Magnetic Fe₃O₄-FeB Nanocomposites with Promoted Cr(VI) Removal Performance

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Abstract

In this study, amorphous FeB alloy modified magnetite nanocomposites (Fe₃O₄-FeB) were facilely synthesized by interfacial reduction of commercial Fe₃O₄ nanoparticles with NaBH₄. TEM, CS-STEM integrated with EDS, Mössbauer spectroscopy analysis confirmed the formation of Fe₃O₄-FeB, where a shell of amorphous FeB nanoparticles with 2-4 nm in size was surrounded on the inner magnetite Fe₃O₄ part. Fe₃O₄-FeB displayed a promoted Cr(VI) removal efficiency compared with the bare Fe₃O₄ counterpart, the interfacial reduced Fe₃O₄ nanoparticles with hydrogen and/or with hydrazine hydrate. XPS analysis evidenced that reduction of Cr(VI) on surface of the Fe₃O₄-FeB was the major contribution to the Cr(VI) removal. Tafel polarization analysis of the Fe₃O₄-FeB and aqueous boron species measurement indicated that high Cr(VI) removal efficiency with Fe₃O₄-FeB was highly depended on amorphous FeB alloy shell, in which boron element containing free electrons could accelerate the electron transfer from Fe to the adsorbed Cr(VI), as well reduce Fe(III) to Fe(II) and thus promote the Fe(III)/Fe(II) cycles. The efficient Cr(VI) removal under a wide range of pH values and its easy magnetic separation make the Fe₃O₄-FeB be a potential for Cr(VI) contaminated water

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treatment.

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1. Introduction

The appearance of chromium in aquatic and soil systems has elicited much attention because of its potential to cause serious threat to human health [1-3]. Cr(VI) with high oxidative property is toxic to plants, animals, and human beings because of its weak adsorption on mineral/soil surfaces [1-4]. Hence, WHO and USEPA set maximum acceptable guideline concentrations of 50 and 100 $\mu\text{g}\cdot\text{L}^{-1}$ for total chromium in drinking water respectively [5]. However, Cr(VI) concentrations in Cr(VI)-bearing wastewater and Cr(VI) contaminated natural water resources are far more than the allowable threshold level [6]. Therefore, it is imperative to develop new materials and effective methods for Cr(VI) remediation.

Adsorption is an efficient and economical technology for dealing with Cr(VI) contaminated problem [4-5]. Fe_3O_4 is the most attractive adsorbent according to its simply magnetic separable advantage compared with conventional separation [7]. The Cr(VI) adsorption process over Fe_3O_4 was considered to be an endothermic and spontaneous process which involved reduction reaction on the surface because the ferrous ions (Fe(II)) that exists in magnetite can in theory function as reductant for Cr(VI) [7,8]. For example, Hu's research reported that structured Fe(II) in the magnetite could initiate the surface reduction of Cr(VI) to Cr(III), and subsequently chelated Cr(III) by surface hydroxyl (-OH) groups of Fe_3O_4 to form a complex solid during the Cr(VI) removal process using Fe_3O_4 particles as adsorbent [8]. However, Fe(II) on the surface of magnetite

and even in the crystal lattice are not easy to release and react with Cr(VI), the Fe_3O_4 adsorbent has the disadvantage of small adsorption capacity or slow adsorption rates for Cr(VI) removal.

Therefore, a series of strategies such as functionalization, immobilization, and modification with Fe_3O_4 have been applied to realize a high efficiency of Cr(VI) removal [9-13]. For instance, Jiang's group found the HA coated Fe_3O_4 adsorbent exhibited enhanced Cr(VI) removal activity and was easily separated by application of a magnetic field [11]. Yuan and his coworkers demonstrated that a ternary magnetic composite consisting of reduced graphene oxide, polypyrrole and Fe_3O_4 nanoparticles could reduce Cr(VI) to the low-toxicity Cr(III) by the nitrogen species of polypyrrole [12]. Additionally, Xu's group synthesized Fe^0 - Fe_3O_4 nanocomposites embedded polyvinyl alcohol/sodium alginate beads which exhibited an excellent reactivity in Cr(VI) removal [13]. Obviously, these modification methods of Fe_3O_4 adsorbents are complicated, and organic composites such as HA with functional groups could cause some adverse environmental consequences [14]. More recently, it was reported that the doped boron could facilitate Cr(VI) reduction by boron-doped-diamond (BDD) cathodic electrodes [15], but the role of boron in Cr(VI) reduction was still unknown.

In this study, we synthesized amorphous FeB alloy modified magnetite nanocomposites (Fe_3O_4 -FeB) via reduction of commercial Fe_3O_4 nanoparticles with NaBH_4 solution and investigated their promoted Cr(VI) removal performance. We found that amorphous FeB alloy was the major contribution to the high Cr(VI) removal efficiency of magnetic Fe_3O_4 -FeB, in which boron element containing many free electrons accelerated the electrons transfer from Fe to Cr(VI) as well promoted the Fe(III)/Fe(II) cycles.

2. Experimental Section

2.1 Chemicals. Commercial Fe_3O_4 nanoparticles (50-150 nm in size, BET $8.82 \text{ m}^2\cdot\text{g}^{-1}$) was purchased from Beijing DK nano-technology Co. Ltd., China. Sodium borohydride (NaBH_4), sodium hydroxide (NaOH), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), hydrochloric acid (HCl , 98%), anhydrous ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), 1, 10-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2\cdot\text{H}_2\text{O}$) and other reagents were obtained from National Medicines Corporation Ltd. in China. All the chemicals were of analytical grade and were used as received without further purification. High purity argon gas ($\text{Ar} \geq 99.9\%$) was provided by Hubei Minghui gas company, China. Deionized water was used throughout the experiment.

