



Mechanism investigation of anoxic Cr(VI) removal by nano zero-valent iron based on XPS analysis in time scale

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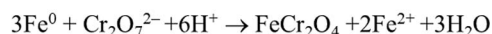
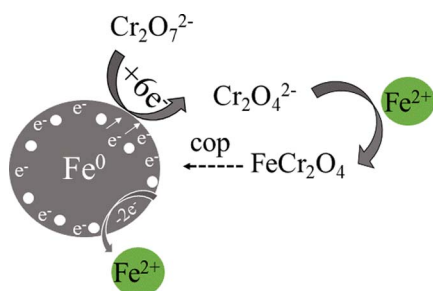
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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, nanoscale zero-valent iron (nZVI) with a considerably high surface area ($182.97 \text{ m}^2 \cdot \text{g}^{-1}$) and featured morphology of chain structure has been synthesized and well characterized. The as-prepared nZVI can totally remove Cr(VI) under anoxic condition after 20 min reaction, whereas only 43% of Cr(VI) was removed after 60 min reaction under oxic condition. Noteworthy, the nZVI exhibits excellent removal capacity of Cr(VI) (123.85 mg/g) and fast removal rate ($0.017 \text{ g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), much better than those reported in the literatures except for that reported by Li et al. (2008) [1]. Experimental results have confirmed that only FeCr_2O_4 with low compactness was generated under anoxic and acidic conditions in the new process. And it is evident that the formation of the passivation layer which contains oxides and hydroxides (or (oxy)hydroxides) of iron and chromium were well hindered. Furthermore, the as-prepared nZVI has shown fast removal of traced Cr(VI) from the Cr-spiked drinking water or actual Cr-contaminated lake water. Accordingly, we proposed a new reaction process of Cr(VI) reduction by nZVI under anoxic condition. And we firstly make clear the detailed process of Cr(VI) removal by the as-prepared nZVI via X-ray photoelectron spectrometer (XPS) analysis in time scale. Meanwhile, the excellent Cr(VI) removal performance of the as-prepared nZVI could be attributed to (i) the high surface area, (ii) large quantity of active sites of nZVI, and (iii) fast electron transfer from the nZVI/ FeCr_2O_4 to Cr(VI). The present work not only provides the potential materials for the application to the rapid and high-

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efficient removal of Cr(VI) from aqueous solution, but also proposed a new avenue for hindering the passivation of Fe⁰. And a detailed mechanism of the Cr(VI) removal by nZVI was proposed for the first time.

1. Introduction

Continuous contamination from heavy metals has become a significant and extensively-attended worldwide problem [2,3]. Among these heavy metals, hexavalent chromium (Cr(VI)) is one of the most poisonous one that is highly toxic to humans, animals, plants and microorganisms, and widely exists in aquatic, terrestrial, and soil systems, generated from tannery operations, chemical manufacturing, mining, and ore processing [4–6]. According to the report in the literature, chromium pollution is the third among the top 10 most toxic pollution problems in the world [7]. In USA, the maximum permitted concentration of Cr(VI) in drinking water is less than 0.1 mg·L⁻¹ (USEPA). Therefore, it is urgent to develop efficient technology for the removal of Cr(VI) in order to meet with the strict regulation standard. Generally, adsorption and/or reduction methods was used to remove Cr(VI) from water [8–10]. For the adsorption process, Cr(VI) was just transferred from aqueous environment to the surface of solid adsorbents but no toxicity alleviation [8]. And the Cr(VI) species on the surface of solid adsorbents can be again released to the aquatic environment because of the unstable bond of Cr(VI) and adsorbents and its high mobility [11]. Different from the adsorption method, the reduction of Cr(VI) to Cr(III) is a well-recognized and effective method to remove Cr(VI) from aqueous solutions. It is mainly due to the reduction process can convert Cr(VI) to Cr(III), which is a less mobile and less toxic form of Cr.

During the last two decades, nano zero-valent iron (nZVI) has attracted extensive attention as a Cr(VI)-reducing agent because nZVI possesses some significant advantages, such as large surface area, low cost, environmental benign and high in-situ reactivity with Cr(VI) [4,12,13]. However, nZVI also shows the evident drawbacks of poor dispersion and easy to deactivation under operational conditions, leading to its rapid loss of reactivity, low stability and high processing costs. Therefore, efficient modifying or manipulating nZVI is deemed as a vital way to enhance nZVI removal efficiency and restrain its surface passivation, which can benefit its further practical application.

