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Cr(VI) Adsorption and Reduction by Humic Acid Coated on Magnetite

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ABSTRACT

Easily separable humic acid coated magnetite (HA-Fe3O4) nanoparticles are employed for effective adsorption and reduction of toxic Cr(VI) to non-toxic Cr(III). The adsorption and reduction of Cr(VI) is effective under acidic, neutral, and basic pH conditions. The chromium adsorption nicely fits the Langmuir isotherm model and the removal of Cr(VI) from aqueous media by HA-Fe3O4 particles follows pseudo-second-order kinetics. Characterization of the Cr-loaded HA-Fe3O4 materials by X-ray absorption near edge structure spectroscopy (XANES) indicates Cr(VI) was reduced to Cr(III) while the valence state of the iron core is unchanged. Fe K-edge extended X-ray absorption fine structure spectroscopy (EXAFS) and X-ray diffraction measurements also indicate no detectable transformation of the Fe3O4 core occurs during Cr(VI) adsorption and reduction. Thus, suggesting HA on the surface of HA-Fe3O4 is responsible for the reduction of Cr(VI) to Cr(III). The functional groups associated with HA act as ligands leading to the Cr(III) complex via a coupled reduction-complexation mechanism. Cr K-edge EXAFS demonstrates the Cr(III) in the Cr-loaded HA-Fe3O4 materials has six neighboring oxygen atoms likely in an octahedral geometry with average bond lengths of 1.98 Å. These
results demonstrate easily separable HA-Fe$_3$O$_4$ particles have promising potential for removal and detoxification of Cr(VI) in aqueous media.

INTRODUCTION

The presence of chromium (Cr) in aquatic systems and drinking water sources is a serious threat to the environment and human health. The United States Environmental Protection Agency set maximum contaminant limits for total chromium in drinking water of 100 µg/L$^{1}$ and the World Health Organization set a more strict threshold of 50 µg/L$^2$. Exposure to chromium has detrimental health consequences on humans and has been linked to carcinomas of the respiratory organs, mutations$^3$, chromosomal aberrations$^4$, and DNA damage$^5$. The introduction of chromium into aquatic environments occurs from both natural sources and anthropogenic activities. The world-wide production of iron chromium oxide, FeCr$_2$O$_4$, was 23.3 million tons in 2011$^6$. The toxicity, solubility, and mobility of chromium are highly dependent on the oxidation state of the metal. Speciation of chromium in aqueous media occurs predominately between Cr(VI) and Cr(III). Although Cr(III) is an essential micronutrient in the human body, Cr(VI) is highly soluble in aqueous media, acutely toxic, mutagenic, and carcinogenic$^7$. Reduction of the Cr(VI) to Cr(III) is critical in the detoxification of Cr(VI)-contaminated media and effective treatment processes. Treatment strategies and current removal methods typically involve reduction of Cr(VI) to Cr(III) followed by adsorption and subsequent separation of the Cr laden absorbent using filtration or other methods$^8,^9$.

Iron based materials have received significant attention for environmental applications and treatment of a variety of pollutants and toxins from aqueous solutions$^{10, 11}$. Iron magnetic nanoparticles are attractive for remediation applications as they possess high surface areas, are
inexpensive, and easily separated and recovered by simply applying an external magnetic field. Magnetite, the most magnetic of naturally occurring minerals, is a mixture of Fe(II) and Fe(III) and exists in sediments in natural aquatic systems. Bare magnetite, Fe$_3$O$_4$ nanoparticles have been successfully applied for remediation of Cr(VI)-contaminated waters. The Fe(II) in magnetite can initiate the reduction of Cr(VI) to Cr(III), and the Cr(III) can subsequently be chelated by OH groups at the surface of iron oxide to form an inner-sphere surface complex. In addition Cr(III) can form precipitates such as Cr(OH)$_3$ and Fe$_x$Cr$_{1-x}$(OH)$_3$ in aqueous solutions. However, these materials are not effective under basic conditions and the Fe(II) present in magnetite is highly susceptible to auto-oxidation forming Fe(III) materials with reduced magnetic properties. Thus the reduction of Cr(VI) by Fe(II) based nanomaterials will lead to a decrease in the magnetic properties of the materials which in turn could limit the effectiveness of separation using a magnetic field. The uses of bare nanomaterials are promising for water treatment, however they are susceptible to agglomeration and real-life applications are controversial because bare nanoparticles can be toxic.

