeneous simulation tank.

In addition, the average concentration of pollutants at all sampling ports in the homogeneous simulated tank at the start of remediation was used as the initial concentration C_0' , and the average concentration of pollutants at all sampling ports in the simulated

tank at different cumulative aeration times was used as C' , and C_0'/C' was used as a relative average concentration to quantitatively characterize the remediation efficiency of zero-valent iron-reactive recirculation wells. C_0'/C' as a relative average concentration, the zone to quantitatively characterize the remediation efficiency of zero-valent iron-reactive recirculation wells, the results are shown in Fig. 12 above. the change of relative average concentration can be divided into the following three main stages.

(1) The rapid removal phase of benzene and toluene during the initial 0-1 h of aeration, where the average concentrations of benzene and toluene decreased by 65% and 36%, respectively, to 35.21 mg/L and 130.24 mg/L, with average removal rates of 1.35 mg/min and 1.18 mg/min, respectively.

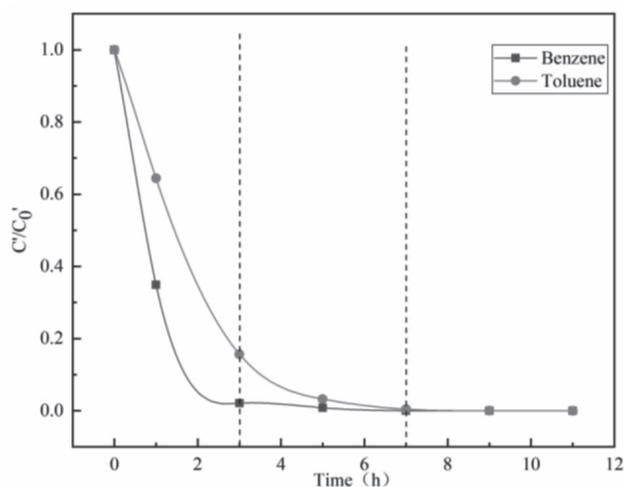


Fig. 12. Fitting results for the average concentration of benzene and toluene at different aeration times in homogeneous simulation tank.

(2) The relative average concentrations of benzene and toluene fluctuated and decreased during the 1st-7th hours of cumulative aeration, and the relative average concentrations of benzene and toluene decreased by 99% and 99% after 7 h of cumulative aeration, with the average concentrations reaching 0.02 mg/L and 0.89 mg/L, respectively.

(3) After the cumulative aeration of 9, benzene and toluene were no longer detectable in the groundwater in the simulation tank, and the pollutants were completely removed.

Conclusion

The main conclusions from the experiments of zero-valent iron-reactive circulation wells for benzene and toluene remediation in homogeneous and non-homogeneous aquifers are as follows.

(1) Zero-valent iron-reactive circulation wells are effective in remediating benzene and toluene in both homogeneous and non-homogeneous aquifers, but their efficiency in remediating contaminants in homogeneous simulated tanks is completely higher than their efficiency in non-homogeneous simulated tanks.

(2) The process of benzene and toluene remediation by zero-valent iron-reactive recirculation wells is divided into three main parts, starting with a rapid removal phase, followed by a fluctuating decline, and finally, a complete removal.

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Conflict of Interest

The authors declare no conflict of interest.

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