2.2 Preparation Procedure. FeB alloy modified magnetite nanocomposites ($\text{Fe}_3\text{O}_4\text{-FeB}$) were synthesized by treating commercial Fe_3O_4 nanoparticles with NaBH_4 solution. In a typical procedure, NaBH_4 solution with a concentration of $0.34 \text{ mol}\cdot\text{L}^{-1}$ was prepared by dissolving 0.65 g of NaBH_4 in 50 mL of deionized water. Then, 0.1 g Fe_3O_4 powders was added into the NaBH_4 solution to initiate the reactive reaction of Fe_3O_4 and NaBH_4 , the suspension was mechanically stirred for 4 h and then centrifuged (5000 rpm for 5 minutes), the powders were obtained via vacuum filter and washed with deionized water and ethanol and finally dried under argon flow. All the samples were stored in the argon bubbled oxygen-free vials to prevent them from being oxidized. For comparison, counterpart samples were obtained by adjusting the initial concentration of NaBH_4 solution ($0.085\sim 1.36 \text{ mol}\cdot\text{L}^{-1}$) and/or the reaction time (0.5 h ~ 5 h). Two surface modified Fe_3O_4 counterparts were synthesized by reduction of the commercial Fe_3O_4 nanoparticles in gaseous H_2 (3% H_2 / 97% Ar) ($\text{Fe}_3\text{O}_4\text{-H}_2$) and/or via reductive precipitation with hydrazine hydride ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) solution obtained by diluting 2 mL of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (85%) ($\text{Fe}_3\text{O}_4\text{-N}_2\text{H}_4\cdot\text{H}_2\text{O}$) in 40 mL H_2O .

2.3 Characterizations. X-ray diffraction (XRD) was determined with a Bruker D8 Advance X-ray

diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at a scanning rate of 2° min^{-1} in the 2θ range from 15° to 70° . Surface morphology characterization of the Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-FeB}$ nanocomposites before and after Cr(VI) removal was performed on a LEO 1450VP scanning electron microscope (SEM). Transmission electron microscopy (TEM) was carried on a JEOL JEM-2010 electron microscope operating at 200 kV. The samples for TEM were prepared by dispersing the final powders in ethanol; the dispersion was then dropped on carbon-copper grids. Furthermore, the obtained powders deposited on a copper grid were observed by a high-resolution transmission electron microscope (HRTEM). The energy-filtered transmission electron microscopy (EF-TEM) was performed with JEM-ARM200F (GIF quantum 965). X-ray photoelectron spectroscopy (XPS) was recorded with a Kratos ASIS-HS X-ray photoelectron spectroscope equipped with a standard and monochromatic source operated at 150 W (15 kV, 10 mA). BET (Brunauer-Emmett-Teller) surface areas were determined from N_2 physisorption with an RXM-100 advanced catalyst characterization system (ASDI, Inc) using the BJH (Barrett-Joyner-Halenda) and multi-point BET methods. Magnetic hysteresis loops were obtained for the evaluation of their saturation magnetism (M_s), remanence (M_r), and coercivity (H_c) by a vibrating sample magnetometer (VSM, Lake Shore 7307). Mössbauer spectra was recorded using a $^{57}\text{Co}^*\text{:Rh}\gamma$ -ray source ($E_0=14.4 \text{ keV}$) mounted on an electromagnetic drive with a triangular velocity signal. The spectra were least-squares fitted to get the hyperfine parameters (isomer shift δ , quadrupolar splitting Q , and hyperfine field H), the broad hyperfine field distribution was fitted using a histogram of hyperfine field with free weights.

2.4 Cr(VI) Removal Setup. 1000 $\text{mg}\cdot\text{L}^{-1}$ of Cr (VI) stock solution was prepared by dissolving 1.4114 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 500 mL deionized water. The Cr (VI) solution with different initial concentrations was prepared by dilution of the stock $\text{K}_2\text{Cr}_2\text{O}_7$ standard solution with deionized water.

All the experiments were carried out in 100 mL conical beakers containing 40 mL of Cr(VI) solution at 25°C. During a typical Cr(VI) removal process, 0.032 g of Fe₃O₄ or surface modified Fe₃O₄ powders was added into the conical beaker with 40 mL of Cr(VI) solution (8 mg•L⁻¹). The beaker was sealed with rubber screw caps and then transferred into a shaker (HY-5 Rotary shaker, China) with a speed of 200 rpm to initiate the removal process. The initial pH of the Cr(VI) solution was 6.3 without adjusting. In some case, the initial pH of Cr(VI) solution was adjusted to 2.0 and 10.0 with 0.1 mol•L⁻¹ of HCl and 0.1 mol•L⁻¹ NaOH respectively. The Cr(VI) solution samples were collected by a 5 mL syringe at regular intervals and filtered immediately through a 0.45 µm nylon syringe filter for the measurement of Cr(VI) concentration. The influence of 1,10-phenanthroline on the Cr(VI) removal was conducted by adding 3 g•L⁻¹ of 1,10-phenanthroline to the Cr(VI) aqueous solution before introducing the sample powders. After the Cr(VI) removal process, the suspension was transferred to a centrifuge tube and then centrifuged (8000 rpm for 5 minutes using an Eppendorf 5840R Centrifuge) to remove the nanoparticles from the supernatant. The used powders were dried under Ar gas flow for further characterizations.

