Original Research

Study on the Effectiveness of Reactive Circulation Wells for Remediation of Benzene and Toluene Contaminated Groundwater

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Abstract

A static batch test was used to determine the optimal ratio of Fenton's reagent for removing benzene and toluene from contaminated subsurface at a site, followed by a two-dimensional simulation tank experiment, where benzene and toluene were distributed throughout the tank, and then in the groundwater circulation wells. The Fenton's reagent of 0.05 L of 3% H_2O_2 and 6.12 g of $FeSO_4 \cdot 7H_2O$ was added in the ratio of 0.05 L of 3% H_2O_2 and 6.12 g of $FeSO_4 \cdot 7H_2O$, and the reactive circulation wells were initiated at an aeration rate of 15 L/min.The results show:The groundwater circulation close to the circulation wells is highly disturbed, the mass transfer between the gas and water phases is strong, benzene and toluene are preferentially removed, and a remediation area centered on the circulation wells is gradually formed; after 12 h of cumulative aeration, contaminants within a 50 cm radius from the circulation well were below the detection limit. Residual benzene and toluene were concentrated in the area on both sides of the simulation tank, away from the circulation well. The contaminant removal efficiency within the 50-cm radius of influence of the circulation wells was high, and the enhanced remediation of benzene- and toluene-contaminated groundwater by reactive circulation wells using Fenton's reagent as the remediation agent was more effective.

Keywords: groundwater, benzene, toluene, reactive circulation wells

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Introduction

Benzene and toluene are the most common components of organic pollutants in groundwater [1, 2], and groundwater circulation well technology is a more effective in-situ remediation method for removing volatile organic compounds from groundwater [3], which has the significant advantages of low-cost, high-efficiency, and in-situ operation [4], and has been used in recent years in in-situ remediation projects in China [5]. Traditional groundwater circulation wells are divided into aerodynamically driven and hydraulically driven, this paper takes aerodynamically driven circulation wells as the object of study [6, 7], the principle of which is that the aeration head in the circulation well's inner well tube aeration generates less dense gas-water mixtures, migrating upward along the inner well tube, the water level is raised, and the inner and outer well tubes generate a difference in density, and the gas-water mixtures flow out from the upper orifice at the same time that the groundwater continuously flows into the wells from the lower orifice. The gas-liquid mixture is separated at the upper orifice, where clean air blows benzene and toluene out of the groundwater, and the exhaust gases are discharged through the tailpipe. Continuous aeration creates a three-dimensional groundwater cycle around the circulation well [8-10].

Numerous studies have shown that the main factors affecting the remediation efficiency of hydraulic groundwater circulation wells are the hydrogeological characteristics of the target treatment area, the operational characteristics of the groundwater aeration volume, the method of aeration, the location of the aeration, and the composition of the contaminants and their nature [11].Combining the traditional groundwater circulation well technology with in-situ chemical oxidation [12], by adding chemical oxidation remediation agents appropriately in the circulation wells, on the one hand, pollutants can be realized to fully react with the agents during the circulation process of the inner wells from the bottom to the top, and on the other hand, the agents will be mass-transferred to the radius area of influence of the groundwater circulation [13] to achieve further pollutant removal within the area of influence around the circulation wells [14], and to enhance the overall remediation efficiency of the pollution control area [15].

In this study, Fenton's reagent, which is effective in the remediation of benzene and toluene, was selected as the chemical oxidation remediation agent [16, 17], and the amount of additive in the simulation experimental device was precisely calculated to avoid the problem of secondary contamination caused by overdose of the reagent [18]. The optimization of the reactive recirculation wells was achieved through the addition of the reagent into the inner wells of the traditional recirculation wells [19], and the attenuation of benzene and toluene was explored under the enhanced effect of Fenton's reagent. The results of the study are very inspiring for expanding the remediation efficiency of traditional groundwater recirculation wells by optimizing the well structure or coupling other remediation technologies within the wells, and also provide a basis for the application of reactive groundwater recirculation wells to benzene and toluene contaminated sites in engineering practice.

