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Nanoscale zerovalent iron decorated on graphene nanosheets for Cr(VI) removal from aqueous solution: Surface corrosion retard induced the enhanced performance

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HIGHLIGHTS

- NZVI/GNS is designed and synthesized for treating Cr(VI) polluted water.
- NZVI/GNS exhibits higher efficiency than that of bare NZVI.
- The Cr(VI) removal efficiency is dependent on the GNS amount in NZVI/GNS.
- The synergistic effect cooperatively enhances the performance of NZVI/GNS for Cr(VI) removal.

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ABSTRACT

Chemical reduction technology based on nanoscale zerovalent iron (NZVI) is an effective method for in-situ remediation of Cr(VI)-polluted water. However, it is difficult to overcome the associated surface passivation during the reaction process, thus losing the reduction reactivity. In this study, a novel system based on the NZVI/graphene nanosheets (NZVI/GNS) is constructed for the effective removal of Cr(VI) in water. Immobilization of NZVI onto graphene improves the stability of the NZVI, while graphene coupling facilitates the electron transfer in the NZVI and retards the surface passivation of the NZVI, thus enhancing the performance of the NZVI toward Cr(VI) removal. The NZVI/GNS exhibits significantly higher activity toward Cr(VI) removal than that of bare NZVI. The Cr(VI) removal efficiency is closely correlated to the graphene amounts in the NZVI/GNS. Based on X-ray photoelectron spectroscopy (XPS) and steady-state polarization measurements, the mechanism of Cr(VI) reduction reaction with the NZVI/GNS has been unraveled as well.

1. Introduction

Nowadays, water pollution has become a serious environmental problem for the global society. Especially, the heavy metals polluted water is becoming a serious threat to human health and ecological environment. Chromium (Cr) is a kind of major contaminants mainly resulting from activities and industries of mining, metallurgy, electroplating, leather tanning, printing, pigments, and polishing [1,2]. In fact, chromium has been identified as priority pollutant and carcinogen by the United States Environmental Protection Agency (EPA). At present, considerable attempts have been made for the development of the advanced treatment technology for efficient Cr(VI) removal and remediation [3–6]. For example, adsorption is an effective and economical method for the removal of heavy metals in water. Recent work has been shown that the ligand embedded diverse mesoporous materials are very effective for the removal of metal ions [7–12]. However, these adsorbent materials often display no reduction ability toward the detoxification of Cr(VI)-contaminated media by transformation of Cr(VI) to Cr(III). Chemical reduction technology based on the nanoscale zerovalent iron (NZVI) has attracted the increased attention due to its significant advantages of large surface area, simplicity, low cost, and high in-situ reactivity with Cr(VI) [13–15]. However, the NZVI has poor dispersion and is easy to corrosion under operational conditions, which will lead to its instability and rapid loss of reactivity, thus increasing the processing costs. Therefore, efficiently manipulating the NZVI to improve the removal efficiency and retard the surface corrosion should be key but challenging issues for its further practical application.

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At present, the research interest mainly focuses on the modification of the NZVI. For example, the surfactant and polymer electrolyte are introduced into the NZVI system to effectively prevent the agglomeration of the NZVI by means of the electrostatic repulsion or steric hindrance [16,17]. Alternatively, loading the NZVI on the solid supports, such as clays [18,19], carbonaceous materials [20,21], biopolymers [22,23], and oxides [24,25], is also an effective method to reduce the agglomeration, increase the reaction active sites, and improve the processing efficiency of the NZVI. However, these strategies aim at improving the dispersion and stability of the NZVI, they are rarely involved the mechanism in reduction reaction of Cr(VI) with the NZVI. Generally, the effective regulation of electron transfer in the NZVI is essential to improve the performance of reduction reaction with the NZVI. Of note, such reduction reaction process is accompanied by the surface passivation phenomenon of the NZVI. The passivation layer deposited on the NZVI surface can prevent the electron transfer from NZVI to Cr(VI), which is the critical step resulting in the loss of reactive activity. Therefore, efficiently balancing the electron transfer behavior and the surface passivation of the NZVI during reduction process is determining the reactivity of the NZVI toward Cr(VI) removal.

Owing to its large specific surface area, great mechanical strength, and low manufacturing cost, graphene has been considered a promising candidate as a new two-dimensional carrier to support metal nanoparticles (NPs) [26,27]. The combination of graphene with the NZVI could realize the enhanced performance for Cr(VI) removal, which has been experimentally demonstrated by recent studies [25,28]. However, to the best of our knowledge, there has been no report on the mechanistically study the role of graphene in improving reactivity for Cr(VI) reduction. In this work, we construct a novel NZVI/graphene nanosheets (NZVI/GNS) system for the effective removal of Cr(VI) in water. Immobilization of NZVI onto graphene improves the stability of NZVI, while graphene coupling facilitates the electron transfer in the NZVI and retards the surface passivation of the NZVI, thus enhancing the performance of the NZVI toward Cr(VI) removal. The NZVI/GNS exhibits significantly higher activity toward Cr(VI) removal than that of bare NZVI. The Cr(VI) removal efficiency is found to be closely correlated to the amount of graphene. The X-ray photoelectron spectroscopy (XPS) and steady-state polarization measurements are also performed to clarify the mechanism of Cr(VI) reduction reaction with the NZVI/GNS.

