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Research on groundwater remediation process modeling and effect assessment method for contaminated site based on finite difference method

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Abstract With the continuous development of groundwater remediation technologies for contaminated sites, selecting appropriate remediation technologies and evaluating their effectiveness are the keys to achieving water resource protection and sustainable utilization. In this paper, the groundwater remediation process was simulated by the finite difference method, and the effect of remediation by permeable reaction wall (PRB) coupled with pumping-injection hydraulic control technology was evaluated. The study used the steady flow model and solute transport model to simulate the groundwater flow field and contaminant migration process in groundwater. Before and after the remediation, the pollutant concentrations of Fe and Mn changed significantly, with the maximum concentration of Fe decreasing from 0.351 mg/L to 0.011 mg/L before remediation, and the maximum concentration of Mn decreasing from 0.239 mg/L to 0.007 mg/L, which complied with the groundwater standards, respectively. By modeling contaminant removal under eight scenarios, the results showed that the coupled remediation technology increased the removal rate by 3.96 to 4.99 times compared to the single PRB remediation technology. The removal efficiency reached up to 80.25% in all scenarios. Therefore, the coupled remediation technology has significant effect in groundwater remediation of contaminated sites and provides effective technical support for practical application.

Index Terms Groundwater remediation, PRB technology, coupled remediation, finite difference method, contaminant removal rate, solute transport

I. Introduction

Groundwater resources are one of the important freshwater resources, which are essential for maintaining the ecological balance of the earth and human life [1], [2]. However, in recent years, with the rapid development of industrialization and urbanization, groundwater has been seriously polluted, and the pollution sources mainly include industrial wastewater, agricultural drainage, and domestic sewage, which seriously threaten the environment and human health [3]-[5]. Therefore, the remediation of groundwater pollution in polluted sites is crucial to protect people's life and health and ecological environment [6].

Currently, there are many kinds of technologies to remediate groundwater resources, including physical methods, chemical methods, bioremediation, barrier technologies, etc., and appropriate technologies can be selected according to different pollution situations [7], [8]. However, since groundwater pollution management is a complex task, it requires the support of comprehensive evaluation methods and models [9]. Qualitative and quantitative evaluation methods can evaluate the extent of groundwater pollution, while environmental risk evaluation methods can synthesize the risk of pollution to human health and ecological environment [10], [11]. The establishment of groundwater flow models, diffusion simulation models and risk assessment models can better guide the management of groundwater pollution [12], [13]. Through the comprehensive application of these methods and models, groundwater pollution problems can be managed scientifically and effectively to protect the safety of groundwater resources and ecological environment [14], [15].

In this study, a novel coupled remediation technology is proposed based on the finite difference method, combining the permeable reaction wall (PRB) technology with the pumping-injection hydraulic control technology, and its application in the groundwater remediation of petrochemical contaminated sites is simulated and evaluated in terms of its effectiveness. The performance of the coupled remediation technology is evaluated by modeling groundwater flow and solute transport, and simulating the contaminant migration and removal processes under different remediation scenarios. This coupled remediation technology combines the PRB technology with the pumping-injection hydraulic control technology, which can effectively improve the contaminant removal efficiency, especially for the remediation of petrochemical contaminated sites with significant advantages.

II. Groundwater treatment process analysis

In recent years, the situation of groundwater pollution has become more and more serious, in order to guarantee the safety of water quality and the sustainable utilization of water resources, groundwater pollution remediation is imperative. Selection of appropriate pollution treatment technology can effectively deal with groundwater pollutants in polluted sites and realize water purification.

II. A. Extraction processing technology

Pump-and-treat is one of the most commonly used groundwater remediation techniques. Through the construction of pumping wells, contaminated groundwater is transported to the surface, and after qualified treatment, the remediated groundwater is injected or discharged into the corresponding pipeline network or water body in situ. The advantages of pump-out treatment are that the technology is simple and easy to operate, and the early treatment of groundwater remediation with a larger scope of contamination and a greater depth of contaminants is quick and effective.