Experimental Materials and Equipment

Experimental Materials and Medicines

The powdered sand used in the experiment was purchased from a sand quarry in Suzhou, sieved after drying for particle size (0.0625 mm~0.0039 mm), pH = 7.06. The clay was taken from a plot of land in Suzhou, and crushed after drying. The classification of sand and clay is based on GB/T 50145-2007 Standard for Engineering Classification of Soil. The grain size of quartz sand is 0.6~1 cm. The particle size of activated carbon was 1.18-2.36 mm. 3% H_2O_2 was produced by Shandong Lilcon Medical Technology Co. and $FeSO_4 \cdot 7H_2O$ was analytically pure, produced by Tianjin Yongda Chemical Reagent Co.

Experimental Set-Up

Analogue Tanks

The simulation tank is made of acrylic, with dimensions of 135 cm×40 cm×100 cm (L×W×H), and consists of three parts, namely, the left water distribution tank, the middle simulated water-containing tank, and the right drainage tank, with the length of the water distribution tank and the drainage tank being 10 cm, and the length of the simulated water-containing tank being 115 cm. A total of 45 sampling ports were located on the front side of the simulation tanks, with adjacent ports 11 cm apart, and the water distribution and drainage channels were filled with quartz sand to provide uniform water distribution and drainage. The simulation tank was filled with powdered sand with a thickness of 54 cm and the powdered sand was covered with 6 cm of clay. The recirculation wells were placed in the center of the sixth and seventh columns of the sampling ports on the front of the simulation tank, and the tailpipes of the recirculation wells were connected to the activated carbon adsorption tank. A schematic diagram of the simulation tank is shown in Fig. 1.

Reactive Circulation Wells

Circulation well mainly includes inner well pipe, outer well pipe, flange, well cover, upper and lower flower holes, sealer, tail gas pipe, dosing pipe, aeration head and aeration pipe and other structural components. The total length of the circulation well is 63 cm, the
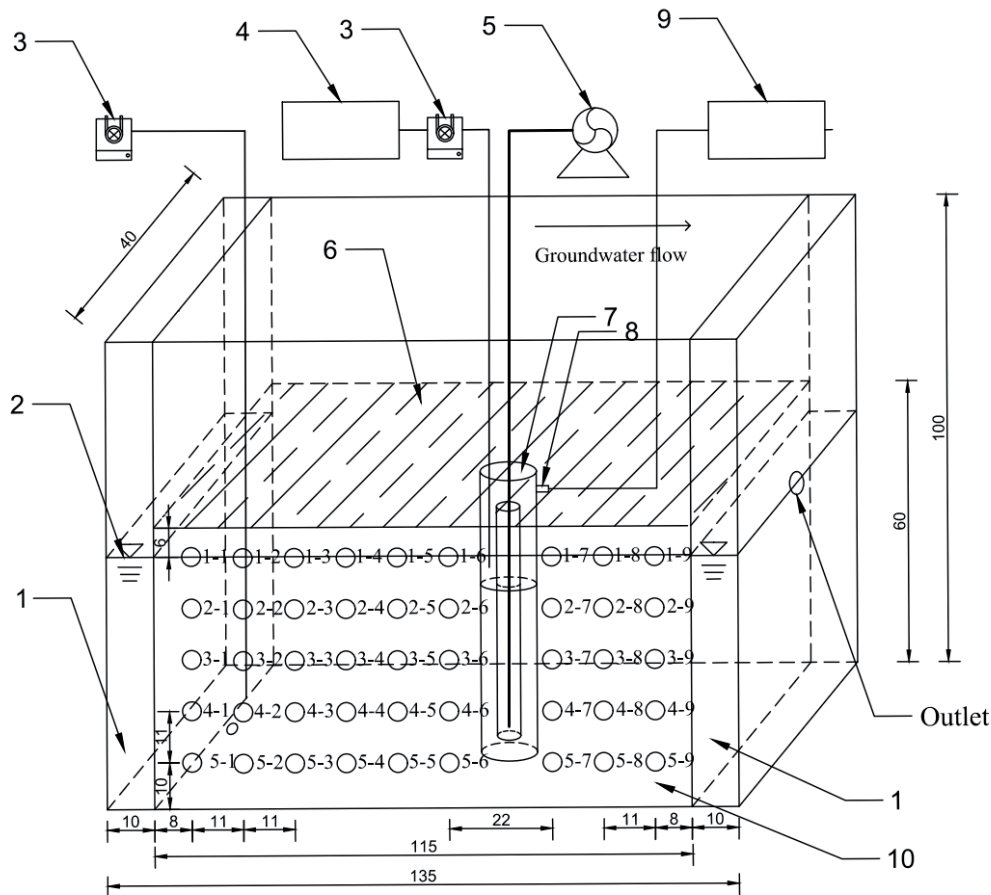
1、Quartz sand 2、Simulated groundwater level 3、Peristaltic pump 4、Fenton Kit 5、Aeration pump 6、Clay
7、Circulation well 8、Exhuast pipe 9、Activated carbon adsorption box 10、Aquifer（Powder sand）