The coating of nanomaterials with organic substrates is a strategy to reduce their toxicity. Surface modification of iron magnetic nanoparticles can also inhibit the auto-oxidation of the iron core. A number of naturally occurring and synthetic organic materials have been employed for surface modification to enhance the adsorption selectivity and capacity. Recent study demonstrates surface modification of magnetic iron oxide nanoparticle can exhibit a natural protective effect and lower the inherent toxicity associated with nanomaterials. Humic acid coated magnetite (HA-Fe$_3$O$_4$) has been synthesized and is promising materials for the removal of heavy metal cations and organic contaminants. These HA-Fe$_3$O$_4$ materials are remarkably stable under ambient conditions, resistant to auto-oxidation and maintain their magnetic properties.
properties. The HA-Fe$_3$O$_4$ materials exhibit only slight leaching of iron and limited desorption of HA from the iron core $^{27}$.

HAs are derived from plants and microbial residues, and ubiquitous in natural aquatic environments. A variety of organic functional groups, notably carbonyl, carboxylate, phenol and hydroxyl groups are present in HA materials. Because of the different types and large numbers of functional groups, HA can effectively complex a variety of metal ions. HA has a high affinity for magnetite due to surface complexation-ligand exchange reactions between the HA functional groups and surface hydroxyl groups of magnetite $^{28}$. Magnetite particles which are completely covered by HA exhibit characteristics of HA as opposed to properties associated with metal oxides $^{29}$, low pH of point of zero charge and negatively charged under solution pH $>$ 3 inhibits their agglomeration.

HA-Fe$_3$O$_4$ hybridized materials have tremendous potential for water purification; however, their application has only been reported for the removal of a limited number of positively charged metal cations without observation of any redox conversion$^{27,30}$. Alkali-metal and alkaline-earth cations bind to humic acid primarily by electrostatic interactions. Our study represents the first report on the potential application of HA-Fe$_3$O$_4$ removal of an oxyanion, specifically toxic Cr(VI). The Fe(II) core and HA can in theory function as reductants for Cr(VI) under environmental conditions $^{31,32}$. Herein HA-Fe$_3$O$_4$ nanoparticles are applied for the removal Cr(VI) from aqueous solution. Detailed characterization of the Cr loaded HA-Fe$_3$O$_4$ materials indicate Cr(VI) is reduced to Cr(III) by HA on the surface of HA-Fe$_3$O$_4$, and the functional
groups associated with HA act as ligands for Cr(III) via a coupled reduction-complexation mechanism. Cr(III) has six neighboring oxygen atoms arranged in an octahedral geometry. Our results provide a fundamental understanding of the chemistry of the HA-Fe₃O₄ in the reductive complexation and immobilization of Cr(VI) from aqueous media. The HA appears to insulate the iron core from auto-oxidation and electron transfer with Cr(VI), preserving the magnetic properties of these materials with the HA mediated conversion of carcinogenic Cr(VI) to non-toxic Cr(III). HA-Fe₃O₄ particles are easily separated following treatment by application of a magnetic field. Our results demonstrate their tremendous potential for removal and detoxification of Cr(VI) in aqueous media.

**MATERIALS AND METHODS**

**Materials**

Potassium chromate (99.8 %), sodium hydroxide (99.4 %), trace metal grade nitric acid (67-70 %), ammonium hydroxide (29.15 %), and ferric chloride tetrahydrate (100.8 %) were purchased from Fisher. Ferrous chloride tetrahydrate (≥ 99.0 %) and HA (sodium salt, CAS no. 68131-04-4) were obtained from Sigma. All the solutions were prepared with Millipore filtered water (18 MΩ · cm) produced from a nanopure diamond lab water system (Barnstead Thermolyne Corporation, Dubuque, IA).