2.5 Analysis Methods. The concentration of Cr(VI) in aqueous solution was measured by using 1,5-diphenylcarbazide method [16]. This method is not sensitive to Cr(III) species. Chromium reagent 1,5-diphenylcarbazide was mixed with 5 mL of filtrate for 5 min. The absorbance of generated Cr(VI)-diphenylcarbazide product was determined by using a UV-vis spectrometer (UV-2550, Shimadzu, Japan) at a wavelength of 541 nm. Total chromium (Cr(VI) and Cr(III)) in solution was measured with a flame-atomic absorption spectrometer (Flame-AAS, 5100, PerkinElmer, USA). The concentration of Fe(II) was determined with 1,10-phenanthroline method by using UV-vis spectrophotometer (UV-2550, Shimadzu, Japan) at a wavelength of 510 nm [17]. The

Fe(II) standard solutions were prepared from anhydrous ferrous chloride solution (FeCl_2 , 99.9%). Total Fe was determined by atomic absorption spectrophotometer (AAS). Elemental analysis was carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES) at wavelengths of 249.77 nm. The pH of the solution was measured at the same regular intervals during the Cr(VI) removal. Electrochemical experiments were performed by a CHI-660B electrochemical system (Shanghai, China) at room temperature. Tafel scans were performed to measure the free corrosion potentials. The work electrode made of 5 mg samples was placed in 50 mL of $50 \text{ mmol} \cdot \text{L}^{-1}$ Na_2SO_4 electrolyte solution in a 100 mL beaker containing a calomel reference electrode and a Pt counter electrode. All the Tafel diagrams were obtained by polarizing the work electrodes $\pm 200 \text{ mV}$ with respect to their open circuit potentials. All the potentials in the Tafel diagrams were with respect to the standard hydrogen electrode (SHE).

3. Results and Discussion

3.1 Characterizations. SEM images indicated that both the commercial Fe_3O_4 and the NaBH_4 treated Fe_3O_4 were irregular nanoparticles in size of 80-150 nm, the morphology of nanoparticles did not change after the NaBH_4 treatment (Figure 1a and 1b). XRD patterns suggested that the phase and crystalline of the commercial Fe_3O_4 and the NaBH_4 treated Fe_3O_4 were all indexed to cubic Fe_3O_4 (JCPDS file No. 19-0629) (Figure 1c) [18]. However, the BET surface areas of the Fe_3O_4 nanoparticles increased from $8.8 \text{ m}^2 \cdot \text{g}^{-1}$ to $15.4 \text{ m}^2 \cdot \text{g}^{-1}$ after the NaBH_4 treatment (Figure 1d), suggesting that the reaction of Fe_3O_4 and NaBH_4 happened and the NaBH_4 treatment could change the superficial structure of Fe_3O_4 nanoparticles.

TEM images confirmed Fe_3O_4 before and after NaBH_4 reaction were all nanoparticles with the

sizes in the range of 80-150 nm (Figure 2a, 2d), this is consistent with the SEM results. Higher magnification TEM images showed that the surface of the commercial Fe₃O₄ was smooth (Figure 2b), on contrast, NaBH₄ treated Fe₃O₄ nanoparticles exhibited an uneven surface where many tiny particles were observed (Figure 2e), this could explain the increased BET surface areas after the reduction by NaBH₄. HRTEM analysis further revealed the single-crystal nature of the Fe₃O₄ nanoparticles before and after NaBH₄ treatment (Figure 2c, 2f), a lattice spacing of 0.296 nm was corresponding to the distance between (220) crystal planes of cubic Fe₃O₄ (JCPDS file No. 19-0629) [19, 20]. The TEM and HRTEM results confirmed the superficial reaction between Fe₃O₄ and NaBH₄, this agreed with the BET analysis.

Moreover, the morphology and composition of Fe₃O₄ nanoparticles before and after NaBH₄ treatment were investigated by EF-TEM and element mapping analysis (Figure 3). The commercial Fe₃O₄ was with smooth surface (Figure 3a), while an uneven surface with numerous nanoparticles was observed in the NaBH₄ treated Fe₃O₄ sample (Figure 3e). The EF-TEM element mapping analysis indicated that Fe and O elements were observed in the bare Fe₃O₄ (Figure 3b and 3c) and NaBH₄ treated Fe₃O₄ nanoparticles (Figure 3f and 3g). The bare Fe₃O₄ was free of boron element (Figure 3d), interestingly, homo-distributed boron element was only found in Fe₃O₄ sample after NaBH₄ reduction (Figure 3h). This result suggested tiny nanoparticles containing B element were formed on the surface of the NaBH₄ treated Fe₃O₄. The boron was not distinguished by XRD, TEM, and HRTEM analysis because of its amorphous nature.

The crystallite size was also determined from the diffraction peaks using the Scherrer formula (Eq. 1), and interplanar spacing d_{hkl} was determined by Bragg's law (Eq. 2)

$$D = \frac{K \cdot \lambda}{\omega \cdot \cos \theta} \quad (1)$$

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \quad (2)$$

Where D is the crystallite size (nm), λ is the wavelength of the monochromatic X-ray beam (0.154056 nm), ω is the full width at half-maximum (FWHM) value of X-ray diffraction lines under consideration (see Fig. 1c), K is a constant (equal to 0.9), and θ is the half diffraction angle of 2θ (degree). The particle size and interplanar spacing d_{hkl} of commercial Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-FeB}$ are determined at the peak D220, the particle size were calculated to be 110.2 nm for commercial Fe_3O_4 and 105.6 nm for $\text{Fe}_3\text{O}_4\text{-FeB}$ respectively, these values are slightly smaller than those obtained from TEM analysis.