II. B. Chemical remediation techniques

Chemical remediation is a method of removing contaminants from groundwater by using a chemical reaction between an oxidizing/reducing agent and the contaminant to convert the contaminant into a less toxic or non-toxic product. Chemical remediation techniques used in groundwater remediation are usually implemented by in situ injection. In-situ chemical oxidation/reduction remediation technology can be applied to the remediation of various types of contaminated sites, can be synchronized to deal with a variety of pollutants, this method for many volatile, semi-volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), fuel hydrocarbons, and heavy metals, PCBs, pesticides, etc., has a better treatment results.

II. C. Electric restoration techniques

Electric remediation technology is a kind of in-situ remediation technology, mainly adopting electrochemical power remediation, which utilizes the kinetic principle of electric power to remediate the pollutants, through the use of DC voltage in the contaminated area to form a gradient electric field, and under the action of the electric field, the target pollutants move towards the vicinity of the electrodes through the processes of electro-migration, electroosmosis, and electrodeposition, so as to enable the free metal ions in the groundwater to migrate in a specific direction, so as to achieve the The goal of centralized treatment of pollutants.

II. D. Multiphase extraction techniques

Multi-phase extraction (MPE) is to extract soil gas, groundwater and non-aqueous phase liquid (NAPL) from underground contaminated areas to the ground by means of vacuum extraction, and then carry out phase separation and treatment operations, so as to achieve the purpose of controlling and remediating the organic pollutants in the soil and groundwater.MPE has less disturbance to the ground environment, and has a better treatment effect when dealing with organic pollutants with high volatility and easy to flow (such as petroleum, chlorinated hydrocarbons), and has a high remediation efficiency. MPE is less disturbing to the ground environment, and has better treatment effect in dealing with volatile and mobile organic pollutants (e.g. petroleum, chlorinated hydrocarbons) with high remediation efficiency and large impact area, and the operation can be accompanied by aerobic biodegradation reaction, which greatly improves the remediation efficiency.

II. E. Microbial remediation techniques

Microbial remediation involves injecting into the contaminated groundwater the substances necessary for microbial survival activities, such as carbon, nitrogen, phosphorus and oxygen, so that the microorganisms can adequately degrade the pollutants in the groundwater and convert the pollutants into harmless end-products, thus realizing the purpose of removing the pollutants. Microbial remediation relies on microorganisms to decompose pollutants, which is usually slow, and the remediation rate is affected by microbial activity, which is not easy to control. In addition, due to the complexity of the biological reaction, some pollutants will inhibit or even kill the microorganisms, which is more demanding on the environment.

II. F. Permeable Reactive Wall Technology

Permeable reaction wall (PRB) technology is a passive groundwater remediation technology, whose mechanism is to install permeable active material walls underground to intercept the pollutant plume, and when the pollutant plume flows through the reaction wall, the pollutant reacts with the reaction medium in the wall physically, chemically, or biologically, so as to realize the purpose of purifying groundwater. The permeable reaction wall is another sense of barrier technology with low cost and better adsorption effect, which has good effect on heavy metals, BTEX (benzene, toluene, ethylbenzene, xylene), inorganic anions, chlorinated hydrocarbons, and radioactive substances.

III. Rehabilitation techniques and study areas

Based on the above analysis of groundwater contamination remediation technologies, this paper adopts permeable reaction wall coupled pumping-injection hydraulic control technology, combined with finite difference method, to simulate the groundwater remediation process of the contaminated site and evaluate its remediation effect.

III. A. Rehabilitation techniques

PRB coupled pumping-injection hydraulic control technology (hereinafter referred to as “coupled remediation technology”) consists of three parts: PRB unit, pumping-injection hydraulic control unit and groundwater treatment reaction unit.