**Preparation of bare Fe₃O₄, HA-Fe₃O₄ and Cr-loaded HA-Fe₃O₄**

The bare Fe₃O₄ and HA-Fe₃O₄ materials were prepared according to a published method. Iron solutions of FeCl₂ · 4H₂O (3.0 g) and FeCl₃ · 6H₂O (6.1 g) were dissolved in 100 mL of water. The iron mixture was heated to 90 °C in a 250 mL round bottom flask equipped with a reflux condenser. The reaction solution was magnetically stirred throughout the reaction process. Ten
mL of 25% ammonium hydroxide and 50 mL of 1.0% HA solution (for HA-Fe₃O₄ synthesis) were added to the mixture rapidly and sequentially. The mixture was aged at 90 ± 5 °C for an additional 30 min. The solid products were washed with water and dried to constant weight in a vacuum oven at ~ 40 °C. The vacuum-dried particles were stored in a vacuum desiccator.

HA-Fe₃O₄ particles (0.5 g) were added to 50 mL of 1.0 mM potassium chromate solution in a 250 mL Erlenmeyer flask. For the adsorption experiments, the effects of dosage of HA-Fe₃O₄ particles and the initial concentration of Cr(VI) were studied. The solution pH was adjusted using 5% aqueous solutions of NaOH and HNO₃. The experiments were carried out on an orbit shaker (Lab-line instrument Inc., model 3520) with continual mixing at 300 revolutions per minute (RPM) for 4 hrs in a temperature-controlled laboratory. Samples were separated from the suspension with a handheld permanent magnet, washed with ~ 10 mL water four times, and dried in a vacuum oven at ~ 40 °C to constant weight. A control experiment was carried out for the blank solution (without Cr(VI)) of 0.5 g HA-Fe₃O₄ in 50 mLs of water. The solution separated from the particles will be referred to as the decanted solution. The total Cr and total organic carbon (TOC) in the decanted solution were measured using an atomic absorption spectrophotometer (AAS) (Perkin-Elmer AA600) and Shimadzu TOC-VCSH total organic carbon analyzer, respectively. The chromium in the decanted solution can include free Cr and Cr bound to HA (released from the HA-Fe₃O₄ particles and not extracted during magnetic separation of the particles). The decanted solution was filtered through Macrosep advance centrifugal devices (3K molecular weight cut-off) at 5000 RPM to remove residual humic acids complexing Cr. The Cr in the resulting filtrate was determined by AAS to distinguish free Cr and Cr bound to residual HA present in solution. The adsorption kinetics were analyzed by
pseudo-first order kinetics (eq.1), pseudo-second order kinetics (eq.2) and intraparticle diffusion model (eq.3), respectively.

\[
\ln\left(\frac{C_0}{C}\right) = k_1 t
\]  

where \(k_1\) is the rate constant of pseudo-first order model (min\(^{-1}\)), \(t\) is time (min), \(C_0\) is the initial concentration of Cr(VI) and \(C\) is the concentration of Cr(VI) at the specific time.

\[
\frac{dQ_t}{dt} = k_p (Q_e - Q_t)^2
\]

where \(k_p\) is the rate constant of pseudo-second-order model (g/(mg · min)), \(t\) is the reaction time (min), \(Q_t\) is the amount of adsorbate adsorbed per unit mass by HA-Fe\(_3\)O\(_4\) at the specific time (mg/g), and \(Q_e\) is the adsorption capacity at adsorption equilibrium (mg/g), respectively.

\[
Q_t = k_{id} t^{1/2} + c
\]

where \(c\) is the intercept and \(k_{id}\) is the intraparticle diffusion rate constant.

The data was modeled with Langmuir adsorption isotherm\(^{34}\).

\[
\frac{C_e}{Q_e} = \frac{1}{b Q_m} + \left(\frac{1}{Q_m}\right) C_e
\]

where \(C_e\) is the equilibrium chromium concentration in solution, \(Q_e\) is the adsorption capacity at adsorption equilibrium (mg/g), \(b\) and \(Q_m\) are the Langmuir adsorption constant (L/mg) and maximum capacity of adsorbent (mg/g), respectively.

