Coating Fe₃O₄ Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water

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Humic acid (HA) coated Fe₃O₄ nanoparticles (Fe₃O₄/HA) were developed for the removal of toxic Hg(II), Pb(II), Cd(II), and Cu(II) from water. Fe₃O₄/HA were prepared by a coprecipitation procedure with cheap and environmentally friendly iron salts and HA. TOC and XPS analysis showed the as-prepared Fe₃O₄/HA contains ~11% (w/w) of HA which are fractions abundant in O and N-based functional groups. TEM images and laser particle size analysis revealed the Fe₃O₄/HA (with ~10 nm Fe₃O₄ cores) aggregated in aqueous suspensions to form aggregates with an average hydrodynamic size of ~140 nm. With a saturation magnetization of 79.6 emu/g, the Fe₃O₄/HA can be simply recovered from water with magnetic separations at low magnetic field gradients within a few minutes. Sorption of the heavy metals to Fe₃O₄/HA reached equilibrium in less than 15 min, and agreed well to the Langmuir adsorption model with maximum adsorption capacities from 46.3 to 97.7 mg/g. The Fe₃O₄/HA was stable in tap water, natural waters, and acidic/basic solutions ranging from 0.1 M HCl to 2 M NaOH with low leaching of Fe ($\leq 3.7\%$) and HA ($\leq 5.3\%$). The Fe₃O₄/HA was able to remove over 99% of Hg(II) and Pb(II) and over 95% of Cu(II) and Cd(II) in natural and tap water at optimized pH. Leaching back of the Fe₃O₄/HA sorbed heavy metals in water was found to be negligible.

Introduction

Water pollution by toxic heavy metals occurs globally (1). Strict environmental regulations on the discharge of heavy metals and rising demands for clean water with extremely low levels of heavy metals make it greatly important to develop various efficient technologies for heavy metal removal. Recent research focused on the development of novel absorbents with enhanced adsorption rate, capacity, and selectivity for the target metals, and numerous sorbents such as mesoporous silicas, zeolites, biomass, and biopolymer were developed for the removal of heavy metals (2–5). The unique properties of nanosorbents are providing unprecedented opportunities for the removal of metals in highly efficient and cost-effective approaches, and various nanoparticles and dendrimers have been exploited for this purpose (6–8). Although the biomedical applications of magnetite

nanoparticles were extensively researched (9–12), only limited research on its application in the environmental area were reported (13–17). While magnetite (13) and maghemite (14) nanoparticles were applied to the removal of Cr(VI), chitosan-bound Fe₃O₄ magnetic nanoparticles were prepared for the removal of Cu(II) ions (15). Ngomsik et al. (16) gave a mini review on the application of magnetic nanoand microparticles in the removal of metals in wastewaters. Recently, monodisperse Fe₃O₄ nanocrystals were exploited to remove arsenic from water with magnetic separations at very low magnetic field gradients (17). By reducing the diameter of Fe₃O₄ nanocrystals from 300 to 12 nm, the removal efficiency of As(III) and As(V) increased by orders of magnitude. Self-assembled 3D flowerlike iron oxide nanostructure materials were demonstrated to have an excellent ability for the removal of As(V), Cr(VI), and Orange II from water (18). More recently, superparamagnetic Fe₃O₄ nanoparticles with a surface functionalization of dimercaptosuccinic acid were developed for the removal of toxic soft metals such as Hg, Ag, Pb, Cd, and Tl (19).

Bare magnetite nanoparticles are very much susceptible to air oxidation (20) and are easily aggregated in aqueous systems. Recent research indicated that humic acid (HA) has high affinity to Fe₃O₄ nanoparticles, and sorption of HA on the Fe₃O₄ nanoparticles enhanced the stability of nanodispersions by preventing their aggregation (21, 22). Abundant in natural aqueous systems, HA has a skeleton of alkyl and aromatic units that attach with carboxylic acid, phenolic hydroxyl, and quinone functional groups (23). As these functional groups have high complex capacity with heavy metal ions, HA was applied to remove heavy metal ions from water (24). Binding of HA to metal oxides influences the sorption behavior of both HA and metal oxides (25–28). This is because the adsorption of HA results in a polyanionic organic coating on metal oxides and thus essentially altering the surface properties of the particles (21, 22, 25, 29–33). Sorption of heavy metals in a complex system of HA metal oxide particles is complicated, and there are numerous experimental and modeling studies (29, 31, 32) devoted to this subject since the publication of a seminal paper (33). The adsorption capacity for metal ions with the complexes of HA and iron oxides was reported to be larger than that with the respective iron oxides and HA alone, though there are some metal ion dependent deviations from additivity rule (32).

