Mini review on the application research of nanoscale zero valent iron in water treatment

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Mini review on the application research of nanoscale zero valent iron in water treatment

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Abstract: *Nanoscale zero-valent iron (nZVI) is highly efficient in environmental pollution control technology, owing to its unique zero-valent iron core-iron oxide surface, which exhibits exceptional adsorption and reduction properties. This paper provides a comprehensive understanding of the physical and chemical properties of* nano-*iron, with a primary focus on the preparation of nZVI. While nZVI finds extensive application in sewage treatment, it also demonstrates outstanding performance in the remediation of soil organic matter and heavy metal pollution, delivering excellent results and displaying good fluidity.*

Keywords: Nanoscale zero valent iron; Preparation method; Wastewater treatment; Modification; Mechanism of action

1. INTRODUCTION

Nanomaterials, with dimensions between 1 and 100 nm, exhibit unique properties due to their small size, making them essential in various industries [1,2]. Among these nanomaterials, nano-zero-valent iron (nZVI) stands out for its high specific surface area, tiny size, rapid reactivity, strong reducibility, and exceptional adsorption capabilities [4].

In this article, we focus on nZVI, its preparation, and applications in environmental pollution control. We explore its core-shell structure, with a dense zero-valent iron core and an iron oxide or hydroxyl iron outer shell, enabling both reduction and adsorption functions.

We also discuss the pioneering work of Glavee et al. [5], who used sodium borohydride to synthesize nZVI, and subsequent research by Zhang et al. [6].

Throughout the article, we examine nZVI's role in soil and groundwater remediation, organic pollutant removal, and heavy metal detoxification, highlighting its significant contributions to pollution control technologies [7].

2. PREPARATION METHOD OF NANOSCALE ZERO-VALENT IRON

The preparation method of nano-zero-valent iron can be divided into two types: decomposition method and synthesis method according to the shape change of nZVI[8]. The decomposition method is to convert large particles of iron into nano-scale particles. The synthesis method is opposite, and the molecular level or even smaller iron, converted to nanoscale. Common preparation methods are shown in Table 1.

3. APPLICATIONS OF nZVI IN WASTEWATER TREATMENT

3.1. Removal of heavy metals

Heavy metals are a class of poisonous adulterants that have a serious impact on mortal and other natural health [16]. However, it'll seriously contaminate the water body, if heavy metals wastewater from different diligence is continuously discharged into gutters and lakes without treatment. In order to break this problem, people have started exploration on nano- zero- valent iron, because nano- zero- valent iron has the advantages of strong exertion, rapid-fire response, and high junking effectiveness, which has gradationally attracted wide attention [17,18].

Adsorption-co-precipitation: For metal cations whose standard electrode potential is lower than that of iron, such as Zn^{2+}, Ba^{2+}, etc., Nanoscale zero-valent iron can be adsorbed on its surface, but they cannot be directly reduced. At this time, nano-zero-valent iron will react with water to generate a large number of hydroxide ions (OH^-), which will change the acidity and alkalinity of the particle surface, thereby combining with heavy metal ions to form a precipitate, which will be fixed on nano-zero-valent iron particles [19].

Table 1. Summary of nZVI preparation methods

No.	*Production Method*	*Characteristics*	*Particle size (nm)*	*Reference*
1	Liquid phase reduction method	Compared with other methods, it is suitable for laboratory-level research and is easy to prepare	Approx 50	[9]
2	Liquid phase reduction method	Significantly increased effective reactive surface area and stability of nZVI	29.9	[10]
3	Mechanical ball milling method	High reactivity, stability and flowability of particles	<100	[11]
4	Mechanical ball milling method	Effectively prevents nZVI from agglomerating and forming larger particles, keeping it nanoscale	<100	[12]
5	Electrodeposition method	Ultrasound can reduce the degree of particle aggregation and facilitate the generation of smaller particles	1~20	[13]
6	Green synthesis method	Extracted from plants is non-toxic and more environmentally friendly	100	[14]
7	Laser pyrolysis method	The core-shell morphology of iron-carbon nanocomposites may be affected by the gas flow in the reaction zone, and the particle size is extremely small.	3~7	[15]

Reduction-co-precipitation: suitable for metals that do not exist in water in the form of cations, such as metal Cr. nZVI can quickly reduce Cr (VI) to Cr(III), and precipitate and fix it on the surface of nZVI[20].