This technology usually places the PRB unit at the downstream boundary of the contamination plume. Under the action of groundwater flow, the pollutants are first adsorbed and degraded by the PRB, and the pollutants that are not adsorbed and degraded continue to migrate downstream along with the groundwater flow, and are captured and pumped out by pumping wells downstream of the PRB, and then transported through pipelines to injection wells upstream of the contamination plume to re-inject and drench the air-packed zones and the aquifers, and the remaining pollutants are removed by the PRB and pumped out again by the PRB under the action of the groundwater flow. Under the action of groundwater flow, the residual pollutants are again adsorbed and degraded by the PRB, and the cycle is repeated until the remediation goal is realized. In order to effectively reduce the content of pollutants in the water entering the air inclusion zone and aquifer, a surface water treatment reaction unit is added to the pumping-injection hydraulic control unit to further adsorb and degrade the groundwater pumped out from the pumping wells prior to re-injection to drench the air inclusion zone and aquifer.

III. B. Study area

The actual site is located in a petrochemical contaminated site, which includes 4 plots to be remediated, among which A2~A4 plots have plant roads and ex-situ thermal desorption equipments on the ground, and there are more gas pipes and water supply and power supply lines underground, which makes the implementation of coupled remediation technology more difficult, and A1 plots have no roads, fences and equipments on the ground, and there are no gas pipes and water supply and power supply lines under the ground, and there are 2 existing observation wells with monitoring data in the plot, so A1 plot was selected as the study area. There are two observation wells in the plot with monitoring data, so plot A1 is selected as the study area, with an area of about 500 m² and a circumference of about 100 m. It is located in the alluvial plain in front of the mountain, with flat topography, complete surface, and homogeneous soil lithology. The area where the study area is located has a warm temperate semi-humid monsoon continental climate, with an annual rainfall of about 579 mm, an average annual temperature of 12.5-14.2°C, and no surface water bodies such as rivers and reservoirs.

IV. Numerical modeling of groundwater at contaminated sites

IV. A. Groundwater Stabilization Flow Model

IV. A. 1) Model generalization

This paper studies the groundwater remediation works and effects of contaminated sites. Therefore, according to the hydrogeological conditions and stratigraphic lithology of the study area, the shallow groundwater system is generalized as a single-layer homogeneous, anisotropic submersible aquifer. In the study area, the dynamic change of groundwater is relatively stable over the years, and it is assumed that the shallow groundwater system in the study area is a stable-flow groundwater system due to the limitation of observation data.

IV. A. 2) Boundary conditions

The study considers only a single submerged aquifer, and after investigating the hydrological data of the region, the groundwater exchange is basically in a stable state, the artificial exploitation is small, and the type of groundwater cycle is mainly of infiltration-runoff type. The study area is a complete hydrogeological unit, of which the northwestern boundary is the surface water divide, which is designated as the water-isolation boundary, and the southern and northeastern parts are rivers, which are designated as the fixed-head boundary. The top boundary of the model is the surface Quaternary System, and the shallow submersible undergoes vertical water exchange with the outside of the system, mainly precipitation infiltration recharge, evapotranspiration discharge, and artificial mining. The shallow diving aquifer lower relative water barrier as the lower boundary of the system is the zero-flow boundary.

IV. A. 3) Stabilized flow model solution

In the course of this study, the model is generalized to a unidirectional homogeneous anisotropic submersible aquifer, therefore, a planar two-dimensional flow two-dimensional diffusion model is used to solve the generalized model. The solution process dissects the study area into square grid cells, and the finite difference method is used for the solution, and the steady flow in the study area can be calculated by Eq. (1):

$$K_{xx}\frac{\partial^2 h}{\partial x^2}+K_{yy}\frac{\partial^2 h}{\partial y^2}+W^{'}=0 \tag{1}$$

In Eq. (1), K_{xx} and K_{yy} denote the permeability coefficients in the X and Y directions of the shallow submersible aquifer, respectively, m/d. W' denotes the vertical recharge coefficient per unit area, m/d.

IV. A. 4) Grid Sections

(1) Regional stable head simulation

The 500m range of plot A1 in the study area was selected as the specific simulation area. Inverse distance square interpolation was performed on the head of 20m×25m grid in the simulation area to obtain the groundwater head value of 1m×1m grid in the simulation area.