In this study, a novel low-cost magnetic sorbent material prepared by coating Fe₃O₄ magnetic nanoparticles with HA was developed for the removal of heavy metal ions from water. The physical and chemical characterization of the synthesized HA coated Fe₃O₄ nanoparticles (Fe₃O₄/HA) was conducted, and the applicability of Fe₃O₄/HA in heavy metal removal was evaluated in view of the sorption kinetic and capacity, effects of water matrices, as well as the material stability.

Experimental Section

Preparation and Characterization of Magnetic Nanomaterials. The bare and HA coated Fe₃O₄ magnetic nanoparticles were synthesized with methods modified from refs 20 and 34. Briefly, 6.1 g of FeCl₃·6H₂O and 4.2 g of FeSO₄·7H₂O were dissolved in 100 mL water and heated to 90 °C, then two solutions, 10 mL of ammonium hydroxide (25%) and 0.5 g of humic acid sodium salt dissolved in 50 mL of water, were added rapidly and sequentially. The mixture was stirred at 90 °C for 30 min and then cooled to room temperature. The black precipitate was collected by filtrating and washed to

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FIGURE 1. IR Spectrum (a) and TEM Image (b) of the prepared $\text{Fe}_3\text{O}_4/\text{HA}$ magnetic nanoparticles.

neutral with water. The obtained black precipitate was $\text{Fe}_3\text{O}_4/\text{HA}$ nanoparticles and was ready for use. Commercial sodium salt of humic acid (HA) from Acros Organics (Morris Plains, NJ) and Aldrich (Sigma-Aldrich, Steinheim, Germany) were used for preparation of $\text{Fe}_3\text{O}_4/\text{HA}$ for comparison the effect of HA source, but $\text{Fe}_3\text{O}_4/\text{HA}$ prepared with Acros HA was used otherwise specified. The bare Fe_3O_4 magnetic nanoparticles were prepared in a similar way except that no HA was added. Characterization of the nanoparticles was described in the Supporting Information.

Procedure of Heavy Metals Sorption. In a typical removal procedure, 10 mg of the as-prepared $\text{Fe}_3\text{O}_4/\text{HA}$ (1 mL of 10 mg/mL $\text{Fe}_3\text{O}_4/\text{HA}$ aqueous dispersion) was added into a 100 mL of mixed solution containing 0.1 or 1 mg/L each of the heavy metals, the mixture was adjusted to pH 6.0 with HCl and NaOH and stirred for 30 min. For removal of metals from real water, however, 50 mg of the as-prepared $\text{Fe}_3\text{O}_4/\text{HA}$ (1 mL of 50 mg/mL $\text{Fe}_3\text{O}_4/\text{HA}$ aqueous dispersion) was added into 100 mL of water. Then the magnetic $\text{Fe}_3\text{O}_4/\text{HA}$ with sorbed heavy metals were separated from the mixture with a permanent hand-held magnets. The residual heavy metals in the solution were determined with ICP-MS (Agilent 7500ce, U.S.). For preparation of the adsorption isotherms of the heavy metals, solutions with varying initial metal concentration of individual metal were treated with the same procedure as above at room temperature (20 °C).