**Characterization**

Transmission electron microscopy (TEM) measurements were run using a Phillips CM-200 (200 kV) for the size of particles. Nitrogen adsorption and desorption isotherms were performed for Brunauer-Emmett-Teller (BET) surface area on a Micromeritics TriStar II 3020 system and HA-Fe\(_3\)O\(_4\) was prepared by purging with nitrogen gas at 80 °C for 4.0 h before analyses. Samples
were separated from the suspension using a handheld magnet, washed with approx. 10 mL of water for four times and dried in a vacuum oven. The FTIR spectra of Cr-loaded HA-Fe$_3$O$_4$ were taken using a Perkin-Elmer 100 FTIR spectrometer. A similar experiment was carried out for the blank solution (without chromium solution) of HA-Fe$_3$O$_4$ (0.5 g HA-Fe$_3$O$_4$ in 50 mL of water) which was also analyzed by FTIR. The total carbon of HA-Fe$_3$O$_4$ particle was measured using a Carlo Erba NA 1500 analyzer. X-ray diffraction (XRD) analysis was carried out on beamline X14A at National Synchrotron Light Source, Brookhaven National Lab (NSLS, BNL). The storage ring was operated at 3.0 GeV with a current of ~ 280 mA. The wavelength of incident beam was set at 0.7785 Å by a saggittal-focusing monochromator. The spot size was ~ 1.5 × 1 mm (horizon vs vertical). A sample filled capillary tube (0.7 mm diameter) was rotated by a spinner on a six-circle Huber diffractometer. The diffraction peaks in the range 4-46 ° were collected using a Si strip position-sensitive detector mounted on the diffractometer.

The X-ray absorption spectra (XAS) were obtained on vacuum-dried samples employing a beamline X19A at NSLS. The storage ring was operated under conditions described above for XRD measurements. The relative energy resolution of X19A was approximately 2 × 10$^{-4}$ for Fe K-edge (7112 eV) and Cr K-edge (5989 eV) XAS measurements, and the harmonics were minimized by detuning double-crystal Si (111) monochromator to obtain a 30 % reduction in the intensity of the incident X-ray. The Fe K-edge spectra and Cr K-edge XAS spectra of reference Cr compounds were collected using a Canberra PIPS-detector in fluorescence mode. Given the relatively low Cr concentrations, the Cr K-edge XAS spectra of Cr-loaded HA-Fe$_3$O$_4$ samples were measured using a 4-elements Si-drift Vortex detector in fluorescence mode. The incident beam was monitored by an ion chamber filled with nitrogen gas. The X-ray absorption spectra were divided into XANES and EXAFS regions. XANES were analyzed by IFEFFIT and
Demeter package\textsuperscript{36}, while EXAFS were analyzed using WinXAS 3.1\textsuperscript{37}. The Cr \textit{K}-edge EXAFS spectrum of KCrO\textsubscript{2} was obtained using FEFF package\textsuperscript{38-40}.

