Research Progress of Improved Methods of Zero-valent Iron

Luyao Wang*, Biao Peng and Shaodong Qu

Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi’an, China
Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi’an, China
Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources of China, Xi’an, China
Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi’an, China

*Corresponding author: luyaowang@shanxidichan.com

Abstract. It has been found that ZVI is cheap and readily available, environmentally friendly, highly active, thoroughly removed, and has a wide range of applications. It can remove a variety of environmental pollutants in wastewater, surface water, groundwater, and drinking water, such as organic compounds, heavy metals and metalloids, oxygen-containing anions. It has been found through research that the activity of ZVI can be improved in various ways. This paper summarizes the research progress of various methods such as ZVI pretreatment, ZVI and material coupling method, UV assisted method, weak magnetic field method, aeration method and particle size reduction, which in order to provide new ideas for the theoretical research and application of ZVI.

Keywords: zero-valent iron, weak magnetic field, aeration, material coupling

1. Introduction

Zero-valent iron (ZVI) has been extensively studied for its removal of pollutants due to its standard oxidation-reduction potential $E_0 = -0.44V$, active property, easy production and low price. Around 1991, Boden, Ontario, Canada took the lead in using nZVI as a permeable reactive wall (PRB) method for the in-situ remediation of contaminated groundwater. Since then, ZVI has been widely used in the repair / treatment of groundwater and halogenated organic polluted wastewater [1].

However, ZVI also exposes its limitations in some research and application: (1) ZVI has low reactivity due to its own inherent passivation layer and relatively low specific surface area; (2) ZVI reactivity decreases with time due to surface passivation caused by oxidation products, such as Fe(OH)$_2$, Fe(OH)$_3$, FeCO$_3$ precipitation; (3) Because H$^+$ participates in the redox reaction of ZVI and the mass transfer limitation due to the precipitation of the passivation film on the metal surface, the reactivity of ZVI decreases sharply with the increase of pH, so the ZVI technology generally works better under acidic conditions; (4) ZVI has low reactivity to certain pollutants such as Se (VI), and has low adsorption and selectivity to certain pollutants, especially organic pollutants; (5) Due to the low reactivity of ZVI, some toxic intermediate products (such as chlorinated hydrocarbons) may accumulate [2]. Researchers have proposed a variety of improved methods for the limitations of ZVI,
such as ZVI pretreatment, ZVI and material coupling, particle size reduction, etc. This article will summarize these improved methods in order to provide theoretical support for the further research and application of ZVI.

2. ZVI pretreatment

The iron material without pretreatment will be covered by the discontinuous passivation layer formed during the redox process. At the same time, the iron material will continue to generate amorphous iron oxide and hydroxyl oxide mixtures during storage. The iron (hydrogen) oxide covered on the surface of the ZVI will hinder the transport of the substance, resulting in a low reactivity of the ZVI in the initial reaction stage. Therefore, if a pretreatment method for removing the passivation oxide layer is added before the initial reaction stage, the number of reactive sites of ZVI chelating pollutants can be increased. The current commonly used pretreatment methods are as follows.

2.1. Pickling

Pickling can remove the passivation layer and improve the reaction activity of nZVI, so that the degradation rate of nitrate, chlorinated organic compounds and nitro aromatic compounds is significantly increased.

2.2. Hydrogen reduction,

Lin and Lo [3] used H2 pretreatment method to reduce the oxide layer at 400°C to carbonize the carbonaceous material on the surface of ZVI, the number of active sites and the adsorption capacity per iron surface area were increased, which in turn improved the cast iron to TCE degradation rate. Liou et al. [4] also used H2 pretreatment to activate ZVI at 400°C. The results showed that the nitrate removal lag period of ZVI after H2 pretreatment disappeared, and the first-order reaction rate constant increased by 4.7 times. However, H2 pretreatment applications may be limited by high temperature conditions.

2.3. Ultrasound method.

Afouni et al. [5] have confirmed that ultrasonic waves can remove oxidation products and precipitates on the surface of iron, thereby increasing the active sites on the surface of iron and increasing the reaction rate. Hung et al. [6] found that ultrasonic treatment of ZVI can increase the degradation rate constant of carbon tetrachloride. Geiger et al. [7] found that ultrasonic waves can increase the surface area of ZVI by 169%, and can also change the ratio of surface materials (such as the ratio of amorphous carbon to carbonyl carbon, iron to oxygen), which are beneficial to the removal of hydroxides. This makes iron more active in reducing dehalogenation. However, the ultrasonic treatment pretreatment consumes too much energy, which is slightly contrary to the original intention of environmental protection.