Results and Discussion

Characterization of $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 . Spectroscopic analysis shows the successful coating of HA on the Fe_3O_4 surface. Infrared spectrum (Figure 1a) shows the C=O stretches of $\text{Fe}_3\text{O}_4/\text{HA}$ at $\sim 1569\text{ cm}^{-1}$, indicating the carboxylate anion interacting with the FeO surface as the C=O

stretches in free carboxylic acid would above 1700 cm^{-1} (19). The band at 1396 cm^{-1} is most likely due to the CH_2 scissoring. For the bare Fe_3O_4 materials, however, no C=O stretches were observed. UV-vis spectrum shows red shift of the maximum absorbance for the $\text{Fe}_3\text{O}_4/\text{HA}$ relative to HA, suggesting the binding of HA to Fe_3O_4 . It is generally believed the binding of HA to Fe_3O_4 surface is mainly through ligand exchange (21, 22, 31).

Based on the measured total organic carbon (TOC) contents in the $\text{Fe}_3\text{O}_4/\text{HA}$ (5.15%) and the HA raw material (45.0%), it was calculated that the as-prepared $\text{Fe}_3\text{O}_4/\text{HA}$ contained 11.4% (w/w) of HA, which is an approximate value as HA was fractionated during its adsorption onto Fe_3O_4 . X-ray photoelectron spectroscopy (XPS) analysis revealed the surface composition (w/w), i.e. 19.3% O, 0.554% N, 79.7% C, and 0.505% S for the HA raw material, whereas 49.43% O, 2.12% N, 33.5% C, and 14.9% Fe for $\text{Fe}_3\text{O}_4/\text{HA}$. Based on the Fe content, it was calculated that the surface of $\text{Fe}_3\text{O}_4/\text{HA}$ contains 79.4% HA, and the HA in $\text{Fe}_3\text{O}_4/\text{HA}$ consists of 62.1% O, 2.67% N, and 42.2% C. Obviously, the O and N contents in the Fe_3O_4 adsorbed HA were significantly higher than that in the HA raw materials, suggesting the HA fractions abundant with O and N-based functional groups were selectively coated on the surface of Fe_3O_4 during the synthesis of $\text{Fe}_3\text{O}_4/\text{HA}$. Likewise, smaller size fractions of HA enriched in acidic functional groups were found to adsorb preferentially on the Fe_3O_4 surface (21). Considering the high synthesis temperature (90 °C), it was also possible that some fractions of HA were degraded to form products with higher contents of O- and N-based functional groups, which adsorbed preferentially on the Fe_3O_4 surface. Nevertheless, inhibition of HA degradation is unnecessary as the purpose of this study is to develop a new material for the removal of heavy metals rather than study the complex nature of HA with metals.

The respective zeta potentials of the as-prepared Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ were measured at varied pH. The pH of zero point charge (pH_{PZC}) of Fe_3O_4 was 6.0, which is close to that reported in literature (15). The pH_{PZC} of $\text{Fe}_3\text{O}_4/\text{HA}$ decreased to ~ 2.3 since the coated HA has abundant carboxylic acid groups. The zeta potential of gray humic acid was also found to be negatively charged in the range of pH 0.5–9.0 (35). The low pH_{PZC} indicates that the $\text{Fe}_3\text{O}_4/\text{HA}$ are negatively charged at the entire environmentally relevant acidity (pH 3–9), which prohibits the aggregation of $\text{Fe}_3\text{O}_4/\text{HA}$ and benefits the sorption of positively charged metal ions.

The respective saturation magnetizations of $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 were 68.1 and 79.6 emu/g, suggesting the content of HA in $\text{Fe}_3\text{O}_4/\text{HA}$ was about 14.5% (w/w) which close to the result from TOC analysis (11.4%, w/w). Separation of $\text{Fe}_3\text{O}_4/\text{HA}$ from its aqueous dispersions can be easily finished in a few minutes with permanent hand-held magnets. The black aqueous suspensions of bare Fe_3O_4 nanoparticles were easily oxidized to brown suspensions without magnetization, whereas no significant change of the saturation magnetization and color was observed after the $\text{Fe}_3\text{O}_4/\text{HA}$ was stored in water for 30 days, indicating the HA coating was able to maintain the saturation magnetization of $\text{Fe}_3\text{O}_4/\text{HA}$ nanoparticles by prohibiting their oxidation.