3. RESULTS AND DISCUSSION

3.1 The pH effect on adsorption and reduction of Cr(VI)

The adsorption and reduction of Cr(VI) with HA-Fe\textsubscript{3}O\textsubscript{4} materials were investigated over a range of solution pH. While the chemical composition, chemical functionalities and physical properties of humic acid materials from different sources can vary significantly, the commercially available humic acid from Sigma was used to coat Fe\textsubscript{3}O\textsubscript{4} in our experiments. The synthesized HA-Fe\textsubscript{3}O\textsubscript{4} materials employed for removal of toxic Cr(VI) are composed of particles with average diameters of \(\sim 15\) nm and BET surface areas \(104\) m\textsuperscript{2}/g. HA-Fe\textsubscript{3}O\textsubscript{4} (0.5 g) was added to Cr(VI) solution (50 mL of 1.0 mM), and the pH was adjusted and the suspension was agitated at 300 RPM. After 4 hrs of mixing, the HA-Fe\textsubscript{3}O\textsubscript{4} particles with adsorbed Cr were separated using a hand held magnet. The solution was retained for analyses of levels of total organic carbon (TOC) and Cr. The levels of TOC are an indication of desorbed HA back into solution from the particles. Less than 2 % total carbon of HA-Fe\textsubscript{3}O\textsubscript{4} was leached under acidic, basic, and neutral conditions. Our results are consistent with a number of reports indicating desorption of HA from such materials is highly unfavorable \textsuperscript{27,30}. To determine the level of Cr associated with HA leached from the HA-Fe\textsubscript{3}O\textsubscript{4} particles, the solution was physically separated from the particles and divided into two fractions. One fraction was subjected to total Cr analysis. The other fraction was subjected to ultrafiltration to remove any residual/leached HA prior to analysis for total Cr. The level of Cr before and after ultrafiltration were comparable, indicating that the leaching HA does not have a critical effect on the chromium in the solution.
The removals of Cr by HA-Fe₃O₄ particles were measured under acidic (pH 4), neutral (pH 7) and alkaline (pH 10) conditions. The particles effectively remove 80-90% of the Cr under acidic, neutral and alkaline conditions as illustrated in Figure 1. While the average removal appears to decrease slightly in moving from acidic to alkaline conditions, the measured removals at different pH are within the reproducibility of the experiments. Iron oxides can be ineffective for the removal of Cr(VI) under basic conditions. The lack of pH effects on the HA-Fe₃O₄ removal of Cr suggests adsorption or binding is not controlled by electrostatic interactions.

Under basic or acidic conditions, hydrolysis at the iron oxide surface can occur; however, under our experimental conditions over a pH range of pH 4 to 10 desorption of HA was insignificant based on low levels of TOC observed in solution. This observation is consistent with the documented high affinity of HA for magnetite via a ligand exchange reaction. The surface properties of the HA-Fe₃O₄ particles are characteristic of the HA with respect to the surface charge and the presence of HA inhibits particle aggregation normally observed in the case of unmodified magnetite. The pH of zero point charge (pH_{PZC}) of bare magnetite is ~7.6, while the measured pH_{PZC} of the HA-Fe₃O₄ and Cr-loaded HA-Fe₃O₄ materials is ~3.3 (Figure 1S), indicating that the adsorption of Cr does not change the pH_{PZC} of HA-Fe₃O₄. The HA-Fe₃O₄ materials are negatively charged except under strong acidic conditions and reportedly effective for adsorption of positively charged ions by electrostatic attraction. However adsorption of negative ions may be inhibited by electrostatic repulsion under alkaline conditions. The pKₐ₁ and pKₐ₂ of H₂CrO₄ are 0.74 and 6.50, respectively. The common chemical species of Cr(VI) in aqueous media, CrO₄²⁻, HCrO₄⁻, Cr₂O₇²⁻, are negatively charged. While adsorption is often governed by electrostatic repulsion and attraction between adsorbent and adsorbate, our results
demonstrate that the repulsive electrostatic interaction between the HA-Fe$_3$O$_4$ and Cr species does not inhibit the removal of Cr(VI) from the solution.

To better understand the adsorption and complexation involved in the removal of Cr(VI) by HA-Fe$_3$O$_4$, the speciation of Cr and Fe in Cr-loaded HA-Fe$_3$O$_4$ were measured using XANES technique. Cr $K$-edge XANES spectra of Cr(III), Cr(VI) and Cr(0) are provided as references for comparison with Cr-loaded HA-Fe$_3$O$_4$ under acidic, neutral and alkaline pH in Figure 2. The spectra of the Cr-loaded HA-Fe$_3$O$_4$ materials are unchanged over the range of pH, the presence of characteristic Cr(III) features and the absence of the strong pre-edge band for Cr(VI) and the broad feature of Cr(0) clearly indicate the predominant specie is Cr(III) in the Cr-loaded HA-Fe$_3$O$_4$. The results confirm that conversion of Cr(VI) to Cr(III) is facilitated by the particles. While bare magnetite has been reported to reduce Cr(VI) $^{43}$, the reduction is fast under acidic conditions but decreases significantly with increasing pH $^{18}$. Chromium $K$-edge XANES spectra indicate that the change of pH under our experimental conditions has no significant effect on reduction of Cr(VI). While a strong pH dependence is observed for bare Fe$_3$O$_4$, the adsorption and reduction of Cr(VI) by HA-Fe$_3$O$_4$ is minimally influenced by solution pH, suggesting the reduction of Cr(VI) by HA-Fe$_3$O$_4$ follows different mechanisms. The results further indicate the adsorption and redox properties of these materials are dominated by the humic acid characteristics and not appreciably influenced by the Fe$_3$O$_4$ core or metal oxide behavior.