Adsorption- oxidation- reduction The junking of As by nano- zero- valent iron is a combination of adsorption, oxidation and reduction. The main forms of As in water are As(V) and As(III). Nano zero- valent iron can reduce As(V) to As(0) and As(III), and can also oxidize As(III) to As(V)[21, 56,57,58].

Due to the small size of nano- ZVI patches and their capability to resettle fleetly in water, they can be flexibly used for in- situ and ex-situ remediation of heavy metals in water. Still, the high price of Nanoscale zero- valent iron, and its easy agglomeration reduces the migration speed, which limits its operation in the factual heavy metals' wastewater treatment. thus, reducing the agglomeration miracle of nano- ZVI is of great significance for its wide operation [22, 60, 61,62, 63, 64].

In summary, due to its great efficiency in heavy metal ion removal, nano-sized zero-valent iron has received a lot of interest in the field of heavy metal ion removal. However, its use is restricted by the expensive cost and the difficulty of reunion, therefore effective improvement methods are required.[23].

3.2. Nitrate removal

Nitrogenous pollutants in water bodies can be divided into two categories: organic and inorganic. Organic nitrogen-containing pollutants are stable in structure, difficult to decompose and transform, and have a long residual time, which poses a greater risk of refractory degradation to organisms [24, 68,69]. Among inorganic nitrogen-containing pollutants, nitrite nitrogen and nitrate nitrogen are the most harmful, which can cause serious damage to human and animal health such as methemoglobinemia, so the discharge of such substances needs to be strictly controlled [25, 70, 71].

In recent years, studies have shown that zero-valent iron shows great potential in reductive removal of nitrate in water [26]. Scientists use nano-zero-valent iron to quickly reduce nitrate in water through chemical reactions, converting it into safer substances such as nitrogen. However, this method also has some disadvantages, such as nano-zero-valent iron cannot completely reduce nitrate to nitrogen, resulting in the production of a large amount of ammonia-nitrogen during the reaction. In addition, the pH value of the reaction system also needs to be strictly controlled, which limits its application range [27, 55, 59]. Future research should concentrate on enhancing the capabilities of nZVI to more effectively convert nitrate to nitrogen and lower the cost of further processing. In order to increase the removal effectiveness of nano-zero-valent iron, scientists must also discover better techniques to regulate the pH level of the reaction system. By doing so, we may more effectively address the issue of nitrogenous pollution in water bodies.[28].

3.3. Removal of organic halogenated compounds

Organohalogenated substances are a class of pollutants ubiquitous in water and soil, mainly produced in the production and use of refrigerants, paints and pesticides [29, 65, 66, 67]. Most of these organic halogenated substances are stable in structure, difficult to degrade and highly toxic, and are easy to accumulate in the human body and the environment, so they are listed as one of the three key organic pollutants in global environmental science research (organic halogenated substances, heterocyclic compounds and polycyclic aromatic hydrocarbons) [30].

As an effective dehalogenation agent, nano-zero-valent iron has attracted global attention and is widely used in the treatment of pollutants such as halogenated alkanes, halogenated aromatics, and PCBs (polychlorinated biphenyls) [31,32]. Studies have shown that nano-zero-valent iron reacts with halogenated hydrocarbons under anaerobic conditions, has strong reducing properties, and can convert some halogenated hydrocarbons into non-toxic substances [33].

Not only that, Nanoscale zero-valent iron is also used to treat p-NCB (p-Chloronitrobenzene) in water. Under certain dosage and initial pH conditions, it can efficiently degrade p-Chloronitrobenzene [34]. At the same time, nano-zero-valent iron can quickly and effectively convert vinyl chloride pollutants into non-toxic ethane and ethylene, and no chlorine-containing intermediate products are produced during the reaction [35].

Nano-zero-valent iron has garnered a lot of attention and is frequently utilized in real-world applications because it has demonstrated significant potential as an efficient pollution treatment technology for the elimination of both organic and inorganic halides [37,38].

4. COMMON MODIFICATION METHODS OF nZVI

Nanoscale zero-valent iron (nZVI) is effective for water pollutant removal but agglomeration limits its efficiency. Modifying nZVI is a possible solution, but current evaluation methods under ideal conditions may not be practical. Economic benefits must be considered due to the influence of material amount on pollutant removal cost [39,40].

Liu et al. [41] introduced the concept of 'electron efficiency,' which assesses the economic advantages of modified nZVI by comparing the electrons consumed during a specific time frame in the reduction process to the electrons supplied by nZVI. This approach aims to optimize costs and maximize electron utilization. However, it is important to note that while electron efficiency offers economic insights, it may not provide an accurate representation of the rate at which pollutants are removed [42].

