Synthesis of Fe-based Nanoparticles by Tea Polyphenols and Their Removal of Hexavalent Chromium

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Abstract. Tea polyphenols were used to synthesize Fe-based nanoparticles (TP-Fe NPs) and remove hexavalent chromium (Cr(VI)) in an aqueous solution. The results demonstrated that 0.92 was the optimal mass ratio of tea polyphenols and FeCl₃, and the addition of polyvinyl alcohol (PVA) as a stabilizer significantly improved the stability of Fe nanoparticle suspension, which can be maintained stable for 60 h. Both scanning electron microscopy (SEM) and X-ray diffraction (XRD) results showed that the sizes of the synthesized Fe nanoparticles, namely, FeO, FeOOH, Fe₂O₃, and organic matter such as quinone range from 50 to 120 nm. TP-Fe NPs effectively remove Cr(VI) in an aqueous solution by reduction and adsorption, and the removal rate surpasses 99.5%. Because of its low cost and high reduction efficiency, TP-Fe NPs has broad application prospects for remediating Cr-contaminated soil and groundwater.

1. Introduction
Rapid industrialization has increased soil and groundwater pollution caused by heavy metals, organic wastes, and industrial wastewater [1]. Because of its strong reactivity, small particle size, and strong mobility in soil and groundwater, nano Fe serves as a remedy for large-scale pollution when injected into soil and groundwater; therefore, it is considered as an ideal environmental remediation material [2]. Multiple studies have been conducted on the remediation of organic pollutants (such as TCE, DCA, and antibiotics) and heavy metals (such as Pb, As, and Cr) in water with Fe-based nanomaterials [3]. Previously, to prepare Fe nanoparticles, the liquid-phase reduction is a commonly used method. Its basic principle is to slowly add strong reducing agents such as NaBH₄ or KBH₄ to a solution of Fe ions under anaerobic conditions to reduce Fe ions into Fe nanoparticles. However, the strong reducing agent used is highly toxic and expensive. Nano Fe produces B(OH)₃ and a large amount of hydrogen in the synthesis process, which is slightly dangerous. These limitations increase the cost of preparing nano iron difficult [2-4].

Recently, a green, environmentally friendly and inexpensive method for preparing Fe nanoparticles by reducing Fe ions using plant extracts has been developed. Many studies used green tea, eucalyptus
leaves, oak, and mulberry extracts to reduce Fe ions and obtain Fe nanoparticles to remove organic dyes, Cr(VI), As(III), Pb^{2+}, and nitrate [5-8]. Plant extracts are rich in hydroxyl and carboxylic groups, which combine with Fe ions and reduce Fe(III) to Fe(II) and zero-valent iron. However, plant extracts in the abovementioned studies are solutions obtained by boiling and filtering leaves in the laboratory; therefore, the preparation efficiency is low. Tea polyphenol extracts from food-grade are widely available and cost-efficient. Using the tea polyphenol extract as a reaction agent can improve the production efficiency of the green synthesis of Fe nanoparticles. Moreover, the green synthesis of nano Fe materials will still have the phenomenon of agglomeration, which limits the migration of nano Fe in groundwater.

In this study, the method of the green synthesis of nano Fe improved, primarily using tea polyphenol extract and ferric chloride as raw materials, and then adding a dispersant to improve the stability of the green synthesis of nano Fe. The prepared suspension of iron nanoparticles (TP-Fe NPs) was used to remove Cr(VI) in an aqueous solution. The properties of TP-Fe NPs and the mechanism of removing Cr(VI) were then explored, which acted a reference for synthesizing nano Fe as environmental remediation materials.

2. Materials and Methods

2.1. Materials

Tea polyphenol extract was purchased from Jinan DongXuan Bioengineering Co., Ltd., with a purity of >95%. Ferric chloride, potassium dichromate, sodium carbonate, diphenylcarbazide, sulfuric acid and phosphoric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Carboxymethyl cellulose (CMC), corn starch (CS), xanthan gum (XG), chitosan (CTS), polyvinyl alcohol (PVA), maltodextrin (MD) and rhamnolipid (RL) were selected as stabilizers. Each stabilizer was prepared with a solution of 10 g/L before use.