BET analysis revealed almost the same surface area for Fe_3O_4 (62 m^2/g) and $\text{Fe}_3\text{O}_4/\text{HA}$ (64 m^2/g). This might be attributed to the fact that HA has highly narrow microporosity which adsorbs no N_2 at 77 K. It was reported that the measured surface area of humic substances (Fluka, Switzerland) was 42.5 m^2/g with CO_2 at 273 K, but less than 1 m^2/g with N_2 at 77 K (36). Noticeably, the similar surface of Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$ suggests these two materials are likely to have a similar primary size.

Figure 1b shows the TEM images of the as-prepared $\text{Fe}_3\text{O}_4/\text{HA}$. The core of the Fe_3O_4 magnetic nanoparticle had a typical size $\sim 10\text{ nm}$, but the entire $\text{Fe}_3\text{O}_4/\text{HA}$ particles contained

aggregates with no uniform size and fractal feature (also see Figure S6 in the Supporting Information). Laser particle size analysis showed an average hydrodynamic size of ~ 140 nm for $\text{Fe}_3\text{O}_4/\text{HA}$ particles, also suggesting the aggregation of the prepared materials in sol solutions. Likewise, Illes et al. (22) also observed that Fe_3O_4 particles with a primary size of ~ 10 nm aggregated to form nonuniform size and fractal aggregates with an average size of ~ 120 nm in sol solutions containing HA. The aqueous suspensions of the as-prepared Fe_3O_4 particles have larger average value (250 nm) and wider range of hydrodynamic size (160–366 nm) than those of $\text{Fe}_3\text{O}_4/\text{HA}$ (140 nm, 104–189 nm) though these two materials have almost the same primary size. These results clearly demonstrate that coating Fe_3O_4 nanoparticles with HA efficiently reduces their aggregation.

Sorption Kinetics. The sorption dynamics of these heavy metal ions to $\text{Fe}_3\text{O}_4/\text{HA}$ were evaluated by adding 0.01 g of the as-obtained $\text{Fe}_3\text{O}_4/\text{HA}$ into 100 mL of a mixed solution containing 0.1 mg/L each of the metal ions (pH 6.0) at room temperature. Results showed that sorption equilibrium was reached in ~ 15 min, which is much longer than those (~ 1 min) in monodispersions of chitosan (15) and dimercaptosuccinic acid (19) coated Fe_3O_4 . The slow kinetics are likely due to saturation of the outer binding sites and slow site–site exchange of heavy metals because of the disordered structure of the HA layer in $\text{Fe}_3\text{O}_4/\text{HA}$.

Effects of Environmental Parameters. The binding of heavy metals to HA is mainly controlled by the source and concentration of HA, metal ion concentration, pH, and other parameters (24, 37–39). Therefore, it is important to study if the variance of these parameters in the environmentally relevant range would influence the removal of heavy metals by $\text{Fe}_3\text{O}_4/\text{HA}$.

Natural Organic Matter. It was reported that with the presence of HA the uptake of heavy metals to hydrous metal oxides is a comprehensive result of numerous interactions (29). If the oxide employed the same sites for binding HA and metals, the binding of HA directly on the oxide surface may decrease the metal adsorption due to the sites blockage and competition. On the other hand, the binding of HA to oxide may favor the uptake of metals because of the complexation between HA and metals, whereas the HA in solution could prevent a fraction of metal from adsorbing to the oxide. Figure 2 shows the influence of natural organic matter, with Aldrich HA as a model, on the removal of metals by the as-obtained Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{HA}$, respectively. With the addition of HA in the range of 0–50 mg/L dissolved organic carbon (DOC), no significant variation of metal removal was observed for $\text{Fe}_3\text{O}_4/\text{HA}$, whereas remarkable change of removals by Fe_3O_4 occurred. Increasing of HA concentration from 0 to 1.1 mg/L DOC gave rise to enhancement of removal, especially for Hg(II) , whose removal increased almost linearly from 42 to 90%. Further addition of HA, however, reduced the metal removals due to part of the metals were bound by the dissolved HA which inhibited their adsorption by Fe_3O_4 . Noticeable drop of Cu(II) removal to 55% occurred with the addition of HA up to 9 mg/L DOC. Experiments showed that further increasing of HA up to 50 mg/L DOC had no further influence on the heavy metal removal for both $\text{Fe}_3\text{O}_4/\text{HA}$ and Fe_3O_4 . These above results indicate that the removal of metals in natural waters by Fe_3O_4 magnetic nanoparticles depends on the content of natural organic matter in water, which also agreed with the literature (29, 31). Since natural water contains 0.5–50 mg/L DOC which consists for 50–70% of humic substances (40), the removal efficiency of heavy metals with Fe_3O_4 magnetic nanoparticles in natural water will inevitably be influenced by the content of natural organic matter. This drawback was overcome with the as-obtained $\text{Fe}_3\text{O}_4/\text{HA}$ nanoparticles, which had high and