Furthermore, ^{57}Fe Mössbauer spectroscopy spectra of the Fe_3O_4 before and after NaBH_4 treatment were recorded at 300 K (Figure 4). Mössbauer spectrum of the bare Fe_3O_4 was fit with two sextets which could be ascribed to paramagnetic high-spin iron(II) and iron(III) in Fe_3O_4 (the corresponding hyperfine parameters were shown in Table 1) [21]. Besides the two sextets related to Fe_3O_4 , the NaBH_4 treated Fe_3O_4 nanoparticles exhibited two broad peaks, which were assigned to poor crystallinity and/or nonhomogeneous composition of the FeB alloy [21-24], implying that the tiny particles formed on the surface of Fe_3O_4 could be amorphous FeB alloys.

XPS spectra were further recorded and analyzed (Figure 5). B element was observed in the NaBH_4 treated Fe_3O_4 sample besides the elements of Fe, O, and C found in the bare Fe_3O_4 (Figure 5a), where the C 1s peak at 284.5 eV could be attributed to the adventitious carbon on the surface of the samples. The peaks at 710.1 and 719.0 eV related to Fe(II) and the shoulder peak at 724.4 eV assigned to Fe(III) suggested the co-existence of Fe(III) and Fe(II) in the bare and NaBH_4 treated Fe_3O_4 (Figure 5b) [24-26]. The calculation of the peak area in core level spectra of Fe 2p gave a ratio of ferrous iron to total iron ($\text{Fe}^{\text{II}}/\text{Fe}_{\text{total}}$) and ferric iron to total iron ($\text{Fe}^{\text{III}}/\text{Fe}_{\text{total}}$) (Table 2). It was found

that the value of $\text{Fe}^{\text{II}}/\text{Fe}_{\text{total}}$ increased from 0.395 to 0.570 after the NaBH_4 treatment, indicating that the amount of ferrous ions on the surface increased with the NaBH_4 reduction. The high resolution B 1s XPS spectra were compared (Figure 5c), the peak in 191.5 and 187.6 eV can be attributed to the oxidized boron species and elemental B in FeB on the NaBH_4 treated Fe_3O_4 respectively. It was observed that the binding energy of elemental B in FeB positively shifted about 0.3 eV in comparison with pure boron (187.3 eV), indicating electron transfer from boron to iron happened in FeB alloys [27-28]. Therefore, on the base of EF-TEM element mapping result, ^{57}Fe Mössbauer spectroscopy analysis, and XPS result, we can reasonably deduce that amorphous FeB alloy modified magnetite nanocomposites ($\text{Fe}_3\text{O}_4\text{-FeB}$) were facilely synthesized by interfacial reduction of commercial Fe_3O_4 nanoparticles with NaBH_4 solution.

3.2 Removal of Cr(VI) with $\text{Fe}_3\text{O}_4\text{-FeB}$ Nanocomposites. The as-prepared $\text{Fe}_3\text{O}_4\text{-FeB}$ was used for the removal of aqueous Cr(VI) at neutral pH of 6.3 (Figure 6). It was observed that Cr(VI) removal was only 5% with the bare commercial Fe_3O_4 , however, the removal efficiency reached to 9%, 85%, and 100% with the $\text{Fe}_3\text{O}_4\text{-FeB}$ obtained after NaBH_4 treatment for 1, 2, and after 3 h respectively within 30 min (Figure 6a). Cr(VI) removal efficiency with $\text{Fe}_3\text{O}_4\text{-FeB}$ first increased with prolonging reaction time from 0 to 4 h, and then kept constancy when the reaction time was more than 4 h. The removal was found to obey a pseudo first-order reaction kinetic equation with high correlation coefficients (Figures 6b). The apparent Cr(VI) removal rate constants (k) were calculated to be 0.01, 0.06, 0.19, 0.27, and 0.28 min^{-1} for $\text{Fe}_3\text{O}_4\text{-FeB}$ obtained at 1, 2, 3, 4, and 5 h, respectively. Moreover, it was found that the Cr(VI) removal efficiency increased with the initial concentrations of the NaBH_4 solution (Figure 6c), the apparent Cr(VI) removal rate constant reached to the highest value of 0.27 min^{-1} when concentration of NaBH_4 was 0.34 $\text{mol}\cdot\text{L}^{-1}$ (Figure 6d). Thus the $\text{Fe}_3\text{O}_4\text{-FeB}$

obtained with 0.34 mol•L⁻¹ of NaBH₄ for 4 h was used in the following mechanistic investigation.