2.2. Synthesis of TP-Fe NPs

The overall preparation process of Fe nanoparticles is as follows. First, 500 mL of 0.1 mol/L FeCl₃ solution was added to the round bottom flask and tea polyphenol solutions of different concentrations are slowly added under a stirring state of 500 rpm, after the solution turned from yellow to black. Then, 10 ml of the stabilizer solution was added and evenly stirred to obtain the TP-Fe NPs suspension. The mass ratio of FeCl₃ to tea polyphenol was controlled by controlling the concentration of the tea polyphenol solution.

This experiment explores the effect of stabilizer types on the stability of nano Fe suspension. When the mass ratio of tea polyphenols and FeCl₃ is 1:1, seven stabilizers (10 ml) are added. After preparation, to select the best stabilizer, the TP-Fe NP suspension was placed in the glass tube, and the sedimentation phenomenon of the nano Fe suspension was regularly observed.

2.3. Characterization of TP-Fe NPs

The TP-Fe NP suspension before and after reaction with Cr(VI) was centrifuged at 6000 rpm for 30 min, and the supernatant was discarded. The precipitates were then characterized after freeze-drying. Scanning electron microscopy (SEM) images were then acquired using a field-emission scanning electron microscope with an energy dispersive spectrometer (SEM-EDS) (SU8010, Hitachi, Japan) at an accelerating voltage of 10 kV. X-ray diffraction analysis (XRD) patterns were collected on an X-ray diffractometer (AXS D8-Focus, Bruker, Germany) equipped with a Cu target at 40 kV and 40 mA.

2.4. Batch experiments

Batch experiments were set up to explore the effects of the reaction time, the ratio of tea polyphenols to ferric chloride, and the dosage of TP-Fe NPs on the removal of hexavalent chromium. Six groups of TP-Fe NPs suspension were prepared constrained by the mass ratio of FeCl₃ to tea polyphenol as 0.18, 0.31, 0.43, 0.62, 0.92, and 1.23. Then, the TP-Fe NPs suspension was added to 25 ml of 50 mg/L
Cr(VI) solution, and the mixture was centrifuged at 3000 rpm for five min after stirring at 200 rpm for a different time. Finally, the supernatant was filtered to determine Cr (VI). The reaction temperature was 5–60 min and the dosage of TP-Fe NPs suspension ranged from 0.2 to 5 mL.

3. Results and Discussion

3.1. Effect of stabilizer on the stability of TP-Fe NPs suspension

Figure 1 shows the images of TP-Fe NPs suspension after adding different stabilizers for 12 and 36 h. TP-Fe NPs suspension with CS, XG, MD, and RL as stabilizers precipitated when the storage time was 12 h, while that with CMC, CTS, and PVA as stabilizers were stable. After 36 h, only PVA-stabilized TP-Fe NPs suspension was stable. From Table 1, which shows the stable time of Fe suspension with different stabilizers, PVA was the best stabilizer for nano Fe suspension and increased the stable dispersion time of TP-Fe NPs to 60 h. PVA was a water-soluble polymer, which dispersed in a solution to facilitate the formation of a viscous or gel matrix/network via hydrogen bonding and polymer entanglements, thereby inhibiting the polymerization and precipitation of Fe nanoparticles [9]. To avoid aquifer blockage, the stability of nano Fe suspension was suitable for its long-term migration in the aquifer; therefore, PVA was the most suitable stabilizer.

Figure 1. The images of TP-Fe NPs suspension after adding different stabilizers for 12 h and 36 h

| Stabilizers | None | CMC | CS | XG | CTS | PVA | MD | RL |
|------------|------|-----|----|----|-----|-----|----|----|
| Time (h)   | 3    | 15  | 5  | 7  | 15  | 60  | 5  | 5  |