Fig. 1. Schematic diagram of the simulation tank (unit: cm).

length of the outer well pipe below the flange cover is 60 cm, the outer well pipe has an outer diameter of 12 cm, the length of the upper perforation of the outer well pipe is 10 cm, the length of the lower perforation of the outer well pipe is 6 cm, the length of the inner well pipe is 49 cm, and the inner diameter of the inner well pipe is 5 cm.Small holes are made in the top of the well cap, and the infusion tube is placed between the inner and outer well tubes through the small holes, and the mouth of the infusion tube is placed in the middle of the upper flower hole. The schematic diagram of the circulation well is shown in Fig. 2.

When aeration is in progress, the contaminated groundwater enters the circulation well from the lower flower hole of the well pipe outside the circulation well, and after aeration in the aeration head the contaminated groundwater rises along the well pipe inside the circulation well to the upper flower hole of the circulation well, where it contacts and reacts with Fenton's reagent and flows out of the well.
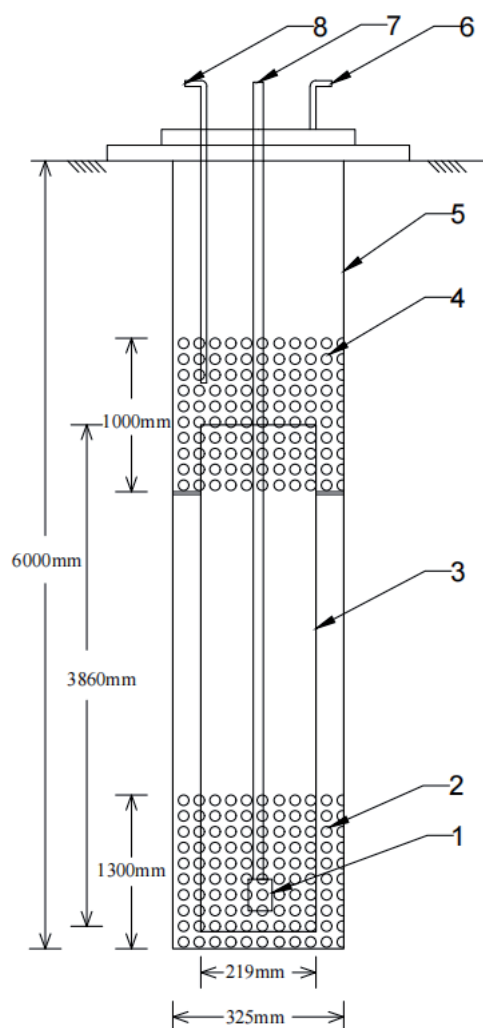
Experimental Methods

Experimental Method of Fenton's Reagent Repair Effect

The experimental water was benzene- and toluene-contaminated groundwater from a contaminated site in Suzhou, with a concentration of 40.61 mg/L for benzene and 38.34 mg/L for toluene.

Determine the ratio of Fenton's reagent hydrogen peroxide and divalent iron, take five 1 L beakers, respectively, add 500 ml of experimental water, control the molar ratio of H_2O_2/pollutant = 5:1, respectively, according to the molar ratio of H_2O_2/Fe^{2+} = 2:1, 4:1, 6:1, 8:1, 10:1 to the beaker with 3% H_2O_2 and $FeSO_4 \cdot 7H_2O$, stirring for 12 h and then take the sample The samples were taken after 12 h. The changes in benzene and toluene concentrations were measured.

Determine the ratio of hydrogen peroxide to contaminants in Fenton's reagent, take five 1 L beakers, add 500 ml of contaminated groundwater from the site, control the molar ratio of H_2O_2//Fe^{2+} = 2:1, and add

1、 Aerator 2、 Lower Floral Hole 3、 Internal well pipe 4、 Upper Floral Hole 5、 External well pipe 6、 Exhust pipe 7、 Aerator pipe 8、 Dosing tube

Fig. 2 Circulation well structure.

