Review on remediation of contaminated groundwater by Fe^0-PRB technology

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Abstract. PRB technology is a new groundwater remediation technology, which is currently in the pilot test stage in China. Zero-valent iron is one of the most commonly used fillers in permeable reaction walls. In this paper, the principle and structure of PRB technology, the working principle of zero-valent iron in PRB, the preparation method and the optimization and improvement of application technology, the application examples at home and abroad and the prospect of PRB technology are introduced.

1 Introduction

Groundwater resources are important living resources for human beings. The pollution of surface water and the scarcity of resources make groundwater resources more precious. As a result of long-term non-standard operation of enterprises and factories in industrial activities and leakage of storage equipment and pipelines, pollutants seep down and cause groundwater pollution, which has a negative impact on human life and health. With the promulgation of《the Action Plan for The Prevention and Control of Soil Pollution》 in 2016, the remediation of soil and groundwater has gradually attracted the attention of people at all levels and of all kinds in China.

At present, groundwater remediation technologies include natural attenuation monitoring technology, groundwater ectopic remediation technology, groundwater in-situ remediation technology, phytoremediation technology, electrodynamic remediation technology, permeable reactive barrier remediation technology, etc. [1]. Among them, the permeable reactive barrier (PRB) technology is favored by researchers because of its simple engineering facilities, long duration, low cost and good effect [2]. PRB technology, which uses zero-valent iron as filler, has been widely used and continuously improved and optimized by researchers.

PRB technology uses the wall filled with reaction medium to block the pollutants in the pollution plume, and uses the filling medium to have physical, chemical, biological and other reactions with the pollutants to degrade the pollutants, so as to achieve the purpose of groundwater remediation. In China, PRB technology has not been commercialized yet, and is currently in the laboratory research and pilot test stage.

Liu Jun et al. [3] took quartz sand as the carrier and made iron oxide crystallize on it to treat organic silicon wastewater and synthetic pharmaceutical wastewater. Under optimized operating conditions, the removal rate of COD and TOC could reach 80% and 85%, and the reduction amount of total iron (Fe^{3+}) could reach 26%. Gao Fang et al [4] to hydroxyapatite as the carrier, the simple and feasible through chemical solution of the hydroxyapatite prepared nZVI composite material removal of uranium (Ⅵ), the effect is remarkable.

This paper introduces the principle and structure type of PRB technology, the working principle of zero-valent iron in PRB, the preparation method and the optimization and improvement of application technology, the application examples at home and abroad and the prospect of PRB technology.

2 Permeable reaction wall technology

2.1 The principle of PRB

PRB technology is a kind of filling technology, the permeable wall grid reaction medium permeable response, in the process of groundwater repair, placed in the downstream of groundwater, reaction gate on the vertical of plume in the natural hydraulic gradient through the response under the action of grid and adsorption, precipitation with fillings, biodegradation and redox reaction, remove the pollutants in the groundwater, and the groundwater meets the standards [5].

Common treatment forms and principles of PRB technology are as follows:

(1) Adsorption type: The permeable reaction wall uses the adsorbent as the filling medium. When the pollution plume flows through the reaction wall, adsorption, ion exchange, surface complexation and other reactions occur. Common adsorption materials include zeolite [6], activated carbon, silicoaluminate, etc.

(2) Precipitation type: The permeable reaction wall uses the precipitant as the filling medium. When the pollution plume flows through the reaction wall, the

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precipitation reaction occurs and precipitates are generated, so it is trapped. Common precipitators include calcium carbonate and hydroxyapatite [7].

(3) Oxidizing reduction prototype: the permeable reaction wall uses oxidizing agent or reducing agent as the filling medium. When the pollution plume flows through the reaction wall, it is oxidized or reduced into non-toxic valence or precipitation and removed. Common filling media include hydrogen peroxide, calcium peroxide, ozone, sodium persulfate, zero-valent iron [8], etc.

(4) Biodegradable: The filling medium in the Bio-PRB[9] mainly provides microorganisms with carbon source, oxygen, electron acceptor and other substances suitable for growth, so that microorganisms can degrade pollutants better.