FIGURE 2. Influence of humic acid in aqueous solutions on the removal of heavy metals by the as-prepared $\text{Fe}_3\text{O}_4/\text{HA}$ (a) and Fe_3O_4 (b). To 100 mL of aqueous solution containing 0.1 mg/L Hg(II) , Pb(II) , Cd(II) , and Cu(II) (pH 6.0) was added 10 mg of $\text{Fe}_3\text{O}_4/\text{HA}$ or Fe_3O_4 .

FIGURE 3. Influence of pH on the removal of heavy metals by the as-prepared $\text{Fe}_3\text{O}_4/\text{HA}$ (a) and Fe_3O_4 (b). To 100 mL of aqueous solution containing 0.1 mg/L Hg(II) , Pb(II) , Cd(II) and Cu(II) (pH 6.0) was added 10 mg of $\text{Fe}_3\text{O}_4/\text{HA}$ or Fe_3O_4 .

almost constant removal efficiencies (93–98%) for heavy metals in the entire studied range of HA (0–100 mg/L).

pH. By using $\text{Fe}_3\text{O}_4/\text{HA}$ (Figure 3a), the removals of Cu(II) , Hg(II) , and Pb(II) decreased slightly from 96–97% to 90–94% with increasing pH from 2 to 9. The slight reducing of removals might be attributed to the slight desorption of HA from $\text{Fe}_3\text{O}_4/\text{HA}$ with the increasing of pH (29, 31), and the freely dissolved HA can competitively complex with metal ions in the solution phase and thus reduce their adsorption onto $\text{Fe}_3\text{O}_4/\text{HA}$. By using Fe_3O_4 (Figure 3b), however, the

TABLE 1. The pH, Concentration of TOC, Fe, and Heavy Metals in Water and the Removal (%) after Treating 100 mL of Water with 50 mg Fe₃O₄/HA

matrix	pH	TOC (mg/L)	Fe (μg/L)	Ca		Mg		Cu		Cd		Hg		Pb	
				IC ^a	removal	IC ^a	removal	IC ^a	removal	IC ^a	removal	IC ^a	removal	IC ^a	removal
tap water	7.8	2.59	59.6	82.9	11.4	23.0	6.96	1.077	86.0	1.001	96.8	1.011	99.8	1.006	99.4
ground water	6.4	1.64	51.1	86.4	13.4	31.8	8.18	1.005	99.7	1.002	92.1	1.012	99.8	1.005	99.5
river water	7.6	3.50	56.7	86.6	16.3	14.1	9.93	1.008	86.0	1.001	92.3	1.011	99.9	1.005	99.4
lake water	7.2	11.7	76.8	124	0	8.50	0	1.011	82.4	1.001	91.7	1.011	99.2	1.006	99.4
sea water	7.7	1.52	895	107	3.7	288	0	1.040	79.3	1.009	99.0	1.013	99.9	1.020	99.0

^a Initial concentration (mg/L) measured after spiked with 1 mg/L each of Cu, Cd, Hg, and Pb.

removal of Cu(II), Hg(II), and Pb(II) was remarkably low at pH < 6.0 (pH_{PZC} of Fe₃O₄). This can be attributed to positive surface charge of Fe₃O₄ that declined the sorption of positive metals. It is noteworthy that at pH over the pH_{PZC} of Fe₃O₄, the removal of Hg(II) was only 65% though the removal of Cu(II) and Pb(II) were over 90%. Because of the weak complex formation between HA and Cd(II), the adsorption of Cd(II) is mainly to the metal oxide rather than the HA coating (33). Therefore, for both Fe₃O₄/HA and Fe₃O₄ the removal of Cd(II) increased with pH and agreed with literature (29), in which it was reported that the adsorption to hematite/HA increased with pH. Based on Figure 3, it can be concluded that the contribution of HA to the removal of Pb(II) and Cu(II) was pH dependent and can be as high as 70–80% at pH 3.