It is expected that both adsorption and reduction of Cr(VI) co-happen with Fe₃O₄-FeB due to its high BET surface area (15.4 m²•g⁻¹) and strong electron donor nature of FeB. The adsorption process induced by electrostatic, hydrophobic and hydrogen bond interaction depends strongly on solution pH values, because pH could determine the surface charge of Fe₃O₄-FeB and the form of Cr(VI) species. HCrO₄⁻ is the dominant species between pH 2 and 6; the form shifts to CrO₄²⁻ and Cr₂O₇²⁻ if pH rises to above 6, and CrO₄²⁻ is the only existence when pH >7.5. We found that Fe₃O₄-FeB could realize totally Cr(VI) removal in 20 min at a broad pH range from 2-10 (Figure 7a), because the positive surface charge makes it easier to attract the negative Cr(VI) species when pH is under the pH of zero point charge (Figure 7b) [5]. Moreover, the effect of initial Cr(VI) concentrations (4-32 mg•L⁻¹) on Cr(VI) removal with Fe₃O₄-FeB was investigated (Figure 7c). Cr(VI) removal efficiency reached 100% within 1.5 h when Cr(VI)_{initial} was of 4, 8, 16, and 32 mg•L⁻¹, the amount of Cr(VI) absorbed per unit mass of the adsorbent was evaluated by using the mass balance equation (Eqs. 3-4) [4].

$$q_t = [(C_0 - C_t)V] / W \quad (3)$$

$$t / q_t = 1 / (k_1 q_e^2) + t / q_e (k_0 = k_1 q_e^2) \quad (4)$$

Where q_t (mg•g⁻¹) is the amount of Cr(VI) adsorbed per gram of adsorbent at time t (min), C_0 is the initial concentration of Cr(VI) in the solution (mg•L⁻¹), C_t is the concentration of Cr(VI) at time t of adsorption (mg•L⁻¹), W is the mass of the adsorbent used (g), and V the volume of the solution (L), k_1 (g•mg⁻¹•min⁻¹) is the rate constant of the pseudo-second-order model of adsorption, and k_0 (mg•g⁻¹ min⁻¹) is the initial adsorption rate. The maximum Cr(VI) adsorption capacity of the Fe₃O₄-FeB was found to be 10.04 mg•g⁻¹ (Figure 7d and Table 3), which was even higher than that of

the Fe@Fe₂O₃ nanowires previous reported (7.78 mg•g⁻¹) with an initial Cr(VI) concentration of 8.0 mg•L⁻¹ [4] and other common used adsorbents (Table 4), suggesting the high Cr(VI) removal efficiency with the as-prepared Fe₃O₄-FeB.

To get mechanistic information on the adsorption of Fe₃O₄-FeB, Langmuir isotherm and Freundlich isotherm models were used to fit the data. The Langmuir isotherm model is applicable for monolayer adsorption on a surface containing a finite number of binding sites. The linear form of Langmuir equation is written as Eq. 5:

$$\frac{C_t}{q_t} = \frac{1}{Q^0 b} + \frac{C_t}{Q^0} \quad (5)$$

Where Q^0 (mg•g⁻¹) is the monolayer adsorption capacity and b (L•mg⁻¹) is the constant related to the energy of adsorption.

The Freundlich isotherm model, which is based on the assumption that the adsorption occurs on a heterogeneous adsorbent surface [32], can be represented as Eq 6:

$$\ln q_t = \ln K_f + \frac{1}{n} \ln C_t \quad (6)$$

Where K_f (mg•g⁻¹) and $1/n$ (L•g⁻¹) are the constants characteristics of the system, indicating the adsorption capacity of the sorbent and the intensity of the adsorption.

The linear plots of C_t/q_t versus C_t (Langmuir plot) and $\ln q_t$ versus $\ln C_t$ (Freundlich plot) were drawn at four different concentration of Cr(VI) (4, 8, 16, 32 mg•L⁻¹) (figures not shown), and Q_0 , K , K_f , n of Langmuir and Freundlich model parameters are shown in Table 5. The regression coefficients for Langmuir ($R^2 > 0.99$) were higher than those for Freundlich model ($0.79 < R^2 < 0.91$), indicating a better fitting with the Freundlich model.

In general, Cr(VI) removal with the Fe₃O₄-FeB is related to physical adsorptive process and chemical reductive reactions, in which both iron (Fe) and boron (B) in the FeB alloys could react

with Cr(VI). As the bare Fe₃O₄ nanoparticles could not remove Cr(VI) (Figure 6a), we deduced that the chemical reactions of Cr(VI) and FeB alloys dominated Cr(VI) removal process with Fe₃O₄-FeB. In order to convince this deduction, we prepared two interfacial reduced Fe₃O₄ powders which were Fe₃O₄ treated by hydrogen (H₂/Ar) (Fe₃O₄-H₂) and hydrazine hydride (N₂H₄•H₂O) (Fe₃O₄-N₂H₄•H₂O) respectively. The Fe₃O₄-H₂ and Fe₃O₄-N₂H₄•H₂O showed a similar morphology to commercial Fe₃O₄ nanoparticles (Figure 8a and 8b). XRD patterns of the Fe₃O₄-H₂ and Fe₃O₄-N₂H₄•H₂O samples suggested that hydrogen treatment and hydrazine hydride treatment could not change the phase and crystalline of Fe₃O₄ (Figure 8c). High resolution Fe 2p XPS spectra confirmed the formation of Fe(II) on the surface of the Fe₃O₄-H₂ and Fe₃O₄-N₂H₄•H₂O samples (Figure 8d), where Fe^{II}/Fe_{total} ratios of the Fe₃O₄-N₂H₄•H₂O (0.546) and Fe₃O₄-H₂ (0.486) were much higher than that of the bare commercial Fe₃O₄ (0.395), indicating that superficial reduction happened after treating Fe₃O₄ with N₂H₄•H₂O and H₂/Ar. However, we found that Cr(VI) removal was not increased with Fe₃O₄-H₂ and Fe₃O₄-N₂H₄•H₂O compared with the commercial Fe₃O₄ (Figure 9), indication that B element in the Fe₃O₄-FeB played key role on their effective Cr(VI) removal performance.