2.2 Positioning

Single-processing system PRB and multi-unit processing system PRB are currently applied PRB structure types. Among them, the single treatment system PRB includes two basic types: continuous wall PRB, funnel-guide door PRB, and improved types such as water-barrier wall-in-situ reactor PRB and siphon PRB. The multi-unit processing system PRB consists of series and parallel structures.

2.2.1 Continuous wall PRB

Continuous wall PRB is the most basic PRB structure. In its application, pervious grille should be placed vertically in the downstream of groundwater, and the pollution plume should flow through the reaction wall and react with the filling medium under the action of natural hydraulic gradient, so as to finally get the outlet meeting the requirements. The action process does not change the flow direction of groundwater, and has a small impact on geology. The overall structure is relatively simple, and this structure is suitable for the contaminated site with a relatively small range of pollution plume [10].

2.2.2 Funnel - guide door type PRB

The funnel-gate type PRB is composed of a water barrier funnel, a water barrier gate and a treatment unit. The water barrier funnel is embedded in the water barrier layer to prevent seepage into the surrounding clean groundwater area due to the large pollution plume area. The water barrier wall is used to control and guide the underground water flow to collect, and the filled reaction medium is used to remove pollutants. This structure type is suitable for the contaminated site with relatively shallow landfill depth and large pollution plume range. Its advantage is that the filling media are all used in the reaction funnel, so the reaction is concentrated and the filling medium quality is less required. The disadvantage is that it will change the groundwater flow direction to some extent and interfere with the natural groundwater flow field [11].

2.2.3 The modified PRB

The water barrier wall - in-situ reactor PRB uses the water barrier wall to divert contaminated groundwater into the inlet of the upper end of the in-situ reactor. The contaminated water enters the reactor and flows downward under the action of gravity and fully reacts with the filling material. Finally, the water flows out through the drain pipe.

The siphon PRB uses the natural hydraulic gradient to introduce the polluted groundwater into the reaction chamber [12]. After the reaction is completed, the groundwater in the reaction chamber will be discharged by siphoning. The advantages of this structure type are low operating cost and small floor space. Disadvantages are small scope of application and high requirements for installation technology [13].

2.2.4 The modified PRB

The multi-unit processing system includes series and parallel structure types. The series multi-unit treatment system is composed of multiple permeable reaction walls in series. The filling medium in the permeable reaction wall can be the same or different, depending on the pollution component contained in the pollution plume, so as to achieve the purpose of removing multiple pollutants simultaneously. The parallel multi-unit treatment system is composed of several permeable reaction walls in parallel. The system is mainly used in the case that the pollution plume is relatively wide and the pollution component is relatively single.

3 Fe^0-PRB

3.1 Technical introduction to zero valent iron

Zero-valent iron can react with organic and inorganic pollutants in groundwater [14], and reduce high-priced inorganic pollutants to low-priced non-toxic or precipitated ones. It provides electrons for organic pollutants, converts them into non-toxic substances, and eventually achieves the purpose of water treatment.

3.2 Preparation of nanometer zero valent iron

At present, the common preparation method of nZVI is liquid phase reduction. Strong reducing agent was added to Fe^{2+} or Fe^{3+} water solution to reduce Fe^{2+} or Fe^{3+} to Fe^0. The most common reducing agent is $NaBH_4$. The preparation process of nZVI is simple and easy to operate, and the product has a good effect. However, it is easy to be oxidized by air and other oxides in the process of operation, usually under the protection of nitrogen. The reaction equation is as follows:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0(s) + 3H_2BO_3^- + 12H^+ + 6H_2(g) \quad (1)$$

$$Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0(s) + 2B(OH)_3 + 7H_2(g) \quad (2)$$

3.3 Optimization and improvement of zero valent iron application

Zero-valent iron has strong reductibility and large specific surface area. In the process of removing pollutants in water, it is easy to be oxidized to form oxides to cover its surface, which reduces the specific surface area of the reaction, hindering the further progress of the reaction and unable to mineralize pollutants in water. At present, there are two common improvement methods. One is the carrier fixation method, in which nZVI is loaded on the carrier to make its particles disperse and reduce agglomeration. Second, surface modification can reduce agglomeration of particles and increase stability.