Currently, the modification of the nZVI has been regarded as one of conventional method to overcome the shortcoming of nZVI [14–16]. For example, the surfactant and polymer electrolyte are widely used to effectively prevent the agglomeration of the nZVI via the electrostatic repulsion or steric hindrance [17]. In addition, loading nZVI onto the solid supports, such as inorganic compounds and clay minerals [18–21], diatomite [22], polymers [23–25], nanostructured carbons [26–28], and silica-based molecular sieves [29,30], organic compounds [31,32], is also an effective method to reduce the agglomeration, resulting in improving the efficiency of the nZVI. However, to the best of our knowledge, the process of removal of Cr(VI) using nZVI is always accompanied by the surface passivation phenomenon of nZVI in the reported method [33,34]. And the passivation layer on the iron surface can hinder the mass transfer and electron transport from nZVI to Cr(VI) mainly because the passivation layer generally consists of oxides and hydroxides (or (oxy)hydroxides) of iron and chromium. And these constituents show excellent compactness and insulativity, which results in the loss of reactive activity. Therefore, a crucial technique should be applied to overcome the associated surface passivation of nZVI during the reaction process in order to improving the reactivity of the nZVI toward Cr(VI) removal.

As one of the earliest method used to pretreat virgin ZVI, acid washing can remove the passive oxide layer, which results in enhancing the reduction rates of Cr(VI) [35]. However, compared with the unwashed ZVI, some reports have shown that acid washing would deteriorate the performance of ZVI toward the removal of Cr(VI) in long-

term tests [36,37]. H₂-reducing pretreatment was also considered as an efficient method to improve the performance of nZVI to the removal of Cr(VI) because the pretreatment of H₂ can increase the number of reactive sites and the BET surface area of nZVI [38]. But the application of H₂-pretreatment would be limited by the high temperature requirement for the reaction to occur. Similarly, as a direct approach, the application of ultrasonic energy can efficiently remove the passivation layer on the surface of nZVI and thus restore the reactivity of nZVI [39]. But the method of sonication pretreatment needs a large amount of energy, which was high-cost and not a facile method to overcome the disadvantages of nZVI. Therefore, it is necessary to study a new, low-cost and environmental-friendly method to avoid the passivation of iron and maintain the reactivity of nZVI.

In this work, nZVI with large surface area was synthesized via an improved method. The removal of Cr(VI) using the as-synthesized nZVI under different conditions were systematically investigated. Some factors, such as temperature, pH, nZVI dosage, Cr(VI) concentration, and co-existing cations and anions, as well as the bubble of different gas (O₂, air and N₂), were researched to illustrate their effect on the removal efficiency and stability of the as-synthesized nZVI for the removal of Cr(VI). X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to confirm the reaction products. Furthermore, for the first time, XPS analysis in time scale was used to make clear the mechanism for Cr(VI) removal using the as-prepared nZVI under anoxic conditions. Furthermore, in order to confirm the potential application of the as-prepared nZVI in the removal of traced Cr from the Cr-spiked drinking water or actual Cr-contaminated lake water, some simulated experiments were investigated, and the magnetic property of the nZVI after 2 h reaction with Cr(VI) was also tested. Herein, we hope to report a new method to prepare nZVI with featured morphology, fast Cr(VI) removal rate and superior Cr(VI) removal capacity under anoxic and acidic condition, and puts forward a new process for hindering the passivation of Fe⁰.

2. Experimental

2.1. Materials

All the chemicals used in this study were analytical grade and all solutions were prepared using deionized water (resistivity 18.2 MΩ·cm). Cr(VI) solution was made up from the potassium dichromate (K₂Cr₂O₇) purchased from the Aladdin. Ethyl alcohol, sodium nitrate (NaNO₃), sodium sulfate (Na₂SO₄), copper dichloride (CuCl₂), and Ferrous sulfate hepta-hydrate (FeSO₄ 7H₂O) were purchased from the Xilong scientific co., LTD. Potassium borohydride (KBH₄) were purchased from Shanghai Macklin Biochemical Technology co., LTD. The pH was adjusted with either HCl or NaOH of 1 mol/L.

2.2. Preparation of nZVI particles

The nZVI particles were synthesized by liquid phase reduction method. Briefly, 4.978 g FeSO₄·7H₂O was dissolved in 100 mL deionized water in 250 mL four-neck flask in water bath at 50 °C. In order to remove dissolved oxygen, nitrogen (N₂) was bubbled in the reaction process with mechanical stirring. Different from the report in the literature [39], in order to obtain nZVI with little sizes and large surface area, we increase the amount of potassium borohydride and increase the dripping speed of KBH₄. Briefly, 3.0 g KBH₄ was dissolved in 80 ml deionized water and then gradually dripped (10 mL/min) into ferrous solution until no significant H₂ generation under N₂ atmosphere. The

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