3% H_2O_2 and $FeSO_4 \cdot 7H_2O$ to the beakers at the molar ratio of H_2O_2/contaminants = 5:1, 10:1, 15:1, 20:1, 25:1, respectively. The samples were taken after 12 h of stirring to determine the changes in pollutant concentration.

Experimental Methodology for Reactive Recirculating Well Rehabilitation Simulation Tanks

The experimental water used was benzene and toluene contaminated groundwater from a contaminated site in Suzhou, with benzene concentration of 40.61 mg/L and toluene concentration of 38.34 mg/L. The simulated groundwater flow direction was from left to right, and the simulated groundwater flow rate was 0.05 m/d through the simulation tank, with an adjusted groundwater level of 54 cm.When the pollutant is fully distributed in the simulation tank, it is done as the initial pollution concentration.Fenton's reagent is formulated according to the static batch test results and the initial contamination concentration. The completed Fenton's reagent is added to the dosing device and injected through a peristaltic pump between the inner and outer well tubes of the circulating wells, and the dosing time is completed within five minutes.

The aeration head was set at the lower 1 cm of the well pipe in the recirculation well and aeration was carried out at a flow rate of 15 L/min. Samples were taken at 1 h, 3 h, 5 h, 8 h, 12 h, 16 h, 20 h and 24 h of aeration, respectively, to determine the changes in benzene and toluene concentrations.

Sample Analysis Methods

The concentrations of benzene and toluene in the samples were determined using the "HJ 639-2012 Water Quality Determination of Volatile Organic Compounds Blow Trap/Gas Chromatography-Mass Spectrometry", and the models of the instruments used and the parameters of the tests are shown in Table 1 below.

Table 1. Instrument models and test parameters.

| No.	Instrument name	Models	Company	Parametric
1	Gas chromatograph	7890B/5977B	Aglient	Inlet Temp.: 220ºC Injection mode: Split-flow injection (split-flow ratio = 30:1) Carrier gas: Nitrogen (5.10); flow rate:1.0 ml/min)
2	Ion source	EI source	/	Ion source temperature: 230 ºC; Ionization energy: 70 eV; Solvent delay: 2.0 Min; Interface temperature: 280 ºC
3	Purge trap	ATOMXxyz	TELEDYN	The control temperature is room temperature; Purging flow rate: 40 ml/min; Blow down time:11 mi; When dry blowing:1 min; Pre-desorption temperature:180 ºC; Desorption temperature:190 ºC; Desorption time:2 min; Baking temperature:200 ºC; Baking time: 6 min

a)

b)
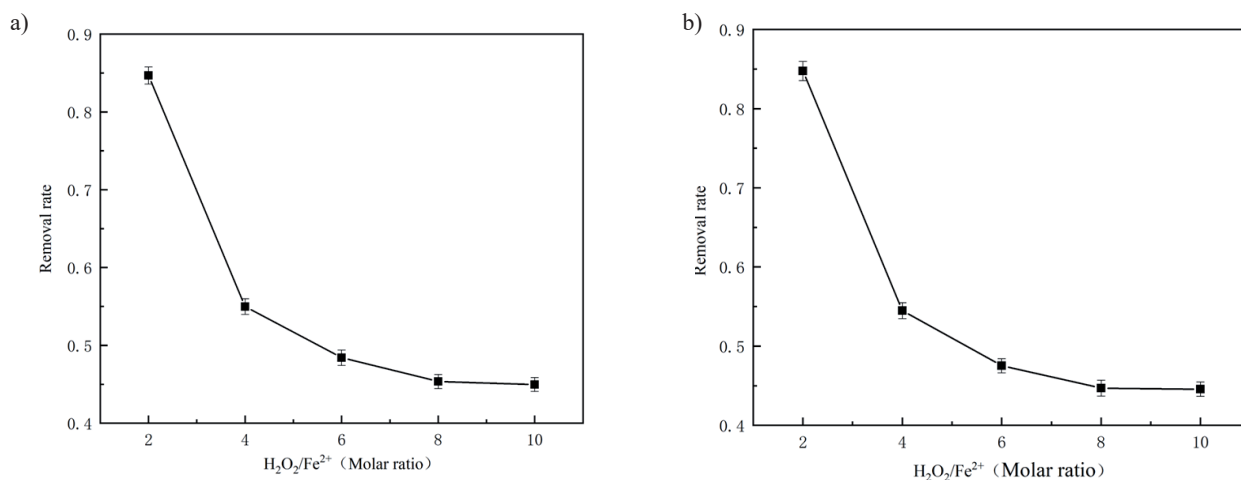
Fig. 3. Effect of variation in the molar ratio of H_2O_2 and Fe^{2+} on the effectiveness of remediation. a) Change in benzene removal rate, b) hange in toluene removal rate.