Fe(II) and HA have similar reduction capacities and are capable of reducing Cr(VI) $^{44}$. To determine the involvement of Fe(II) in the core of the HA-Fe$_3$O$_4$ in the reduction of Cr(VI), iron XANES spectra were obtained Figure 2S demonstrates that no detectable change is observed in
the valence states of iron during the reduction of Cr, suggesting Fe(II) in HA-Fe₃O₄ is not responsible for Cr(VI) reduction. Changes in the valence state of Fe₃O₄ are reported during reduction of Cr(VI) by unmodified Fe₃O₄. The presence or addition of dissolved iron to HA material can lead to Cr(VI) reduction, however our results indicate the Fe₃O₄ core is not appreciably transformed during the reduction of Cr(VI) under our experimental conditions. A relatively high concentration of HA (31 g/L) was employed for the synthesis of the HA-Fe₃O₄ particles. Complete surface coverage of magnetite can be obtained at solution concentrations of 20 mg/L HA. Under our experimental conditions it appears the HA effectively insulates the iron core, prohibits the interaction of Cr(VI) and Fe(II), and thus Cr(VI) is reduced by HA.

HA contains a variety of functional groups, including substituted phenols, α-hydroxyl carboxylic acids, oxalic acid, and α-carbonyl carboxylic acids, which are capable of initiating the reduction of Cr(VI) to Cr(III). Chromium(III) can be chelated by the functional groups in HA and a coupled reduction-complexation mechanism between the functional groups in HA and Cr(VI) is proposed.

3.2 The local coordination environment

The effects of temperature, ionic strength and background electrolytes have been previously explored to determine the thermodynamic and kinetic parameters for the reduction of Cr(VI) by different soil humic substances (SHSs). The rate equations for the reduction of Cr(VI) by SHSs were applicable over a range of pH, ionic strength and background electrolytes. The rates for SHSs reduction of Cr(VI) were not appreciably influenced by changes in ionic strength and background electrolytes. EXAFS was carried out for detailed structural information of the chromium binding in HA-Fe₃O₄ system, the coordination number (N), bond length (R) and the Debye-Waller value (σ²) of Cr in Cr-loaded HA-Fe₃O₄ are presented in Figures 3-A, 4-A, and
Table 1S. The typical bond lengths of Cr(III)-O and Cr(VI)-O are 1.98 ± 0.01 Å and 1.63 ± 0.03 Å, respectively. The measured Cr-O bonds in the Cr-loaded HA-Fe₃O₄ materials are identical to the literature values for Cr(III)-O bonds with bond lengths of 1.98 Å, summarized in Table 1S. The bond length further demonstrates Cr(VI) is reduced to Cr(III) upon adsorption to HA-Fe₃O₄ materials. The local coordination environment of Cr(III) is the same at different solution pH under our experimental conditions. The coordination number of Cr(III) is 6, likely an octahedral geometry. Given the heterogeneous mixture of functional groups in HA, a variety of ligands are involved in the complexation of Cr(III). The carboxylate, quinone and phenolic groups are abundant in HA and have an affinity to complex with a central Cr(III) atom.