Salinity. Increasing of salinity from 0 to 3.5% NaCl (the salinity of seawater) had no significant effects on the removal of metals by Fe₃O₄/HA. This is because the salinity has no significant effect on the adsorption/desorption between HA and iron oxide (29, 31), and the complexation of the target metals with chloride ions was much weaker than with HA.

Coexisted Ions. The influence of commonly coexisted ions on the removal of heavy metals was studied with Ca²⁺ and PO₄³⁻ as model cations and anions, respectively. Neither the presence of Ca²⁺ (0–100 mg/L) nor the PO₄³⁻ (0–10 mM) has any significant influence on the removal of the studied heavy metals. The binding of HA to heavy metals is stronger than to Ca²⁺ (24, 31), and the sorption of heavy metals to HA is much stronger than to PO₄³⁻. Thus the presence of Ca²⁺ and PO₄³⁻ has no effect on the sorption of heavy metals to Fe₃O₄/HA.

Effect of Real Water Matrix. Real waters spiked with 1 mg/L each of the target metals were used to further evaluate the effects of different matrices on the removal efficiency of heavy metals. Table 1 shows the initial concentration and the removal efficiencies of Ca, Mg, Cu(II), Cd(II), Hg(II), and Pb(II) after treatment with the as-prepared Fe₃O₄/HA. For all the studied waters, the observed removals of Hg(II) and Pb(II) were over 99% and were negligibly influenced by the concentrations of TOC, Ca, and Mg. This can be attributed to the high complexation capability of HA with these two metal ions. The removal of Cu(II) and Cd(II) was pH predominant (Figure 3). The highest Cu(II) removal was observed in groundwater which has the lowest pH, whereas the highest Cd (II) removal was observed in tap water with the highest pH. Further experiments showed the removal of Cu(II) and Cd(II) elevated to over 95% by adjusting these waters to pH 6.0 and 8.0, respectively. The very low removals for Ca (0–16%) and Mg (0–10%) shown in Table 1 demonstrated their weak binding to HA, and it is for this reason that the removals of the target heavy metals were not affected by the presence of 124 and 288 times of Ca and Mg, respectively. No scale or fouling on the Fe₃O₄/HA was observed after treatment of these waters, suggesting Fe₃O₄/HA selectively adsorbed heavy metals.

Adsorption Capacity. The adsorption capacities of the as-obtained Fe₃O₄/HA to metal cations were measured individually at pH 6.0 with 10 mg/L of Fe₃O₄/HA and varied

metal concentration (0.01–5 mg/L), and the data of the heavy metal adsorbed at equilibrium (q_e , mg/g) and the equilibrium metal concentration (C_e , mg/L) were fitted to the Langmuir adsorption model

$$q_e = q_m b C_e / (1 + b C_e) \quad (1)$$

where q_m is the maximum adsorption capacity corresponding to complete monolayer coverage and b is the equilibrium constant (L/mg). The data fit well to the model with correlation coefficients (r^2) in the range of 0.98–0.99, and maximum adsorption capacity of 46.3, 50.4, 92.4, and 97.7 mg/g for Cu(II), Cd(II), Pb(II), and Hg(II), respectively. The b values (L/mg) indicated a descending series of affinity to the Fe₃O₄/HA as follows: Cu(II) (22.4) > Cd(II) (18.3) > Pb(II) (14.8) ≈ Hg(II) (14.6). It is noteworthy that the stability constant for metal–HA complexes are pH and ionic strength dependent (39), hence the maximum adsorption capacities for the metals might have different value in different aqueous system. As a comparison, the adsorption isotherms of Pb(II) with the commonly used activated carbon adsorbents was also determined in the same way as with Fe₃O₄/HA, and much lower q_m (3.3 mg/g) was observed. The q_m for Cu(II) with the proposed Fe₃O₄/HA was also higher than that with chitosan-bound Fe₃O₄ magnetic nanoparticles (21.5 mg/g) (15).