Analysis of Results

Analysis of Experimental Results on the Restoration Effect of Fenton's Reagent

Analysis of Experimental Results for Different H_2O_2 and Fe^{2+} Molar Ratios

Groundwater ORP increased from -134 mV to 457 mV and pH decreased from 6.85 to 3.84 before and after the addition of Fenton's reagent at molar ratios H_2O_2/contaminant = 5:1 and H_2O_2//Fe^{2+} = 2:1.

Fixing the molar ratio of H_2O_2 and pollutants as 5:1 and varying the molar ratio of H_2O_2 and pollutants, the concentration of each pollutant after 12 h of reaction is shown in Fig. 3 as a graph of the change in the molar ratio of H_2O_2 and Fe^{2+}.

As can be seen from Fig. 3, when the H_2O_2/pollutant molar ratio = 5:1, varying the H_2O_2/Fe^{2+} molar ratio, the removal of pollutant concentration decreases

Table 2. Variation of pollutant concentration with molar ratio of H_2O_2 and pollutant.

No.	Molar ratio of H_2O_2 to pollutant	Benzene concentration (mg/L)	Toluene concentration (mg/L)
1	5:1	6.220	5.840
2	10:1	0.001	0.062
3	15:1	0	0
4	20:1	0	0
5	25:1	0	0

Table 3. Variation of pollutant removal rate with molar ratio of H_2O_2 and pollutants Molar ratio of H_2O_2 and pollutant.

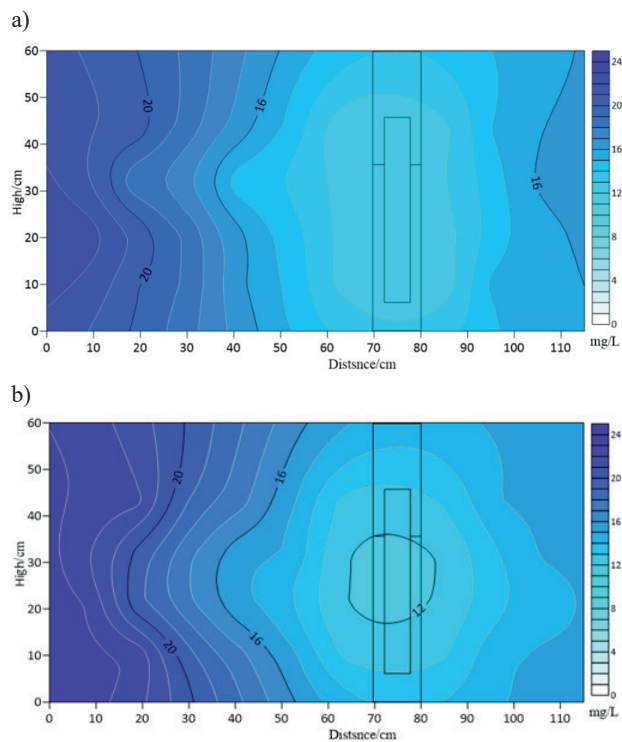| No.	Molar ratio of H_2O_2 to pollutant	Benzene removal rate	Toluene removal rate
1	5:1	84.68%	84.77%
2	10:1	99.99%	99.84%
3	15:1	100.00%	100.00%
4	20:1	100.00%	100.00%
5	25:1	100.00%	100.00%

a)

b)