3.3 Crystal transformation

FTIR analysis was employed to study the binding of HA on magnetite surface (Figure 3S). The free C=O stretching peak typically occurs ~ 1700 cm⁻¹, however upon complexation with Fe₃O₄ the C=O_{HA} bond is weakened and the IR band shifts to the right. The observed peak at ~ 1560 cm⁻¹ is assigned to the C=O_{HA} and is indicative of complexation of the C=O_{HA} by the magnetite surface. HA has a high binding affinity to magnetite, and subsequent desorption is very difficult. The adsorption of Cr does not appear to affect the interaction between HA and Fe₃O₄ under acidic, neutral and alkaline pH conditions as indicated by the unchanged C=O band. Distinct or unique differences in the IR spectra of HA-Fe₃O₄ at pH 4.0, 7.0, and 10.0 with or without Cr(VI), were not observed under our experimental conditions and within the resolution of the FTIR instrument. While EXAFS indicated Cr bonds to HA through oxygen ligands, the small number of HA functional groups directly involved in Cr binding, relative to the large
number and broad strong adsorption bands of the bulk material did not allow us to distinguish changes in the IR adsorption bands upon Cr adsorption.

XRD was employed to assess the crystal lattice of Fe$_3$O$_4$ core in HA-Fe$_3$O$_4$ after loading with Cr(VI). The peak position and relative intensity match the literature well and demonstrate no change in lattice of iron core is observed (Figure 5) $^{53}$. The XRD spectra show no detectable difference between the original HA-Fe$_3$O$_4$ and Cr-loaded HA-Fe$_3$O$_4$, and iron XANES (Figure 2S), imply no transformation from magnetite to maghemite during removal of Cr(VI). The dissolution of maghemite can lead to the formation of goethite $^{18}$; however no goethite was detected under our experimental conditions. Fe K-edge EXAFS (Figure 3-B, 4-B, and Table 2S) indicate there was no significant difference in the iron core of the original HA-Fe$_3$O$_4$ and Cr-loaded HA-Fe$_3$O$_4$ $^{54}$. Therefore, the iron core of HA-Fe$_3$O$_4$ is unchanged during Cr adsorption and reduction processes.

**Adsorption kinetics and adsorption isotherm**

Adsorption and kinetic studies can provide valuable parameters for the modeling specific treatment processes. The equilibrium constant and adsorption isotherm were measured at constant HA-Fe$_3$O$_4$ concentration (0.8 g/L) while varying initial Cr(VI) concentrations from 1-5 ppm. The adsorption equilibrium was achieved by shaking the HA-Fe$_3$O$_4$ suspension at 300 RPM for 120 min. The adsorption was equated to the change in chromium concentrations in the aqueous phase. The adsorption did not fit pseudo-first order kinetics ($R^2 < 0.54$), but is nicely modeled by pseudo-second order kinetics with a high coefficient of determination ($R^2 > 0.98$) for the plots of $t/Q_t$ versus $t$. The kinetic data was analyzed using an intraparticle diffusion model,
indicating that the adsorption of Cr(VI) occurs in two phases: the surface adsorption and intraparticle diffusion, followed by a redox reaction (Fig 4S).

Langmuir adsorption model was employed to assess the adsorption capacity of HA-Fe₃O₄ for Cr. Langmuir adsorption isotherm assumes that the adsorbent surface has a specific number of equivalent sorption sites, and the monolayer adsorption occurs without interaction between sorption sites. The adsorption of chromium by HA-Fe₃O₄ is nicely described by Langmuir isotherm with a good coefficient of correlation ($R^2 = 99\%$). In the current study, the maximum adsorption capacity, $Q_m = 3.37 \text{ mg/g}$ for chromium is significantly lower than that observed for adsorption of cationic species on the same materials²⁷. These observed differences are rationalized by the fact that HA-Fe₃O₄ particles are negatively charged under our experimental conditions and thus contributions to the adsorption capacity from attractive electrostatic interactions for cationic species can enhance the adsorption capacity while repulsion between chromate and HA-Fe₃O₄ will lower the adsorption. The observed adsorption constant for chromium $b = 23146 \text{ L/mg}$ is higher than those observed for cationic species, consistent with a high chromium bonding strength on HA-Fe₃O₄. Structural characterization indicates the formation of a strongly bound chromium octahedral complex, Such complexes should be resistant to leaching and thus are attractive for removal applications.