(2) Inverse distance square interpolation

The spatial interpolation method is one of the effective tools to study the spatial variability characteristics and distribution of groundwater properties, and has been widely used in the field of groundwater resources. The inverse distance weighted method (IDW) belongs to the deterministic local interpolation method, and the spatially continuous groundwater depth data can be obtained after interpolation of the existing water level depth data. The basic principle is that the interpolation method is weighted by the distance between the interpolation point and the actual observed sample point, and the closer the actual observed sample point is to the interpolation point, the greater the weight is given, and its weight contribution is inversely proportional to the distance. The estimation formula is:

$$z=\sum_{i=1}^{n}\frac{z(x_i)}{d_i^p}/\sum_{i=1}^{n}\frac{1}{d_i^p} \tag{2}$$

where z denotes the water level value at the grid point, m. $z(x_i)$ denotes the ith measured water level value, m. n denotes the number of measured water level points involved in the calculation. d_i denotes the distance between the grid point and the ith station, m. P denotes the parameter, P=2 is used in this study.

IV. A. 5) Boundary and initial conditions

According to the hydrogeological investigation report of the project area, the quaternary system in the project area is very developed and widely distributed, mainly for the river impact cone and river floodplain deposition, up to 40-90m thick, according to the results of seepage experiments, its permeability coefficient is 0.031-0.039m/d. The quaternary system under the Cretaceous system, red mudstone, sandstone central conglomerate, up to 500m thick, with weak water permeability, does not contain tax or localized stagnant water. They are weakly permeable, do not contain tax or localized stagnant water, and form the relative water-insulating base plate of the Quaternary submersible aquifer in the area.

The porous diving aquifer of Tetrahymena Loose Rock is mainly dominated by alluvial deposits, with relatively uniform distribution of grain size, and no significant difference in hydrogeological parameters such as horizontal permeability coefficient, degree of water supply and porosity. The survey results show that the horizontal permeability coefficient is in the range of 3-7m/d, and the porosity is $0.1<n<0.2$. The average value is chosen as the initial parameter for simulation.

The surface elevation is used as the initial water level for the flow field simulation, and the source and sink items include atmospheric precipitation, river drainage, evaporation drainage, etc. Each source and sink item is converted to the corresponding intensity according to the requirements and assigned to the corresponding grid cell. During this study, 20m×25m grid cells were used in the evaluation area to simulate the regional steady flow field. Considering the small pollution source (area of 500m²) during this study, after obtaining the regional-scale stable head, the head point of 50m around the well site was selected, and the inverse distance square interpolation was used to construct the 1m×1m local-scale grid cell.

IV. B. Solute transport simulation

IV. B. 1) Mathematical modeling of solute transport

Considering that the horizontal scale of the study area is much larger than the vertical scale, and there is an artificial clay impermeable layer at the bottom of the field area, based on the finite difference method, a two-dimensional flow two-dimensional diffusion model is selected to simulate the pollutant transport process in the study area, as shown in equation (3):

$$\frac{\partial C}{\partial t}=D_x\frac{\partial^2 C}{\partial x^2}+D_y\frac{\partial^2 C}{\partial y^2}-\frac{\partial(V_xC)}{\partial x}-\frac{\partial(V_yC)}{\partial y}+\omega \tag{3}$$

where, D_x is the horizontal hydrodynamic dispersion coefficient, m²/d. D_y is the vertical hydrodynamic dispersion coefficient, m²/d. V_x is the groundwater flow rate in the horizontal direction, m/d. V_y is the groundwater flow rate in the vertical direction, m/d, and w is the source of contamination, mg/L.

IV. B. 2) Initial concentration field

Twenty groundwater monitoring points were set up in the study area, and the monitoring results showed that the differences in the concentrations of ammonia nitrogen and COD in groundwater in the area were not significant. Due to the small number of monitoring points, the error of using interpolation method to solve the initial concentration field of pollutants in the study area is large. Therefore, during the study, the initial concentrations of ammonia nitrogen and COD in the area were set to 0 mg/L, and the simulated concentrations were the contributing concentrations of a petrochemical contaminated site.

