Synthesis of Guar Gum Stabilized Nanoscale Zero-valent Iron for Cr (VI) Removal in Water

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Abstract. Guar gum was used in the preparation of a new stabilized nanoscale zero-valent iron (nZVI), as a biodegradation stabilizer. The TEM results showed that the nanoparticles were coated by guar gum, and average particle size was 87.4 nm; XRD results showed that guar gum stabilized nZVI was α-nanoFe0. The batch test results showed that the degradation rate of guar gum stabilized nZVI was 12 times than 200 mesh reduced iron powder. Guar gum could hinder the formation of Fe(III)-Cr(III) precipitate by chelating Fe(III), consequently enhanced the reduction of Cr(VI) to Cr(III).

1. Background
More than 10% of our products are related to chromium[1,2], it is also widely used in fur, textile printing and dyeing, mining and smelting, chemical, pigment, pharmaceutical and other industries[3-5]. Cr(VI) serious pollution is caused by unreasonable utilization and emission. There are two main forms of chromium in nature: Cr(III) and Cr(VI), among which Cr(VI) has high carcinogenicity, high toxicity and high mobility, so the remediation technology of Cr(VI) pollution has attracted widespread attention. Conventional Cr(VI) remediation techniques mainly include adsorption, membrane separation, chemical precipitation. Nano-iron applications are a very active research field in environmental pollution remediation technology. Because of its high reaction activity and the ability to repair many kinds of environmental pollutants, it has shown obvious advantages in environmental pollution remediation. However, there are still some problems need to be solved in practical application: the synthesis conditions are difficult to control due to the high activity of nano-iron; iron nanoparticles are small in size and easy to agglomerate and affect the activity; the stability of nano-iron materials is poor, and it is easy to oxidize or even self-ignite in the environment; the substances used in the preparation process have potential pollution to the environment.

Based on the former research experience in preparing nanoparticles and consulting relevant literature[6], we conclude that the formation of uniformly stable nano-irons with particle size must satisfy the following conditions: (1) there are a large number of groups with metal complexation ability in the reaction system, such as hydroxyl, carboxyl, amino, etc., and can form metal-iron colloidal particle precursors with iron ions; (2) dispersed stabilizers added in particle formation can form nanometres and have steric hindrance effect; (3) the amount of reducing agent and the strength of reduction ability also affect the stability and particle size of nanoparticles.
Guar gum is a green polyol biomacromolecule substance (Figure 1). This structure determines that guar gum has strong water absorption characteristics, good solubility in cold water and hot water, wide range of viscosity stability and adaptability, and has good water solubility and crosslinking property. It can be widely used in food, petroleum, chemical products for daily use, paper, textile, construction, medicine, ceramics and other industries. Guar gum contains a large number of hydroxyl groups (-OH), which can form metal iron colloidal particle precursors with iron ions, and it has a more complex spatial structure, which is conducive to the formation of nano-matrices and promotes the formation of nano-iron particles. In addition, guar gum is rich and cheap, has good biocompatibility and biodegradability, and will not produce secondary pollution.

A new nZVI was prepared by a simple liquid phase reduction method using guar gum as a stabilizer. The removal of Cr (VI) from water by guar gum stabilized nano-iron was investigated by batch experiments and satisfactory results were obtained.

2. Experimental part

2.1. Synthesis of guar gum stabilized nZVI
Added a certain amount of guar gum powder into deionized water, and mixed for 40-60 min in water (60-70°C) to obtain 0.5% guar gum solution; added 10 ml aqueous solution containing 0.4467 g FeSO₄·7H₂O into a three mouth bottle, then added 10 ml of 0.5% guar gum solution, removed oxygen with nitrogen for 30 min, and then stirred for 10 min; under stirring, added 10 mL of newly prepared 0.4334 g KBH₄ to the mixed solution. A black nano zero-valent iron solution was obtained by 30-50 min reaction, and the nano zero-valent iron particles were separated by magnetic separation method, washed three times with deoxygenated distilled water, and the stable nano zero-valent iron particles were obtained by vacuum drying. The reaction equation was as follows:

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2Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 \downarrow + 2B(OH)_3 + 7H_2 \uparrow
\]

2.2. Characterization of guar gum stabilized nZVI
The guar gum stabilized nZVI was dissolved in deoxyethanol, and the particle size and morphology were analyzed by transmission electron microscope; Washed and dried under nitrogen protection, measured XRD Spectrum (tube voltage 40kV, tube current 100mA, CuKα radiation, scanning speed 4°/min, scanning range 10-80°) and performed SEM characterization (magnification ×5000 and ×15000); Characterized the valence state of each element in guar gum stabilized nZVI by XPS (full scan spectrum and high-resolution XPS spectrum of Cr and Fe).

2.3. Batch experiments of guar gum stabilized nZVI for Cr (VI) removal in water
Added 40 mg/L of Cr(VI) solution to a 175 mL plasma bottle, added guar gum stabilized nZVI, sealed with polytetrafluoroethylene tape, and placed in a gas bath constant temperature oscillator to shake (220r/min) reaction. At a predetermined time, used a magnet to attract the black particles to the bottom of the plasma bottle. Used a syringe to collect a certain Cr(VI) simulated water sample. The sample was
quickly filtered through a 0.22μm filter membrane. The concentration of Cr(VI) in the sample was measured by diphenylcarbazide spectrophotometry.

### 3. Results and discussion

#### 3.1. Characterization of guar gum stabilized nZVI

The nano-iron particles were spherical or elliptical, forming a grayish-white coating layer around the nano-iron, which was guar gum (Figure 2 (a)). The rapid oxidation of guar gum stabilized nano-iron was not found. The particle size range was between 30 and 200 nm, with an average particle size of 87.4 nm.

The XRD spectrum of guar gum stabilized nZVI (Figure 2 (b)) was a body-centered cubic α-Fe0 crystal plane dispersion diffraction peak at 44.46°, so it could be determined that the composition of nano-iron was α-nanoFe0.

In the process of cleaning the nZVI, a magnet was used for magnetic separation, and the obtained nZVI had obvious agglomeration, and most of the nano-iron in the SEM image (Figure 2 (c)) was in the form of aggregation.

![Figure 2. Characterization diagram of stable nano-iron with guar gum (a .TEM; b.XRD; c.SEM)](image)

#### 3.2. Degradation of Cr (VI) in water with guar gum stabilized nZVI

Under the conditions that the reaction system pH=6.0 and the temperature was 25℃, the newly prepared guar gum stabilized nZVI was added to the Cr (VI) solution with an initial concentration of 40 mg/L, so that the concentration of nZVI was 0.5 g/L, and the reduced iron powder with a concentration of 5 g/L was added under the same reaction conditions. Two different types of zero-valent iron materials had great different effects on the removal Cr (VI) in water (Figure 3(a)). The reduced iron powder had no obvious effect within 80 minutes, and the removal rate was only 0.5%. The removal rate of guar gum stabilized nZVI on Cr(VI) in water was much higher than that of reduced iron powder, and the removal rate of Cr(VI) in 80 min was as high as 70%, which is mainly due to the huge specific surface area and high reaction activity of guar gum stabilized nZVI. The research results show that[12,13], the reaction kinetics of zero-valent iron reduction and removal of Cr(VI) can be described by the apparent first-order reaction kinetics. In order to compare the degradation of the two materials more clearly, used ln (C/C0) to linearly fit the reaction time t to obtain the reaction kinetics fitting diagram (Figure 3 (b)). The apparent
rate constant ($k_{obs}$) of Guar gum stabilized nZVI and reduced iron powder were $6.1 \times 10^{-3}$ min$^{-1}$ and $5.0 \times 10^{-4}$ min$^{-1}$, the former was more than 12 times the latter.

