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Research Progress on Nanoscale Zero Valent Iron Remediation of Heavy Metal Contaminated Soil

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Abstract: With the acceleration of industrialization, the problem of heavy metal pollution in soil is becoming more and more serious, posing a threat to the ecological environment and human health. As an emerging remediation technology, nano-ZVI has shown great potential in the field of remediation of soil heavy metal pollution due to its efficient reduction ability and large specific surface area. In this paper, the research progress of nano-ZVI remediation of heavy metal contaminated soil is reviewed, including the preparation method and modification method of nano-ZVI and its application in the remediation of heavy metal contaminated soil, aiming to provide scientific basis and technical support for the treatment of soil heavy metal pollution.

Keywords: Nanoscale zero-valent iron, soil, remediation, heavy metal pollution, repair material.

1. Introduction

With the rapid development of industry, such as metal smelting, chemical, mining, electroplating, iron and steel, petrochemical, coal and other industrial activities, a large number of heavy metal elements are brought into the atmospheric environment, water environment and soil environment in the form of waste water, waste gas, waste residue, etc., causing serious pollution. Heavy metal pollution has become a global problem, considering the harm caused by heavy metals to plants, animals, ecosystems and human bodies, heavy metal pollution control is imminent. Among the remediation materials for heavy metal contaminated soil, nano-zero-valent iron (nZVI) is a soil remediation material with great development potential due to its strong reducing property and good adsorption capacity.

"Nano" generally refers to particles with a particle size in the scale range of 10 -7 ~10-9 m. At present, the particle size of nZVI prepared at home and abroad is in the range of 12nm~120nm. In general, the smaller the particle size, the more surfaces exposed to the active ingredient Fe, and the larger the contact surface with the contaminant, the better the remediation effect of the contaminant. However, there are also some problems, such as the smaller the particle size, the stronger the reactivity, and the easier it is to inactivate nZVI; Moreover, the processing cost also increases accordingly. The ideal nZVI should have five characteristics: "small particle size", "narrow range", "high sphericity", "low tendency to agglomerate", and "uniform chemical composition". Therefore, nZVI prepared by different methods exhibit different properties. The study of iron reduction can be traced back to the early 80s of the last century, when researchers began to synthesize zero-valent iron. With the deepening of the understanding of the properties of nanoparticles and the continuous improvement of the technology of synthesizing nanoparticles, a large number of nZVIs can be synthesized artificially and applied in the environmental field. This method delivers nZVI to the target location where the soil needs to be remediated, and can effectively reduce the toxicity of harmful heavy metal ions in the soil by using its strong reducibility and adsorption capacity formed by a large specific surface area.

2. The Preparation Method

2.1. The physical preparation method

The main methods for preparing nZVI are physical and chemical methods. Among them, the physical preparation method can be divided into ball milling method, sputtering method, deep plastic deformation method, etc. Through the ball milling process, the iron powder particles can be changed from large to small, and there is no need to add chemical reagents and provide heat sources during the process, and the nano ZVI has good thermal stability. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analysis confirmed that the nano-ZVI crystals did not show significant coarsening after annealing. In this method, iron powder with an average particle size of about 2 μm can be ground for 30 min, so that the specific surface area of the raw material can be increased from 5 m^2/g ~ 10 m^2/g to 35 m^2/g ~ 40 m^2/g, and the particle size can be reduced to 40 nm ~ 60 nm [1]. The nZVI particles prepared by sputtering and deep plastic deformation methods have good uniformity and high purity[2], but the sputtering method has high cost, high energy consumption, and high processing requirements of deep plastic deformation method, which is generally suitable for the production of small-batch nano ZVI particles.

2.2. The chemical preparation method

Chemical preparation of nZVI is a commonly used method in recent years, especially in the scientific research process. The method is further subdivided into: liquid phase reduction method, gas phase reduction method, microemulsion method, pyrolysis carbonyl method, etc. Among them, the liquid-phase reduction method generally uses a strong reducing agent such as KBH_4 or $NaBH_4$ to reduce Fe(II) or Fe(III) ions in solution to Fe(0) particles[3]. A large amount of iron powder can be rapidly obtained by rapidly adding $NaBH_4$

solution to $FeSO_4 \cdot 7H_2O$ solution under mechanical stirring conditions (without N_2 protection). The particle size of the obtained iron powder is 60nm~80nm, and the specific surface area of the particles is in the range of 41.7 m^2/g~68.41 m^2/g.

The gas-phase reduction method uses reducing gases such as H_2, CO, and NH_3 to reduce solid metal iron salts to obtain nZVI particles. The iron particles obtained by this method have good uniformity, good single-phase property, high sphericity and high purity, but the equipment requirements are high and the operation is difficult. For example, Cao et al. used H_2 or NH_3 as the reducing agent, respectively, and reduced $FeCl_2$ in a heat pipe furnace to obtain nanoscale α-Fe particles. The preparation of nZVI by liquid-phase reduction has the advantages of fast reaction rate[4-6], simple process and low price, but the obtained nanoparticles have defects such as uneven particle size distribution and easy agglomeration and oxidation. The nZVI particles obtained by the microemulsion method and the pyrolysis carbonyl method also have the advantages of uniform particle size, small particle size, and less impurities, but the cost is relatively high, and they are generally only used for small-scale experiments.