IV. B. 3) Solute transport parameters

(1) Determination of groundwater flow rate

Considering the submerged aquifer in the study area as a porous medium, Darcy's law is used to calculate the steady flow rate of groundwater. The groundwater flow rates V_x and V_y in the X and Y directions are obtained from equation (4):

$$V_x=-K_x\frac{\partial H}{\partial x},V_y=-K_y\frac{\partial H}{\partial y} \tag{4}$$

(2) Dispersivity determination

Hydrodynamic dispersion coefficient includes mechanical dispersion coefficient and molecular diffusion coefficient, and its calculation formula is shown in equation (5) and equation (6):

$$D_x=D'+(a_LV_x^2+a_TV_y^2)\frac{1}{V} \tag{5}$$

$$D_y=D'+(a_L-a_T)\frac{V_sV_s}{V} \tag{6}$$

where, V is the actual velocity of groundwater, m/d. V_x,V_y are the velocity components of groundwater in the X and Y axes, respectively, m/d. D is the molecular diffusion coefficient, m²/d. a_L is the mechanical dispersion coefficient, m²/d. a_T is the molecular dispersion coefficient, m²/ d.

(3) Determination of source strength

After the operation of a petrochemical contaminated site, the atmospheric rainfall washes the surface layer and seeps down to the bottom of a petrochemical contaminated site, most of which is discharged through the internal leachate drainage system, and the remaining part seeps down through the clay impermeable layer at the bottom and then enters into the shallow submersible aquifer system. The amount of pollutant seepage per unit area of the petrochemical contaminated site is calculated by equation (7):

$$M=K_zJtC_1 \tag{7}$$

where, M is the amount of pollutant infiltration per unit area, mg. K_x is the permeability coefficient of the clay impermeable layer at the bottom of the reservoir, m/d. J is the hydraulic gradient, which is taken to be 1. t is the leakage time, d. C_1 is the concentration of pollutants in the leachate, mg/L. For this simulation, C = 250 mg/L and C_{COD} = 3000 mg/L.

V. Results and discussion

V. A. Simulation of groundwater remediation processes

V. A. 1) Flow field simulation results

After the physical model of the study area was established, the groundwater seepage field was simulated using a steady flow model to correct the initial flow parameters. The groundwater in the simulated area is mainly recharged by atmospheric rainfall, and its groundwater flow field is controlled by the topography, and the groundwater in the area eventually flows to its lowest discharge datum. The simulated groundwater flow field is basically consistent with the topographic conditions, and is mainly influenced by the topographic conditions in the area, with the hydraulic gradient gradually decreasing from south to north. Twenty boreholes were selected as groundwater level observation wells to verify the correlation between the simulated water level and the actual observed water level. The comparison of the simulated groundwater flow field in the study area is shown in Fig. 1, and the scattering points between the simulated water level and the actual water level are distributed near the 45° straight line, and all of them are within the 95% confidence interval, so the simulated flow field is reasonable.

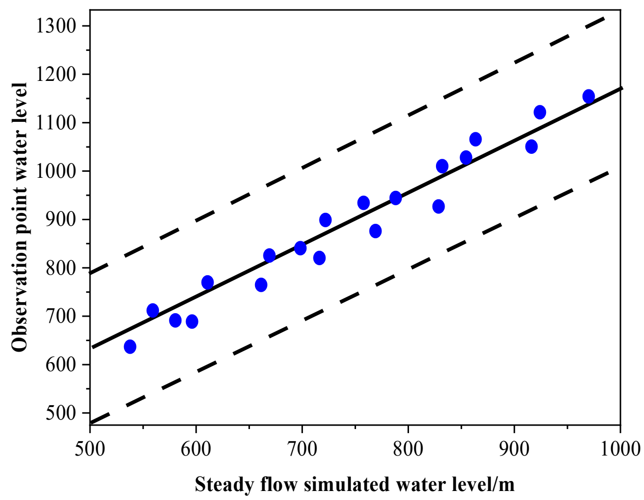

Figure 1: The comparison of groundwater simulation flow field in the research area