2. Experimental

2.1. Materials

Graphite powder, $NaNO_3$, H_2SO_4 (98%), $KMnO_4$, H_2O_2 (30 wt%), $FeCl_3{\cdot}6H_2O$, $NaBH_4$, $K_2Cr_2O_7$, polyvinylpyrrolidone (PVP) and acetone were purchased from Kelong Chemical Reagents Company (Chengdu, China). 1,5-diphenylcarbazide (DPC) was purchased from Aladin Ltd (Shanghai, China). All reagents and chemicals were of analytical grade and used without further purification.

2.2. Synthesis of graphene oxide (GO)

GO was synthesized from natural graphite powder by a modified Hummers method [29]. In a typical procedure, 120 mL of concentrated H_2SO_4 was added into a 500 mL flask containing 5 g of graphite and 2.5 g of $NaNO_3$ and followed by stirring for 30 min inside an ice bath. Then 15 g of $KMnO_4$ was added slowly to the mixture. The rate of addition was carefully controlled to keep the reaction temperature below 20 °C. The mixture was stirred at room temperature overnight. Then, 150 mL of H_2O was slowly added under vigorous stirring. The reaction temperature rapidly increased to 98 °C with effervescence, and the mixture color changed into yellow. The diluted suspension was stirred at 98 °C for one day. Then, 50 mL of 30% H_2O_2 was added to the mixture. For purification, the mixture was washed by rinsing and centrifugation with 5% HCl followed by deionized water for several times. After filtration and drying under vacuum, GO was obtained as a solid.

2.3. Synthesis of graphene nanosheets (GNS) loaded NZVI

In a typical procedure, the required amount of graphite oxide (GO) was dispersed in 20 mL of deionized water by ultrasonication for 30 min. 10 mL of aqueous solution containing $FeCl_3{\cdot}6H_2O$ (0.0348 g) and PVP (0.1716 g) was added into the former GO suspension. The mixture was mechanically stirred for 30 min. 10 mL of $NaBH_4$ (0.6442 g) solution was then added dropwise into the above mixture solution under constant stirring at room temperature. After the reaction of 6 h, the black solid was collected by filtration, washed with ethanol three times, and dried in flowing nitrogen. The obtained samples were denoted as NZVI/GNS-*x*, where *x* represents the mass fraction of GO.

2.4. Characterization

The powder X-ray diffraction (XRD) measurements were recorded on a Rigaku Dmax/Ultima IV diffractometer with monochromatized Cu Kα radiation (λ = 0.15418 nm). The morphology was observed with a JEOL JSM-6510LV scanning electron microscope (SEM) and transmission electron microscope (TEM, FEI Tecnai G20). The elemental composition of the samples were characterized by energy-dispersive X-ray spectroscopy (EDS, Oxford instruments X-Max). Surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin–Elmer PHI 5000C, Al KR). All binding energies were calibrated by using the contaminant carbon (C_{1S} = 284.6 eV) as a reference. The Fourier transform infrared (FTIR) spectrum was measured on a Nicolet 6700 FTIR spectrometric Analyzer using KBr pellets. The specific surface area of the samples was measured by nitrogen adsorption at 77 K using an automated gas sorption analyzer (ASIQ-C, Quantachrome) and calculated according to the Brunauer–Emmett–Teller (BET) method. The point of zero charge (pH_{PZC}) of the adsorbent was determined by the solid addition method [2,30,31]. To a series of 100 mL conical flasks, 45 mL of 0.1 mol L^{-1} NaCl solution was transferred. The initial pH values (pH_i) of the solution were adjusted from 3.0 to 13.0 by adding either 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the NaCl solution. Then, 0.1 g of the NZVI/GNS was added to each flask and the mixtures were agitated at 150 rpm. After 48 h, the final pH values (pH_f) of the solutions were measured. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i. The point of intersection of the resulting curve with abscissa, at which $\Delta pH = 0$, gave the pH_{PZC}.

2.5. Cr(VI) removal experiment

The removal of Cr(VI) in aqueous solution on NZVI/GNS was performed in a batch experiment. A stock Cr(VI) solution (1000 mg L^{-1}) was prepared by dissolving appropriate amount of $K_2Cr_2O_7$ in double distilled water. The experimental solution was obtained by diluting the stock solution with deionized water to the desired initial Cr(VI) concentration. In a typical procedure, 0.02 g of the NZVI/GNS sample was added into 20 mL of Cr(VI) solutions with required initial concentrations and then shaken in a thermostatic shaker at room temperature. At predetermined time intervals, the samples were separated by a 0.45 μm membrane filter. The concentrations of Cr(VI) were determined by a Shimadzu