3. ZVI and material coupling method

When studying the reaction of chlorinated organics with ZVI, Zhang et al. [8] found that ZVI has limited adsorption capacity for PCE and TCE, resulting in a slower slowing rate and a half-life of several days or longer. Therefore, many scholars have proposed the use of reactive materials to improve the performance of ZVI in removing pollutants. For example, many micro-couples are naturally formed between ZVI and activated carbon when the coupling material of activated carbon and ZVI reacts with organic pollutants. Fe²⁺, OH and nascent hydrogen can be released from the electrochemical corrosion reaction, which is highly active in decomposing organic pollutants. This technology has been widely used in the treatment of pesticides, pharmaceuticals and dye wastewater due to its advantages of easy operation, low running cost and high treatment efficiency. In addition, the mixture of granular AC and granular ZVI is also widely used as the active medium in PRB to remove common groundwater pollutants such as chlorinated hydrocarbons. However, the practical large-scale application of ZVI/AC technology was limited due to the time-consuming synthesis
process and the high production cost of AC. Zeolites, natural zeolites and synthetic zeolites are used as industrial adsorbents, soil improvers, ion exchangers and molecular sieves. At the same time, the combination of cationic surfactant-modified zeolite (SMZ) and granular ZVI has also been extensively studied to enhance the sequestration of pollutants through the synergistic effect of adsorption and reduction. Research has shown that the removal rate of PCE and chromate increased by 3-9 times after using SMZ/ZVI. Bentonite can be easily modified by inserting inorganic/organic cations due to increased surface area and more functional groups, and the product is more effective than before. Some scholars mixed organic bentonite with ZVI to remove TCE, and found that the removal rate of TCE was significantly improved. Li et al. [9] pointed out that the use of pillared bentonite can increase the nitrate removal rate of ZVI.

4. UV assisted method
The combined reaction of ZVI and UV can produce Fe$^{2+}$ through the oxidation-reduction reaction of H$_2$O$_2$ radical generated by UV irradiation of H$_2$O and ZVI, which is similar to Fenton reaction and does not require additional H$_2$O$_2$. Son et al. [10] studied the kinetics of 1,4-dioxane degradation using ZVI under UV light. The results show that UV light in the UV-C region is very effective for improving FeO removal of 1,4-dioxane Effective, and 1,4-dioxane is mainly degraded by .OH in the combined reaction. Meanwhile, the research shows that UV irradiation could increase the removal efficiency of arsenate by ZVI from 78% to about 87% within 4 hours.

5. Weak magnetic field method
Weak magnetic field method is to control the mass transfer of the reaction components on the electrode surface by adjusting the shape of the electrodeposited product on the electrode, and thus the reaction rate at the electrode/electrolyte interface can be controlled. The magnetic force may cause convection in the solution and narrowing the diffusion layer, which result in higher current [11]. Due to the application of a DC (direct current) magnetic field (10-20 mT), Jiang et al. [12] increased the SO$_2$ absorption of cast iron scrap by 30-50%. Liang et al. [13] found that the presence of a weak magnetic field significantly accelerated the removal of Se(IV), and extended the pH range of mZVI from 4.0~6.0 to 4.0~7.2.

6. Aeration method
Aeration method, generally speaking, lowering the pH value can accelerate the removal of ZVI pollutants. Hsu et al. [14] proposed combining ZVI with CO$_2$ aeration, and the results show that CO$_2$ aeration can significantly improve the conversion of ZVI to nitrate. In order to reduce the consumption of carbon dioxide and induce a potentially faster pH balance and a faster rate of nitrate reduction, Li et al. [15] used CO$_2$ pressurization to control the pH and the nitrate reduction. The result shows that the CO$_2$ pressurization system can save CO$_2$ in a 30-minute reaction time.

7. Particle size reduction
In the 1990s, Zhang et al. [16] synthesized nano-sized (<100 nm) ZVI (referred to as nZVI). Its large specific surface area and quantum size effect of nanoparticles overcome the problem of low utilization of ZVI activity. The degradation activity of nZVI to pollutants tends to increase several times compared to the granular ZVI. There are four reasons why nZVI is better than general ZVI or mZVI to remove pollutants in water. (1) Because of its large specific surface area, nZVI is more reactive; (2) nZVI can be used for faster degradation of pollutants; (3) the more complete degradation process of pollutants by nZVI can avoid the generation of unnecessary by-products; (4) injecting nZVI into the pollution source is faster and more efficient for groundwater treatment than the groundwater lifting method or the PBR method [17]. nZVI can remove inorganic salts, heavy metal ions, organic compounds and other contaminants by reduction, oxidation, adsorption, precipitation or co-precipitation, so it is widely used in water/soil remediation.
8. Conclusion
The method of using ZVI to remove pollutants in water has wide applicability, thorough removal and environmental friendliness. Changing the particle size of zero-valent iron and increasing its specific surface area can enhance its activity, but its stability becomes worse, which is not conducive to practical application. To overcome this contradiction, the synthesis of ZVI with high activity, high stability, and wide applicability to remove pollutants has always been a hotspot. This paper summarizes six different methods of improving the reactivity of ZVI. The results of the studies show that these methods have improved the removal rate of pollutants by ZVI to varying degrees, especially the coupling of ZVI with materials and the reduction of particle size. In recent years, many scholars have combined these two methods to prepare supported nZVI. Therefore, in the future research, the fusion of multiple methods to improve the performance of ZVI will become a trend. We speculate that in the near future, the application of ZVI will become more and more mature.