3. The Modification Method of Nano-ZVI

3.1. Doping modification

This method is to modify the surface by adding other elements to nZVI to alleviate its easy agglomeration and oxidation, and the commonly used modified elements are metal elements such as Pt, Ag, Cu, etc., as well as non-metallic elements S. For example, Cheng et al. used tea polyphenols and sodium carboxymethylcellulose modified nano-zero-valent iron to remediate hexavalent chromium in soil and water, and the results showed that TPs-nFe0@CMC (CMC/Fe=0.1) is a low-cost, "green" material with good underground fluidity, which can be used for effective in-situ remediation of Cr(VI)[7]. Cao et al. used carboxymethyl cellulose (CMC) to stabilize Fe-Cu nanomaterials, and the results of transmission electron microscopy showed that the particle size distribution of bimetallic particles was uniform, and the composite materials synthesized by CMC were uniformly coated with bimetallic core-shell structure[8]. Qin et al. synthesized bimetallic FeCo nanocomposites in the laboratory by thermal reduction method and used them to remove Cr(VI.) in neutral or alkaline solutions, and the experimental results showed that the particle size of bimetallic FeCo nanocomposites was between 120 and 140 nm, and the concentration of Cr(VI.) could be reduced from 1.0 mg/L to 0.025 mg/L in 1 h at pH=7[9]. Li et al. synthesized S-nZVI by modifying nZVI with S element, and applied it to 2,4,6-trichlorophenol (TCP) in water and soil with good results. Liang et al. prepared S-nZVI by modifying nZVI with S element and applied it to the heavy metals Hg^{2+}, Ag^+, Cu^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+} in water, and the results showed that compared with nZVI, the easy oxidation of S-nZVI was significantly alleviated, and the removal efficiency of heavy metals was significantly increased[10]. Yang et al. synthesized S-nZVI with S element modified nZVI and used it for the remediation of Pb, Cd and As in soil, the results showed that 88% of the aqueous extracted Pb and Cd were converted into reducible, oxidizable and/or reducible forms at 3 h, while for nZVI without S modification, the immobilization rate of Pb and Cd was only 3-56% after 72 h, and S-ZVI significantly reduced the plant utilization rate of Pb, Cd and As[11].

3.2. Surface load modification

Adding some surfactants with dispersion to stabilize nZVI particles, and stabilizing and dispersing nZVI can stabilize them. nZVI particles behave very similarly to colloidal solutions in liquid-phase media. The microscopic processes are as follows: (1) Electric double-layer action. That is, there is an electrostatic interaction between the charge on the surface of the nZVI particle and the heterosexual charge in the solution, forming an electric double layer. By controlling the pH of the solution or by adding an electrolyte, the electric bilayer structure can be changed; (2) Steric hindrance stabilization. Refers to the adsorption of certain polymer compounds on the surface of the particles, preventing closer contact between the particles, allowing the nZVI suspension to be stable. By adding uncharged polymers, the polymer-coated microcellular structure was constructed to improve the stability of the suspension.

4. The Application of nZVI

Heavy metals are widely distributed in nature, and due to the large-scale development of mineral resources, the content of heavy metals in the soil near mining areas and industrial zones is relatively high, and the problem of soil pollution is becoming more and more serious. Duan et al. [12] studied the remediation effect and mechanism of biochar-loaded nano-ZVI on heavy metal contaminated soil, and found that the modified biochar (3:1) treatment group had the best remediation effect on arsenic-contaminated soil, which could significantly increase soil pH, cation exchange capacity and available iron content, and increase the residue content of copper, zinc, arsenic, cadmium and lead. Akintayo et al. [13] remediated Pb and Cd contaminated soil with different concentrations of coconut shell biochar-loaded nano-ZVI and found that it significantly fixed cadmium and lead, and increased antioxidant enzyme activity at low doses. Li et al. [14] studied the fixation of lead in soil by biochar loading nZVI/nFe3O4, and found that 8 g·kg-1 was the optimal amount of fixed lead, which could promote lead immobilization and reduce exchangeable lead under acidic conditions, and BC@nZVI was an environmentally friendly material for remediating lead-contaminated soil. Jin et al. [15] found that the fluidity and bioavailability of lead, cadmium and chromium were significantly reduced by adding biochar/bentonite loaded nano-zero-valent iron composites (BC-BE-nZVI) to lead, cadmium and chromium contaminated soil, forming stable metallogenoids, increasing bacterial richness, soil enzyme activity, and improving soil metabolic function.

5. Conclusion

The emergence of nanotechnology has promoted the development of environmental pollution remediation research to a deeper level. Soil heavy metal remediation technology is changing in the direction of green and low-carbon, from harmless to reduction and comprehensive utilization of resources, and from ex-situ remediation to in-situ remediation. As an effective remediation technology for soil heavy metal pollution, nano-ZVI has broad application prospects. Future research should further explore the environmental behavior and remediation mechanism of nanoiron, optimize the preparation and application technology of nanoiron, and evaluate its environmental safety, so as to realize the wide application of nanoferrotechnology.

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