V. A. 2) Solute transport simulations

Groundwater solute transport processes at a petrochemical contaminated site were simulated and analyzed 1 month before remediation (1-30d) and 1 month after remediation (31-60d) to determine the effects of the characteristic elements Fe and Mn on groundwater. The maximum concentrations of Fe and Mn ions increased rapidly in the 1 month before remediation, and the Fe and Mn pollutant concentrations reached the maximum value at 30 d. After the petrochemical contaminated site was remediated using the PRB-coupled pumping-injection hydraulic control technique, the Fe and Mn pollutant concentrations gradually decreased. The maximum concentration changes of Fe and Mn in the simulated scenarios are shown in Figures 2 and 3. At 1 d, the maximum concentration of Fe was 0.253 mg/L, and then the pollutants gradually increased, and the maximum concentration of Fe reached 0.351 mg/L at 30 d, which exceeded the corresponding groundwater standard limit by 1.17 times. Subsequent to the remediation of the contaminated site, the maximum concentration of Fe ions gradually decreased with time, and the maximum concentration of Fe was 0.011 mg/L at 60 d. The maximum concentration of Mn ions decreased with time, and the maximum concentration of Mn ions decreased with time.

The maximum concentration of Mn ions was similar to that of Fe. At 1d, the maximum concentration of Mn was 0.172mg/L, which exceeded the corresponding standard limit value of 0.10mg/L, and then the maximum concentration continued to rise, and the concentration of Mn reached the maximum value of 0.239mg/L at 30d, which exceeded the corresponding standard limit value by 2.39 times. Subsequent to the remediation of the contaminated site, the maximum concentration of Mn gradually decreased with time, and the maximum concentration of Mn was 0.096 mg/L at 49d, which met the requirements of the corresponding standard limit, and the maximum concentration of Mn was 0.007 mg/L at 60d.