Fig. 4. Graph of initial concentration of pollutants in modelled tanks (unit: mg/L). a) Initial benzene concentration graph, b) Initial toluene concentration graph.
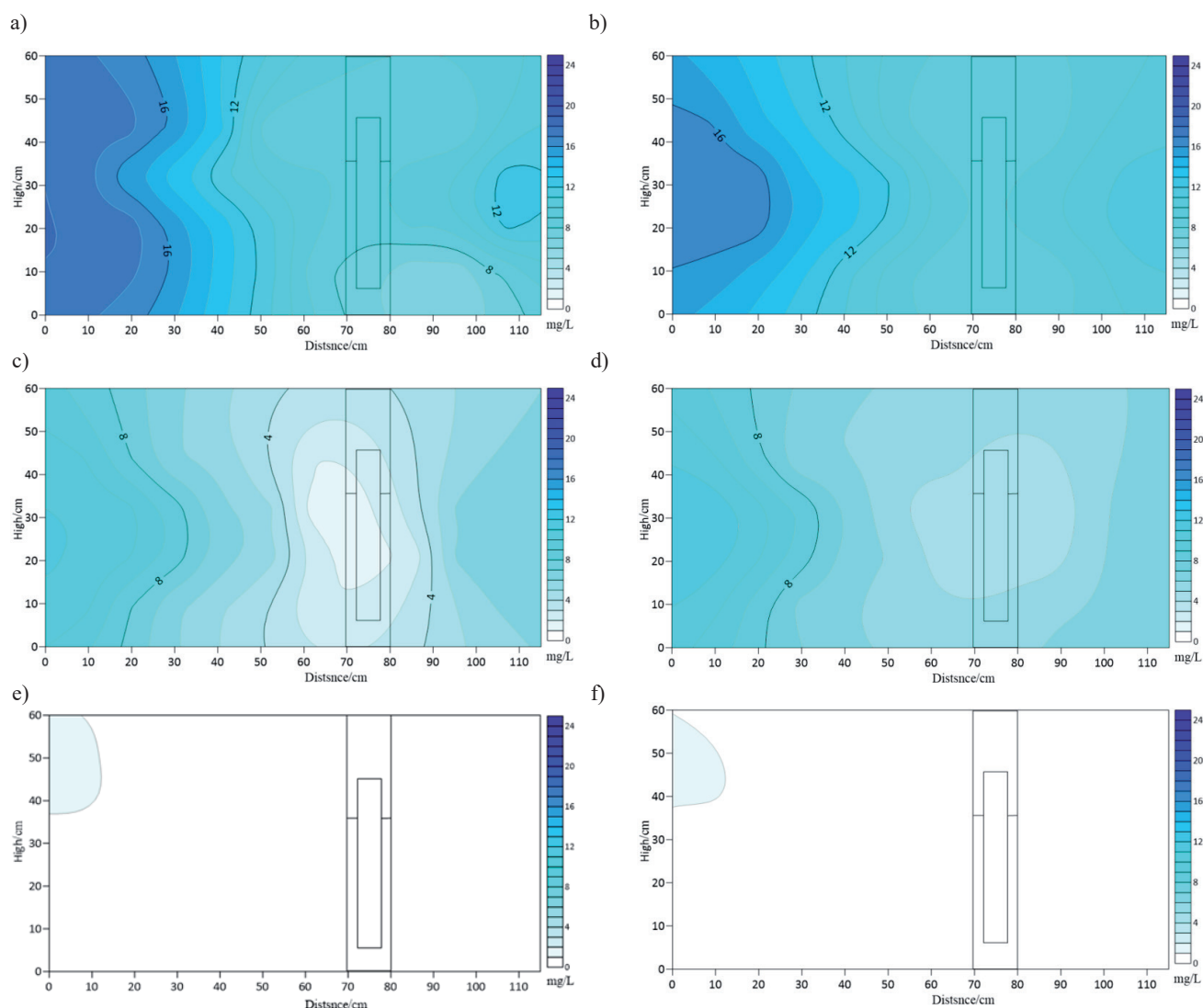
a)

b)

c)

d)

e)

f)

Fig. 5. Variation of benzene and toluene concentration after aeration (unit: mg/L). a) Benzene concentration during 1 h of aeration, b) Aeration 1 h toluene concentration graph, c0 Benzene concentration during 5 h of aeration, d) Aeration 5 h toluene concentration graph, e) Benzene concentration during 12 h of aeration, f) Aeration 12 h toluene concentration graph.

rapidly when the H_2O_2/Fe^{2+} molar ratio becomes larger, which is mainly due to the decrease in the concentration of $/Fe^{2+}$ in the Fenton reagent, and the catalytic effect decreases accordingly, which will curtail the effect of the oxidative removal of benzene and toluene to a certain extent. When $H_2O_2//Fe^2 \ ^+= 8:1$, 10:1, the restoration becomes less effective because the concentration of $/Fe^{2+}$ is too low to provide enough catalyst.