3.3 Role of B in Cr(VI) Removal with Fe₃O₄-FeB Nanocomposites. To understand the role of B element on Cr(VI) removal with the Fe₃O₄-FeB, we measured concentrations of dissolved B species, Fe(II), and Fe(III) in solution during the removal process (Figure 10). It was observed that Fe(II) ions and B species were continuously released to the anoxic aqueous solution, the concentration of aqueous B species and Fe(II) increased to 14.14 and 15.03 mg•L⁻¹ respectively within 30 min, implying that B element and Fe in the FeB alloy involved in Cr(VI) removal. We did not detect any soluble Fe(III) species during Cr(VI) removal process, suggesting reduction of Fe(III) to Fe(II)

occurred in the system, the possible reason was the rapid reaction between Fe(III) and FeB on the surface of the Fe₃O₄-FeB (Figure 10a). It was hypothesized that Fe and B in the FeB alloy, as well as aqueous or adsorbed Fe(II) generated during the Cr(VI) removal could contribute to reductive removal of Cr(VI). To distinguish the role of these reductants on Cr(VI) removal, we employed 1, 10-phenanthroline to complex Fe(II) species. We found the addition of 1, 10-phenanthroline could dramatically suppress Cr(VI) removal efficiencies of Fe₃O₄-FeB. Cr(VI) removal decreased from 100% to 15% within 15 min, the inhibitory efficiency reached 85.8% in the presence of 1, 10-phenanthroline (Figure 10b). This result indicated that Fe(II) species were the main contribution of Cr(VI) removal with Fe₃O₄-FeB.

In order to investigate Cr(VI) removal mechanism with Fe₃O₄-FeB, XPS spectra of Fe₃O₄-FeB before and after Cr(VI) removal (Fe₃O₄-FeB-Cr(VI)) were compared (Figure 11a). The peak in 191.5 eV which was responded to B species disappeared after Cr(VI) removal (Figure 11b), confirming B element in FeB participated in Cr(VI) removal process. Additionally, the high resolution XPS of Fe 2p and Cr 2p revealed that Fe(II) and Fe(III), Cr(III) and Cr(VI) coexisted in the Fe₃O₄-FeB and Fe₃O₄-FeB-Cr(VI) samples (Figure 11c, 11d), confirming that both adsorption and reduction co-happened during Cr(VI) removal process.

Furthermore, we checked electron transfer property by measuring the free corrosion potentials of the commercial Fe₃O₄ and Fe₃O₄-FeB in the presence of 8 mg•L⁻¹ of Cr(VI) with Tafel polarization diagrams. It is known that an electrode of a more negative free corrosion potential value possesses a higher electron transfer rate. The Fe₃O₄-FeB was easier to donate electron than the bare Fe₃O₄ as the free corrosion potentials of the Fe₃O₄-FeB (-0.76 V) was more negative than that of the Fe₃O₄ (-0.68 V) (Figure 12a). Because the reduction step is an electron-transfer process, the high electron-transport

property of FeB facilitates the reaction in a much faster manner, this was evidenced by the fact that Fe₃O₄-FeB showed a superior capacity of producing H₂ over the bare Fe₃O₄ under argon atmosphere (Figure 12b).

3.4 Possible Mechanism of the Promoted Cr(VI) Removal. On the basis of the above experiment results and discussion, we proposed a possible mechanism for the promoted Cr(VI) removal with Fe₃O₄-FeB (Scheme 1). As soon as Fe₃O₄-FeB was exposed to Cr(VI) solution at neutral pH, Cr(VI) in form of Cr₂O₇²⁻ would adsorb on the positively charged surface of Fe₃O₄-FeB via electrostatic interaction. Fe and B of the FeB alloy could reduce Cr(VI) adsorbed on the Fe₃O₄-FeB surface into Cr(III), simultaneously Fe(III) and BO₂⁻ species were generated (Eqs. 7, 8), as evidenced by the XPS analysis. Both Fe and B in the FeB could reduce the generated Fe(III) to form Fe(II) species (Eqs. 9, 10), these generated Fe(II) would also initiate Cr(VI) reduction (Eq. 11), this was confirmed by Tafel polarization analysis and aqueous boron species measurement result. Here boron elements containing many free electrons could accelerate electron transfer from Fe to the adsorbed Cr(VI), as well reduce Fe(III) to Fe(II) and thus promote Fe(III)/Fe(II) cycles, resulting in promotion of Cr(VI) removal efficiency of Fe₃O₄-FeB. Subsequently, Cr(III) species referred to form polymeric Cr(III) hydroxides because of its much less inflexibility. Finally, Cr(VI) could bound into these polymeric Cr(III) hydroxides through Cr(III)-O-Cr(VI) linkages to produce Fe(III)/Cr(III)/Cr(VI) composite oxide layer on the surface of Fe₃O₄-FeB (Eq. 12) [29]. B element may diffuse automatically from the bulk to the surface during the Cr(VI) removal, such diffusion would continue until all the bulk boron was consumed [30].