3.3.1 Carrier fixation method

Using porous media material as the carrier, the nZVI is fixed on the carrier, and the carrier characteristics are effectively utilized to improve the stability and dispersion of the nZVI particles and overcome the defects of the nanoparticles themselves. The commonly used carriers are quartz sand, attapulgite clay, chitosan, zeolite, etc.

CHEN et al. [15] prepared nZVI using activated carbon as the carrier and applied it to dechlorination reaction of hexachlorobenzene (HCB). The experimental results showed that the iron-loaded method could significantly increase the removal efficiency and dechlorination performance of HCB. Wang Hong etc. [16] by chemical liquid phase reduction of attapulgite prepared load zero-valent iron composite material, and optimize the preparation technology of composite materials, the degradation of the experimental results show that the composite material has higher stability and dispersion, improve the processing efficiency of methylene blue.

3.3.2 The surface modification

The surface modification of nZVI is mainly made by adding polymeric polymer electrolyte or surfactant, which can reduce or prevent the charge and dipole suction between nZVI particles, thus preventing the agglomeration between nZVI particles and increasing its stability. The commonly used modification methods include physical assistant method and chemical additive method.

Sun et al. [17] selected polyelectrolyte mixture for surface modification of nZVI particles, and found that the average particle size was only about 15 nm, and that the adsorption capacity and migration capacity were significantly improved. Jing Li et al. [18] modified nZVI simultaneously with non-ionic surfactant polyvinylpyrrolidone and anionic surfactant sodium oleate. The results showed that the working efficiency of zero-valent iron was optimized, the reaction was balanced for 2min, and the removal efficiency was more than 99%.

4 Application cases at home and abroad

4.1 Domestic application cases

The research on PRB technology in China started relatively late and is still in the laboratory research and pilot test stage, which still needs further research and exploration to provide theoretical basis for the realization of commercial application.

Some pilot tests have also been conducted in China. Tian Lei [19] carried out a pilot test of PRB technology for remediation of TCE and toluene contaminated groundwater in an engineering demonstration site in Henan Province with zero-valent iron composite material as filler, with good results. However, the service life of zero-valent iron will be affected by the content of other substances in groundwater. Hou, etc.[20] the construction of underground water in Shenyang in Liaoning province PRB demonstration project, with zeolite as the filling medium pollution treatment of NH_4^+-N, after a period of time, water concentration in accordance with GB/T 14848 《underground water quality standard》 Ⅲ class water quality requirements.

4.2 Overseas application cases

Zero-valent iron PRB technology has been widely used in groundwater remediation abroad [21], with a high success rate, and has been commercialized in European and American countries [22].There have been more than one hundred successful cases of the reaction wall built with zero-valent iron as the filling medium.

A continuous reaction wall with length of 5.5m, depth of 9.7m and thickness of 1.5m was constructed in a contaminated site of Boden Base in Ontario, Canada, using zero-price iron and concrete as fillers to treat TCE and PCE. The final removal rate of TCE and PCE was 90% and 88%[23].A north Carolina Elizabeth city pollution sites using zero-valent iron electroplating workshop for packing construction has a length of 45.7 m, 7.3 m deep, thick 0.6 m of continuous reaction wall removal of TCE and hexavalent chromium, Cr (Ⅵ) concentration of 5 mg/L to did not check out, concentration of TCE by 7 mg/L dropped to less than 0.005 mg/L [24].

5 Outlook

PRB technology is a simple and efficient groundwater remediation technology. After the installation of the reaction wall, almost no additional costs will be incurred except for the necessary maintenance costs. Although PRB technology in China has a late start and is still in the pilot test stage, it has a broad prospect and will be commercialized soon. The problem of groundwater remediation in China has attracted the attention of many experts and scholars, and the widespread application of PRB technology will also become a trend.

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