Analysis of Experimental Results for Different Molar Ratios of H_2O_2 and Pollutants

Fixing the molar ratio of H_2O_2 and $/Fe^{2+}$ and changing the molar ratio of H_2O_2 and pollutants, the concentration changes of each pollutant concentration with the change of molar ratio of H_2O_2 and pollutants after 12 h of reaction are shown in Table 2, and the change of removal rate is shown in Table 3.

As can be seen from Tables 2 and 3, under the premise of fixing the molar ratio of $H_2O_2//Fe^{2+}$, the larger the molar ratio of H_2O_2/pollutant, the better the remediation effect will be, when H_2O_2/Fe^{2+} = 2:1 and H_2O_2/pollutant = 10:1, after the reaction, the concentrations of benzene and toluene are already much lower than the target value of the remediation, and this ratio can satisfy the remediation effect as well as save the remediation cost.

Based on the above analyses, the Fenton reagents injected in the reactive recirculation wells were selected in the molar ratios H_2O_2/contaminant = 10:1 and H_2O_2/Fe^{2+} = 2:1.

Analysis of Experimental Results
of Reactive Recirculation Well Rehabilitation

The concentration of pollutants in the simulation tank was measured before the beginning of the experiment,

and the highest concentration of benzene and toluene in the aqueous phase in the simulation tank was 22.710 mg/L and 22.912 mg/L, and the average concentration was 16.125 mg/L and 16.249 mg/L. The distribution of benzene and toluene concentrations in the simulated tank is shown in Fig 4.

The average concentrations of benzene and toluene in the initial simulation tank were used as the concentrations for the preparation of Fenton's reagent, while the amount of Fenton's reagent dosed was calculated by using three times the volume of the well pipe in the recirculation well as the amount of contaminated groundwater.

The molar ratios of H_2O_2/pollutant = 10:1 and H_2O_2/$Fe2^+$ = 2:1 were selected and the amounts of ferrous sulfate heptahydrate and 3% hydrogen peroxide were calculated to be 6.12 g and 0.05 L, respectively. The injection of the drug was completed within five minutes, and the benzene and toluene concentrations in the simulated tanks at 1 h, 5 h, 12 h, and 24 h after the reaction are shown in Fig. 5.

Contaminant concentrations decline most rapidly near the upper and lower perforations of the reactive recirculation wells, where Fenton's reagent is injected into the recirculation well's inner tubing and recirculated outward through hydraulic exchange between the upper and lower perforations.

As can be seen from Fig. 5, after 1 h of reactive recirculation well rehabilitation, the maximum concentrations of benzene and toluene have decreased to 17.532 mg/L and 16.571 mg/L, and the average concentrations are 12.122 mg/L and 11.496 mg/L; at 5 h of reaction, the maximum concentrations of benzene and toluene have decreased to 10.514 mg/L and 11.751 mg/L, and the average concentrations are 6.397 mg/L and 7.077 mg/L, respectively. As the reaction proceeds, the benzene concentration in most of the sampling ports in the simulation tank is below the detection limit at 12 h. Only benzene and toluene are detected in the upper-left sampling port in the whole simulation tank, but the concentration of pollutants is already very low at this time, which is lower than the target value of the remediation, and it can be assumed that the benzene remediation in the simulation tank is completed at this time.

Conclusions and Recommendations

In the Fenton reagent remediation experiments, when the Fenton reagent was added to the contaminated groundwater, the ORP increased rapidly and the whole system was in a strong oxidisingoxidizing state. After several batches of comparison experiments, it can be seen that the Fenton reagent injected in the reactive circulation wells for the molar ratio H_2O_2/pollutant = 10:1 and H_2O_2//Fe^{2+} = 2:1 can satisfy the remediation effect as well as save the remediation cost.

Conflict of Interest

The authors declare no conflict of interest.

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