3.5 Implications for Cr(VI) Removal in Aquatic Systems. Magnetic properties of the commercial Fe_3O_4 , fresh prepared $\text{Fe}_3\text{O}_4\text{-FeB}$, and used $\text{Fe}_3\text{O}_4\text{-FeB-Cr(VI)}$ were measured at 300K (Figure 13a). All the samples showed a ferromagnetic performance. The fresh prepared $\text{Fe}_3\text{O}_4\text{-FeB}$ exhibited a saturation magnetization value of $84.48 \text{ emu}\cdot\text{g}^{-1}$. Owing to the strong ferromagnetic behavior of $\text{Fe}_3\text{O}_4\text{-FeB}$, the adsorbed Cr(VI) contaminant can be easily separated from aqueous solution by means of an external magnet, which was much simpler than using centrifugation of non-magnetic adsorbents (Figure 13b). We found that Cr(VI) removal efficiency decreased during the re-cycled Cr(VI) removal process with $\text{Fe}_3\text{O}_4\text{-FeB}$ (Figure 13c), because Cr(VI) was mainly reductively removed by electrons donated from Fe and B as soon as adsorbed, followed by an in-situ formation of Cr(III)/Fe(III) oxyhydroxides subsurface layer and simultaneous adsorption of Cr(VI) on this subsurface to generate Cr(III)/Fe(III)/Cr(VI) oxyhydroxides surface. The increased Cr(III)/Fe(III)/Cr(VI) oxyhydroxides shell could inhibit the electron transfer, leading to the decrease of Cr(VI) removal [29]. The used $\text{Fe}_3\text{O}_4\text{-FeB}$ could be regenerated after the re-treatment with NaBH_4 (Figure 13c), suggesting its potential of real application in Cr(VI) wastewater treatment.

4. Conclusions

In summary, $\text{Fe}_3\text{O}_4\text{-FeB}$ has been facilely synthesized by interfacial reduction of commercial Fe_3O_4 nanoparticles with NaBH_4 . The $\text{Fe}_3\text{O}_4\text{-FeB}$ displayed a promoted Cr(VI) removal

efficiency compared with the bare Fe_3O_4 counterpart, the interfacial reduced $\text{Fe}_3\text{O}_4\text{-H}_2$ and/or $\text{Fe}_3\text{O}_4\text{-N}_2\text{H}_4\cdot\text{H}_2\text{O}$. The high Cr(VI) removal efficiency of the $\text{Fe}_3\text{O}_4\text{-FeB}$ was highly dependent on the amorphous FeB alloy, where the boron elements containing many free electrons could accelerate the electrons transfer from Fe to the adsorbed Cr(VI), as well reduce Fe(III) to Fe(II) and thus promote the Fe(III)/Fe(II) cycles. The efficient Cr(VI) removal under a wide range of pH values and its easy magnetic separation make the low-cost $\text{Fe}_3\text{O}_4\text{-FeB}$ to be a potential material for Cr(VI) contaminated water treatment.

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Figure Caption

Figure 1. SEM images of the commercial Fe_3O_4 (a) and powders treated with NaBH_4 (b); XRD patterns (c) and N_2 adsorption and desorption isotherms (d) of Fe_3O_4 and powders treated with NaBH_4 .

Figure 2. TEM and HRTEM images of the commercial Fe_3O_4 (a, b, c), and the NaBH_4 treated Fe_3O_4 (d, e, f).

Figure 3. EFTEM images of the commercial Fe_3O_4 (a) and the treated Fe_3O_4 (e). EFTEM element mapping images of the Fe_3O_4 (b, c, and d) and the treated Fe_3O_4 (f, g, and h).

Figure 4. Mössbauer spectra of the Fe_3O_4 before and after NaBH_4 treatment.

Figure 5. XPS spectra of the Fe_3O_4 before and after NaBH_4 treatment, (a) XPS survey; (b) high resolution of Fe 2p; (c) high resolution of B 1s.

Figure 6. Time profile of Cr(VI) removal with Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-FeB}$ with different treatment time (a), and concentrations (c); plots of $-\ln(C/C_0)$ versus time with samples with different treatment time (b), and concentrations (d).

Figure 7. Time profiles of the initial pH values on Cr(VI) removal with $\text{Fe}_3\text{O}_4\text{-FeB}$ ($\text{Fe}_3\text{O}_4\text{-FeB}$ 0.8 $\text{g}\cdot\text{L}^{-1}$, Cr(VI) 8 $\text{mg}\cdot\text{L}^{-1}$) (a), removal kinetics of Cr(VI) removal at different initial pH values (b), time profiles of the initial Cr(VI) concentrations (4-32 $\text{mg}\cdot\text{L}^{-1}$) on Cr(VI) removal (c), and pseudo-second-order kinetic model, $\text{Fe}_3\text{O}_4\text{-FeB}$ was 0.8 $\text{g}\cdot\text{L}^{-1}$; initial concentrations of Cr(VI) were 4

to 32 mg•L⁻¹ (d).

Figure 8. SEM images of Fe₃O₄-H₂ (a), and Fe₃O₄-N₂H₄•H₂O (b); XRD patterns (c), and XPS spectra (d) of Fe₃O₄-N₂H₄•H₂O and Fe₃O₄-H₂.

Figure 9. Time profile of Cr(VI) removal with Fe₃O₄, Fe₃O₄-FeB, Fe₃O₄-N₂H₄•H₂O, and Fe₃O₄-H₂.

Figure 10. (a) Time profile of concentrations of B, Fe(II), and Fe(III) in solution; (b) time profile of Cr(VI) removal with Fe₃O₄-FeB in the absence or presence of 1,10-phenanthroline.

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Figure 12. (a) Tafel plots; (b) temporal concentration change of hydrogen evolution of Fe₃O₄ and Fe₃O₄-FeB in the system.