![Graph showing degradation and reaction kinetics of Cr (VI) by nZVI and reduced iron powder.](a) Figure 3. The degradation (a) and reaction kinetics of Cr (VI) by nZVI and reduced iron powder (b)

### 3.3. Reaction product analysis

The surface composition of the sample after the reaction of guar gum stabilized nZVI with Cr(VI) was thoroughly analyzed by XPS(Figure 4). The sample surface was dominated by Fe, Cr, O, C elements. The appearance of C peaks should be caused by polluting carbon, while the appearance of Cr peaks indicated that chromium had been separated from water and deposited on the surface of nZVI. The binding energies of Cr$_2$P$_3/2$ and Cr$_2$P$_1/2$ after the reaction of guar gum stabilized nZVI were 574.3 eV and 583.6 eV, respectively(Figure 5(a)). According to the XPS spectrum database, chromium on the surface of the sample existed in the form of Cr(III), that was, an oxidation-reduction did occur on the surface of nZVI, Cr (VI) was reduced to Cr(III). After the reaction, the binding energies of Fe$_2$P$_3/2$ and Fe$_2$P$_1/2$ in the guar gum stabilized nZVI were 706.7 eV and 719.9 eV, respectively(Figure 5 (b)). According to the XPS spectrum database, the iron on the surface of the sample after the reaction mainly existed in the form of Fe(III), and there was no iron in the form of Fe(0) after the reaction. The main reasons are as follows :(1) Cr(VI) acted as a strong oxidant to oxidize nZVI;(2) during the reaction process, the small amount of dissolved oxygen that may existed in the water oxidizes the nano-iron. The research results of Alowitz et al.[14] showed that, as a strong oxidant, Cr(VI) has a relatively obvious passivation effect on nano-iron. Research shows that zero-valent iron can reduce Cr(VI) to Cr(III). Zero-valent iron is oxidized to Fe(III), and the two are deposited on the surface of zero-valent iron in the form of Fe(III)-Cr(III) hydroxide co-precipitation to form a passivation layer; The research results of Li et al.[15] further showed that, the actual structure of the hydroxide passivation layer on the surface of nano-iron is Cr$_{0.667}$Fe$_{0.333}$O$_2$OH or (Cr$_{0.667}$Fe$_{0.333}$)(OH)$_3$, that is, the ratio of Fe to Cr atoms is 0.5. After the reaction, the content of Cr(III) and Fe(III) on the surface layer is 1.14% and 7.38%, respectively. The ratio of iron to chromium is 6.47, which is 12.95 times that of Li et al. This further proves that the guar gum molecules can chelate more Fe(III), which increases the Fe(III) content on the sample surface, which also reduces the co-precipitation of Cr(III) and Fe(III) hydroxides, and then promote the degradation of Cr (VI).
Figure 4. XPS scanning patterns of guar gum stabilized nZVI with Cr (VI)

Figure 5. High resolution XPS spectra of Cr2p (a) and Fe2p (b) of guar gum stabilized nZVI

4. Conclusion
A new preparation method of stable nano-iron was proposed and its degradation performance to Cr (VI) was studied. The following conclusions were obtained:

(1). Guar gum as a food additive, biodegradable macromolecular substances played a vital role in the preparation of nano-iron. A large number of hydroxyl groups in its molecular structure complexed with Fe (II) to form metal colloid precursors to ensure the formation of nano-iron particle nuclei, while the complex spatial structure provided a good steric hindrance effect for the growth of nano-iron particles, and finally obtained the nano-iron with excellent properties;

(2). Average particle size of nano-iron stabilized by guar gum was about 87.4 nm, which had the characteristics of large specific surface area and high reaction activity. The coating of nano-iron particles with guar gum not only enhanced the oxidation resistance of nano-iron, but also increased the chelation of Fe (III), Reduced the effect of passivation on the degradation Cr (VI) of nano-iron;

(3). Guar gum stabilized nZVI had a high degradation ability to Cr (VI), and the substances used in the preparation process had little effect on the environment, so it is helpful to expand the application of nano-iron in the environment.
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