**Implications for Cr(VI) detoxification in natural aquatic systems.**

Since Cr(VI) is toxic and carcinogenic, the reduction of Cr(VI) to non-toxic Cr(III) is highly desirable for treatment of Cr(VI)-contaminated water. Magnetite and HA are capable of reducing Cr(VI). Magnetite effectively reduces Cr(VI) but changes in the valence state of the iron can diminish the associated magnetic properties. HA alone may be effective for removal of Cr(VI) from aqueous media, however recovery of the Cr-loaded HA materials is difficult. The HA-
Fe$_3$O$_4$ materials reported herein are robust and easily separable. Effective adsorption and reduction of Cr(VI) from aqueous media by HA-Fe$_3$O$_4$ materials are demonstrated in our study. The Cr-loaded HA-Fe$_3$O$_4$ materials are easily separated by applying a magnetic field. The adsorption of Cr(VI) is effective under acidic, neutral and basic conditions. Characterization of Cr-loaded HA-Fe$_3$O$_4$ materials demonstrate Cr(VI) is reduced to non-toxic Cr(III) by HA to form an octahedral complex within the HA-Fe$_3$O$_4$ materials. These easily separable materials have a strong capacity for Cr(VI) adsorption and initiate reductive-complexation leading to an immobilized Cr(III) complex. Predictable adsorption and capacity helps in defining conditions to meet specific treatment objectives. HA-Fe$_3$O$_4$ appear to have remarkable potential for the treatment of Cr(VI)-contaminated water. This process has promise for in situ and ex situ treatment for Cr and possibly other metal/metalloids of such forms.

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Supporting Information Available

Zeta potential of bare HA-Fe$_3$O$_4$, HA-Fe$_3$O$_4$, and Cr-loaded HA-Fe$_3$O$_4$ at different pH (Figure 1S), Fe K-edge XANES spectra of iron reference compounds and Cr-loaded HA-Fe$_3$O$_4$ at different pH conditions (Figure 2S), FTIR of HA-Fe$_3$O$_4$ and Cr-loaded HA-Fe$_3$O$_4$ particles from different solution pH (Figure 3S), adsorption of Cr(VI) by HA-Fe$_3$O$_4$ as a function of time (Figure 4S), intraparticle diffusion plots (Figure 5S), summary of chromium K-edge EXAFS fitting parameters, (Table 1S), and a summary of the iron K-edge EXAFS fitting parameters (Table 2S) are shown. This material is available free of charge via Internet at http://pubs.acs.org.
References


List of figures

**Figure 1.** Effect of pH on removal efficiency of chromium by HA-Fe₃O₄. [Cr(VI)]₀ = 1 mM, [HA-Fe₃O₄] = 10 g/L. Error bars represent standard deviation of triplicate runs.

**Figure 2.** Cr K-edge XANES spectra of chromium reference compounds and Cr-loaded HA-Fe₃O₄ at different pH conditions.

**Figure 3.** k³-weighted Cr (A) and Fe (B) K-edge EXAFS spectra.

**Figure 4.** Fourier-transform spectra of Cr (A) and Fe (B) resulting in a radial structure function.

**Figure 5.** XRD patterns of HA-Fe₃O₄ and Cr-loaded HA-Fe₃O₄ particles: (a) HA-Fe₃O₄, (b) Cr-loaded HA-Fe₃O₄ (pH 4), (c) Cr-loaded HA-Fe₃O₄ (pH 7), and (d) Cr-loaded HA-Fe₃O₄ (pH 10).
Figure 1.
Figure 2.
Figure 3.

A. Cr-loaded HA-Fe₃O₄ (pH 4)

B. Cr-loaded HA-Fe₃O₄ (pH 10)
Figure 4.
Figure 5.
Table of Contents (TOC)

Fe₃O₄ core

= humic acid

= Cr(VI)

= Cr(III)