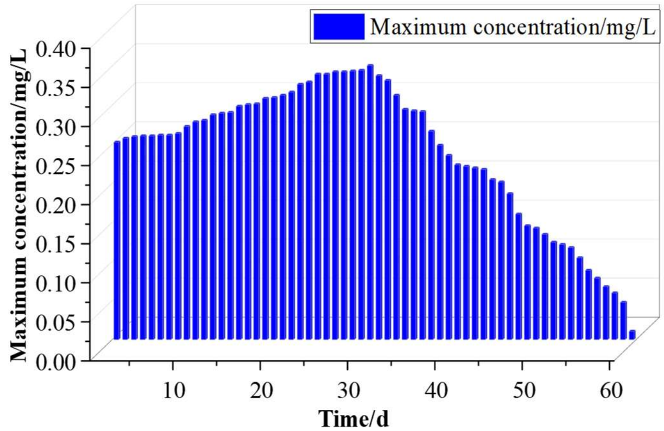

Figure 2: The maximum concentration of Fe in the simulated scenario

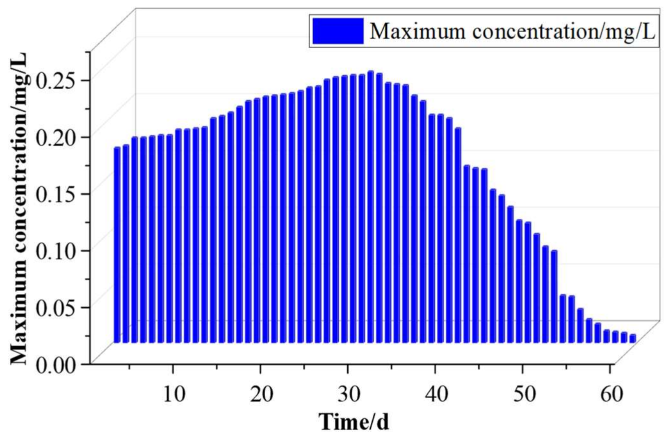

Figure 3: The maximum concentration of Mn in the simulated scenario

V. B. Evaluation of the effectiveness of the rehabilitation

V. B. 1) Technical parameters for coupling repair

The key parameters affecting the pollutant removal rate of coupled remediation technologies mainly include aquifer permeability coefficient K, pumping-injection volume Q, and total technology removal efficiency E. Aquifer permeability coefficients have been set up in the groundwater flow and solute transport models. Eight scenarios for E1 and E2 have been determined based on the relationship between the total technical removal efficiency E and the PRB removal efficiency E1 and the surface water treatment reactor removal efficiency E2. The technical parameters were added to the constructed groundwater flow and solute transport models.PRBs were deployed downstream of the contamination plume, pumping wells were deployed downstream of the contamination plume, and injection wells were deployed upstream of the contamination plume.

V. B. 2) Analysis of restoration effects

The simulation results of the eight scenarios are detailed in Table 1, and it was found that the pollutant removal rate after remediation using coupled remediation techniques reached more than 78%, with the highest pollutant removal rate of 80.25% in Scenario 4, when the PRB removal efficiency, E1, and the surface water treatment reactor removal efficiency, E2, were 70% and 0.80%, respectively.

Table 1: The simulation results of 8 scenarios

Scenarios	E1/%	E2/%	Total initial pollutant/g	Fixed quantity/g	Pollutant removal/%
Scenario 1	55	0.90	4836	978	79.78
Scenario 2	60	0.87	4836	1012	79.07
Scenario 3	65	0.84	4836	973	79.88
Scenario 4	70	0.80	4836	955	80.25
Scenario 5	75	0.76	4836	998	79.36
Scenario 6	80	0.72	4836	1024	78.83
Scenario 7	85	0.65	4836	1040	78.49
Scenario 8	90	0.60	4836	976	79.82

In order to investigate the difference in pollutant removal effect between coupled remediation technology and PRB single remediation technology, the extraction-injection module and surface water treatment reactor module were removed from the model, and only the PRB module was retained to simulate the pollutant removal effect under eight scenarios, and the results of pollutant removal rate comparison are shown in Table 2. It can be seen that compared with the single remediation technology of PRB, the coupled remediation technology can increase the remediation efficiency by 396~3 times. It can be seen that compared with the PRB single remediation technology, the remediation efficiency of the coupled remediation technology can be improved by 3.96~4.99 times.

Table 2: The comparison of the removal rate of pollutants

PRB single repair technique		Coupling repair technique			Enhanced multiple
E1/%	Pollutant removal/%	E1/%	E2/%	Pollutant removal/%	
55	13.32	55	0.90	79.78	4.99
60	13.64	60	0.87	79.07	4.80
65	14.56	65	0.84	79.88	4.49
70	14.86	70	0.80	80.25	4.40
75	15.25	75	0.76	79.36	4.20
80	15.67	80	0.72	78.83	4.03
85	15.83	85	0.65	78.49	3.96
90	15.95	90	0.60	79.82	4.00

VI. Conclusion

In this paper, in the simulation study of groundwater remediation at a petrochemical contaminated site, good remediation results were achieved by combining PRB technology and pumping-injection hydraulic control technology. It was found that the maximum concentrations of Fe and Mn in 1 month before remediation were 0.351 mg/L and 0.239 mg/L, respectively, which exceeded the groundwater standard limits. After the remediation treatment, the concentrations of Fe and Mn decreased significantly, and after 60 days of remediation, the Fe concentration decreased to 0.011 mg/L and the Mn concentration decreased to 0.007 mg/L, which both met the groundwater quality standards.

Further analysis revealed that under different remediation scenarios, the pollutant removal rate of the coupled remediation technology generally exceeded 78%. The highest removal rate reached 80.25%, which was significantly higher than that of the single PRB remediation technology. Specifically, the coupled remediation technology increased the pollutant removal efficiency by 3.96 to 4.99 times compared with the single PRB remediation technology, demonstrating a strong technical advantage.

The results showed that the coupled remediation technology, as an effective groundwater remediation program with high pollutant removal efficiency, can provide new ideas and technical support for groundwater pollution remediation.

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