3.2. Characterization of TP-Fe NPs

Figure 2a shows the SEM image of TP-Fe NPs. Fe nanoparticles are spherical with particle sizes ranging from 50 to 120 nm. Moreover, this phenomenon was observed in previous studies on the green synthesis of Fe nanoparticles [10-12]. From Table 2, EDS analysis shows that TP-Fe NPs primarily contain C, Fe, O, Cl, and other elements. The proportion of C is 41.0%, indicating that organic matter is attached to Fe nanoparticles. According to previous study, tea polyphenols are oxidized to quinones after reacting with Fe³⁺. Quinone attached to the surface of iron nanoparticles can act as a capping agent to prevent iron nanoparticles from being oxidized by oxygen [13]. From Figure 3, XRD patterns showed that TP-Fe NPs primarily contained FeO, FeOOH, Fe₃O₄, and Fe₂O₃, indicating that iron oxides or hydroxides were formed by the reaction of tea polyphenols with ferric ions. In the SEM image of TP-Fe NPs produced after the reaction with Cr(VI) (Figure 2b), the spherical iron nanoparticles disappear. The EDS results demonstrated that the proportion of Cr and K increased after the reaction, indicating that Cr and TP-Fe NPs co-precipitated. The XRD patterns showed that FeO,
FeOOH, and Fe$_3$O$_4$ in the TP-Fe NPs disappeared, and only Fe$_2$O$_3$ remained, which indicated that Fe(II) in the Fe nanoparticles oxidized to Fe(III). From the above information, TP-Fe NPs rapidly reduced Cr(VI) to Cr(III) and formed the composite precipitation of Fe(III)-Cr(III)-organic matter to remove Cr(VI) in water.

![Figure 2. SEM images of TP-Fe NPs before (a) and after (b) reaction with Cr(VI)](image)

| Element | TP-Fe NPs (wt%) | After reaction with Cr(VI) (wt%) |
|---------|----------------|-------------------------------|
| C       | 41.00          | 46.56                         |
| Fe      | 28.85          | 24.65                         |
| O       | 12.49          | 16.93                         |
| Cl      | 17.66          | 8.00                          |
| Cr      | 0              | 2.79                          |
| K       | 0              | 1.07                          |

![Figure 3. XRD patterns of TP-Fe NPs before (a) and after (b) reaction with Cr(VI)](image)

3.3. Removal of Cr(VI) by TP-Fe NPs

Figure 4 shows the removal of Cr(VI) by TP-Fe NPs at different reaction times while showing that the reaction reached equilibrium in 30 min. TP-Fe NPs have a large specific surface area and strong reactivity, and they can rapidly reduce Cr(VI). Figure 5 shows that the higher the dosage of TP-Fe NPs, the higher the removal rate of Cr(VI), and the highest removal rate can surpass 99.5%. The rapid removal of Cr(VI) in TP-Fe NPs prepared by the different proportions of ferric chloride and tea polyphenols varied. With increase in tea polyphenol content, the swift removal of Cr(VI) in prepared
TP-Fe NPs suspension became stronger. When the ratio of tea polyphenols and ferric chloride is >0.92, the removal efficiency of Cr(VI) is similar. The primary reason is that tea polyphenols are electron donors for synthesizing Fe nanoparticles. The more tea polyphenols are used, the more iron nanoparticles are obtained by reducing Fe ions. Because of the high cost of tea polyphenols, when the mass ratio of tea polyphenols and ferric chloride is 0.92, it is the most appropriate.

Figure 4. Removal of Cr(VI) using TP-Fe NPs with different ratio of tea polyphenols and FeCl₃ at different reaction time

Figure 5. Removal of Cr(VI) using TP-Fe NPs with different ratio of tea polyphenols and FeCl₃ at different dosages

4. Conclusions
The conclusions are drawn as follows: Tea polyphenol extract reduced Fe³⁺ to form Fe nanoparticles with a particle size range of 50–120 nm. SEM, EDS, and XRD analyses demonstrated that Fe nanoparticles primarily contain FeO, FeOOH, Fe₂O₃, and organic matter such as quinone. PVA is the best stabilizer for TP-Fe NPs, thus maintaining TP-Fe NPs suspension stable for 60 h. The optimal mass ratio of tea polyphenols and ferric chloride is 0.92. The TP-Fe NPs have a strong reaction activity and removes Cr(VI) at a rate exceeding 99.5%. From this study, TP-Fe NPs can be produced in large quantities by tea polyphenol extract and ferric chloride. This material is environmentally friendly, cost-efficient, and can be extensively used for soil and groundwater environmental remediation.

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