Figure 13. (a) Magnetic hysteresis loop measured at 300K, the enlarged magnetization curve between -800 and 800 Oe (inset); (b) photographs of magnetic separation: (I) 8 mg L⁻¹ Cr(VI); (II) a mixture of Fe₃O₄-FeB with 8 mg L⁻¹ Cr(VI) solution; (III) magnetic separation of Fe₃O₄-FeB from the solution; (c) Reusability of Fe₃O₄-FeB: left, Fe₃O₄-FeB recycled to the next removal without any treating; (b) the recycled solid was retreated by NaBH₄ to the next removal.

Scheme 1. Schematic Cr(VI) removal mechanism with Fe₃O₄-FeB.

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Figure 8. SEM images of $\text{Fe}_3\text{O}_4\text{-H}_2$ (a), and $\text{Fe}_3\text{O}_4\text{-N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (b); XRD patterns (c), and XPS spectra (d) of $\text{Fe}_3\text{O}_4\text{-N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and $\text{Fe}_3\text{O}_4\text{-H}_2$.

Figure 9. Time profile of Cr(VI) removal with Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-FeB}$, $\text{Fe}_3\text{O}_4\text{-N}_2\text{H}_4\cdot\text{H}_2\text{O}$, and $\text{Fe}_3\text{O}_4\text{-H}_2$.

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Scheme 1. Schematic Cr(VI) removal mechanism with $\text{Fe}_3\text{O}_4\text{-FeB}$.

Table 1. Mössbauer spectrahyperfine parameters.

	δ (mm/s)	Q (mm/s)	H (kOe)	Line width (mm/s)	Area (%)	Possible assignment
Fe_3O_4	0.304	-0.0058	488.13	0.2154	57.21	Ordered iron(III)oxide
	0.6594	0.0061	451.97	0.2512	42.79	Ordered iron(II)oxide
Treated Fe_3O_4	0.306	-0.014	487.5	0.225	32.2	Ordered iron(III) oxide
	0.652	-0.017	453.6	0.243	27.0	Ordered iron(II) oxide
	0.199	-0.091	156.2	1.831	35.3	Ordered iron(III)oxide
	-0.560	-0.106	230.4	0.104	1.1	$\text{Fe}_x\text{B}_{1-x}$
	0.924	1.965		0.118	1.4	High-spin iron(II)
	0.211	1.106		0.217	3.1	High-spin iron(III)

* isomer shift δ , quadrupolar splitting Q, and hyperfine filed H

Table 2. Ratio of $\text{Fe}^{\text{II}}/\text{Fe}_{\text{total}}$ and $\text{Fe}^{\text{III}}/\text{Fe}_{\text{total}}$ in Fe 2p core level spectra, and ratio of B in oxides to total ($\text{B}/\text{B}_{\text{total}}$) of the Fe_3O_4 , $\text{Fe}_3\text{O}_4\text{-FeB}$, $\text{Fe}_3\text{O}_4\text{-H}_2$, and $\text{Fe}_3\text{O}_4\text{-N}_2\text{H}_4\cdot\text{H}_2\text{O}$ samples.

	$\text{Fe}^{\text{II}}/\text{Fe}_{\text{total}}$	$\text{Fe}^{\text{III}}/\text{Fe}_{\text{total}}$	$\text{B}/\text{B}_{\text{total}}(\%)$
Fe_3O_4	0.395	0.605	–
$\text{Fe}_3\text{O}_4\text{-FeB}$	0.570	0.430	1.82
$\text{Fe}_3\text{O}_4\text{-H}_2$	0.486	0.514	-
$\text{Fe}_3\text{O}_4\text{-N}_2\text{H}_4\cdot\text{H}_2\text{O}$	0.546	0.454	-
$\text{Fe}_3\text{O}_4\text{-FeB-Cr(VI)}$	0.358	0.642	0.029

Table 3. Theoretical and calculated q_e values, k_2 , and R^2 .

	Calculated q_e (mg L^{-1})	k_2 ($\text{g/mg}^{-1} \text{ min}^{-1}$)	R^2
4	5.01	0.371	0.999
8	10.04	0.211	0.999
16	20.53	0.023	0.999
32	42.59	0.002	0.998

Table 4. Cr(VI) removal capacities of various adsorbents.

Adsorbents	pH	$q_{\max}$ (mg/g)	Ref
Fe ₃ O ₄ -FeB	6.3	38.9	This work
nZVI-Fe ₃ O ₄	3	100	5
Magnetic Nanoparticles (Fe ₃ O ₄)	6	3.5	7
Nanoscale maghemite (Fe ₂ O ₃)	2-3	19.2	8
Polypyrrole magnetic nanocomposite	2	169-264	9
Ethylenediamine-functionalized Fe ₃ O ₄ magnetic polymers	2	60	10
HA-Fe ₃ O ₄	4-10	3.37	11
Reduced graphene oxide-Fe ₃ O ₄ magnetic composites	3	293	12

Table 5. Langmuir and Freundlich isotherm parameters for Cr(VI) removal by Fe₃O₄-FeB.

Cr(VI) mg•L ⁻¹	Langmuir isotherm			Freundlich isotherm		
	Q^0	K	R^2	K_f	n	R^2
	(mg•g ⁻¹)	(L•mg ⁻¹)		(mg•g ⁻¹)	(L•mg ⁻¹)	
4	4.56	401.5	0.99	4.47	34.81	0.91
8	9.09	376.0	0.99	9.08	35.71	0.94
16	15.29	23.1	0.99	17.34	19.67	0.73
32	19.79	5.9	0.99	42.07	4.81	0.79

Graphical Abstract