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References
[1] Timothy  L. Johson, M. M. S., Paul G. Tratnyek, kinetics of Halogenated Organic Compound Degradation by Iron Metal. Environ. Sci. Technol. 1996, 30, 2634-2640.
[2] Chuanbai Wang, W. Z., Synthesizing Nanoscale Iron Particles for Rapid and Complete Dechlorination of TCE and PCBs. ENVIRONMENTAL SCIENCE & TECHNOLOGY 1997, 31, 2154-2156.
[3] Lin, C. J.; Lo, S. L., Effects of iron surface pretreatment on sorption and reduction kinetics of trichloroethylene in a closed batch system. Water Research 2005, 39, (6), 1037-1046.
[4] Liou, Y. H.; Lo, S. L.; Lin, C. J.; Kuan, W. H.; Weng, S. C., Effects of iron surface pretreatment on kinetics of aqueous nitrate reduction. Journal of Hazardous Materials 2005, 126, (1-3), 189-194.
[5] Afounini, G. F.; Clausen, C. A.; Geiger, C. L.; Reinhart; Ruiz, N. E., The use of zero-valent iron and ultrasonic energy for in-situ groundwater remediation. Abstracts of Papers of the American Chemical Society 1996, 212, 110.
[6] Hung, H. M.; Hoffmann, M. R., Kinetics and mechanism of the enhanced reductive degradation of CCl4 by elemental iron in the presence of ultrasound. Environmental Science & Technology 1998, 32, (19), 3011-3016.
[7] Geiger, C. L.; Ruiz, N. E.; Clausen, C. A.; Reinhart, D. R.; Quinn, J. W., Ultrasound pretreatment of elemental iron: kinetic studies of dehalogenation reaction enhancement and surface effects. Water Research 2002, 36, (5), 1342-1350.
[8] Zhang, P. F.; Tao, X.; Li, Z. H.; Bowman, R. S., Enhanced perchloroethylene reduction in column systems using surfactant-modified zeolite/zero-valent iron pellets. Environmental Science & Technology 2002, 36, (16), 3597-3603.
[9] Li, Z. H.; Jones, H. R.; Bowman, R. S.; Helfferich, R., Enhanced reduction of chromate and PCE by pelletized surfactant-modified zeolite/zero-valent iron. Environmental Science & Technology 1999, 33, (23), 4326-4330.
[10] Son, H.S.; Im, J.K.; Zoh, K.D., A Fenton-like degradation mechanism for 1,4-dioxane using zero-valent iron (Fe-0) and UV light. Water Research 2009, 43, (5), 1457-1463.
[11] Hinds, G.; Coey, J. M. D.; Lyons, M. E. G., Influence of magnetic forces on electrochemical mass transport. Electrochemistry Communications 2001, 3, (5), 215-218.
[12] Jiang, J.H.; Li, Y.H.; Cai, W.M., Experimental and mechanism research of SO2 removal by cast iron scraps in a magnetically fixed bed. Journal of Hazardous Materials 2008, 153, (1-2), 508-513.
[13] Liang, L.; Sun, W.; Guan, X.; Huang, Y.; Choi, W.; Bao, H.; Li, L.; Jiang, Z., Weak magnetic field significantly enhances selenite removal kinetics by zero valent iron. *Water Research* 2014, 49, 371-380.

[14] Hsu, C. Y.; Liao, C. H.; Lu, M. C., Treatment of aqueous nitrate by zero valent iron powder in the presence of CO2 bubbling. *Ground Water Monitoring and Remediation* 2004, 24, (4), 82-87.

[15] Li, C. W.; Chen, Y. M.; Yen, W. S., Pressurized CO2/zero valent iron system for nitrate removal. *Chemosphere* 2007, 68, (2), 310-316.

[16] Zhang, W. X., Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research* 2003, 5, (3-4), 323-332.

[17] Comba, S.; Di Molfetta, A.; Sethi, R., A Comparison Between Field Applications of Nano-, Micro-, and Millimetric Zero-Valent Iron for the Remediation of Contaminated Aquifers. *Water Air and Soil Pollution* 2011, 215, (1-4), 595-607.