For the evaluation of nZVI modification, Zhou et al [43]. reviewed the ways to improve the electron selectivity of nZVI and demonstrated the importance of the evaluation of this economic benefit. However, more economical and rapid evaluation methods are still needed. In many studies of ZVI nanoparticles, the methods for evaluating modified materials mainly focus on the exploration of reactivity, stability or toxicity under different physicochemical conditions [44]. However, this disjointed approach to research may lead to disagreements in the evaluation of modified materials [45]. Therefore, the new evaluation method should evaluate the modified nano-zero-valent iron in many aspects (reactivity, stability, mobility, toxicity) and multi-factors to better meet the needs of practical applications [46].

4.1. Load modification

Loading modification is a technique for consistently and evenly dispersing nanoscale zero-valent iron (nZVI) over the surface of other materials, with the aim of preventing nZVI agglomeration and boosting the contact area to encourage the degradation of contaminants. Clay and high surface area carbon materials, which have strong adsorption capabilities and stability, are often utilized loading materials. One key strategy for creating multifunctional nZVI materials is load modification [47].

4.2. Bimetal modification

In order to increase reactivity, particularly for contaminants that need to be dehydrogenated, bimetallic modification involves combining micro zero-valent iron with another metal. Metals including palladium, platinum, nickel, copper, and silver are frequently utilized. Despite being the most effective catalyst, palladium is constrained by its greater price. A less expensive and less harmful option is copper. Even though the bimetal modification can increase the reaction's efficiency, it's important to consider any potential environmental issues that the second metal may bring about. To improve stability and application effects, it may be possible to combine multifunctional nano-zero-valent iron materials with other ways of modification [48].

4.3. Vulcanization modification

By creating a sulfide shell on the surface of nano-zero-valent iron, the modification process known as sulfurized nano-zero-valent iron (S-nZVI) increases the material's specific surface area and reducing power. The use of S-nZVI as an electron transfer medium to effectively transport electrons to target pollutants has the potential to play a part in pollutant remediation [49]. While being salt-tolerant, it has good performance in the removal of heavy metals and organic contaminants. S-nZVI may be made using a one-step approach or a two-step method, with the one-step method having a greater sulfur content and selectivity. Additionally, the bioprecipitation approach for producing S-nZVI eliminates the need of hazardous chemical sulfur reagents. The structure and homogeneity of the iron sulfide determine how long S-nZVI will last, and its outer shell can shield the core from anoxic corrosion and convert heavy metal ions to sulfide throughout the process. This modification technique has drawn a lot of interest in nZVI research and has demonstrated potential for application [50].

4.4. Surface modification

Nanoscale zero-valent iron (nZVI) can be dispersed in water by altering its surface through surface modification with coating molecules. The coating reduces inter-nanoparticle contact force and improves stability through steric hindrance. The surfactant concentration plays a significant role in this process, affecting the liquid's characteristics and surface tension [51,52].

Surface modification alters the charge on nZVI, reducing electrostatic attraction and aggregation. It also increases available surface sites for pollutant concentration reduction. However, surface alteration may limit diffusion channels, hinder electron transfer to pollutants, scavenge active radicals, and prevent dispersion of contaminants [53].

Despite the potential benefits of surface modification, it's essential to carefully consider influencing factors and drawbacks in real applications. Interaction with other substances, such as humic acid, can lead to aggregation and sedimentation of nZVI [54].

5. CONCLUSIONS AND PROSPECTS

Nano-zero-valent iron (nZVI) is a promising technology for remediating pollutants like heavy metals, halogenated compounds, and nitrates in wastewater. However, challenges such as easy aggregation and oxidation need to be addressed. To enhance its efficacy, researchers are modifying nZVI properties to improve performance, reduce costs, and extend its service life.

Though studies have revealed insights into how nZVI and its variants remove pollutants, uncertainties remain due to diverse pollutant structures. Further research is essential to fully understand the process, enabling effective nZVI application in engineering scenarios. The main challenge is applying mature revision techniques to nZVI particles prepared through artificial physical methods, enhancing engineering operations and revolutionizing water pollution mitigation.

In conclusion, overcoming aggregation and oxidation challenges and adopting advanced revision methods will accelerate nZVI's real-world applications. Continued research is crucial to comprehensively explore nZVI's potential, enabling more efficient and environmentally friendly wastewater treatment approaches and contributing to a cleaner and healthier environment.

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