Material Stability. Leaching of sorbent components into the treated water is unfavorable. Although sorption of HA onto iron oxide is favored at low pH (21, 22, 31), we synthesized Fe₃O₄/HA at basic condition to obtain higher resistance to leaching. Instead of in a spherical structure at lower pH, HA existed in a rather linear or stretched structure at higher pH (28) which favored multiple sites binding with Fe₃O₄ and thus reduced the leaching of Fe and HA. Experiments showed that the aqueous dispersed Fe₃O₄/HA (100 mg/L, pH 6.0) gave a free concentration of 0.025 mg/L iron ions and 0.16 mg/L DOC at equilibrium, whereas the free iron ions in an aqueous dispersion of Fe₃O₄ nanoparticles (100 mg/L, pH 6.0) was 0.24 mg/L, which was almost 10-fold of that of Fe₃O₄/HA and suggests that the HA coating markedly improved the stability of Fe₃O₄ magnetic nanoparticles. The low free concentration of HA in Fe₃O₄/HA dispersion agreed with literature (29, 31), which reported that the natural organic matter adsorbed on iron oxide was very difficult to be desorbed at a given pH and ionic composition.

Table 2 shows the leaching of HA and Fe after suspending Fe₃O₄/HA in different fluids. In natural and tap water matrices, the leaching of Fe and HA from Fe₃O₄/HA into the solution phase was below 0.03 and 5.3%, respectively; whereas in acidic/basic solutions ranging from 0.1 M HCl to 2 M NaOH, the leaching of Fe and HA was below 3.7 and 3.5%, respectively. According to the used amount (500 mg/L) and the content of TOC (5.15%) and Fe (64%) in Fe₃O₄/HA, the highest leaching of HA (5.3%) and Fe (3.7%) gave rise to 1.4 mg/L DOC and 12 mg/L Fe in water, respectively. From Figure 2a, it is expected that this low increase of DOC content should cause a negligible laden of heavy metals in water, suggesting

TABLE 2. Leaching of Fe and HA after Suspending 50 mg Fe₃O₄/HA in 100 mL of Different Fluids for 6 h

water matrix	%Fe leached per total Fe	%TOC leached per total TOC
tap water, pH 7.8	0.003	1.1
river water, pH 7.6	0.001	3.4
lake water, pH 7.2	0.04	4.3
ground water, pH 6.4	0.02	5.3
deionized water, pH 6.0	0.03	1.3
0.001 M HCl	1.7	0.2
0.01 M HCl	1.8	0.2
0.1 M HCl	3.7	1.1
0.5 M HCl	11	3.6
1 M HCl	38	15
5 M HCl	100	100
2 M NaOH	0.1	0

the Fe₃O₄/HA is applicable in treating most natural and waste waters. As Fe₃O₄/HA was prepared in basic solutions, no HA leaching was observed in 2 M NaOH, whereas HA was completely leached out in 5 M HCl. It was noteworthy that the leaching of HA in natural waters was similar to that in 0.5 M HCl, which indicates the matrix in natural water also contributed to the release of HA from Fe₃O₄/HA. Overall, the Fe₃O₄/HA was stable in natural waters, tap water, and acidic/basic solutions ranging from 0.1 to 2 M NaOH without observation of break down of nanoparticle clusters and formation of fines.

To test the effect of time on the leaching of Fe₃O₄/HA components and the sorbed heavy metals, Fe₃O₄/HA laden with heavy metals was resuspended in deionized water, and the supernatant was monitored for Fe, TOC, and heavy metal concentration over varied periods of time. Results (Supporting Information Table S1) indicated that the leaching of both the sorbed heavy metals and the material components were negligible. The leaching of the laden heavy metals were time independent and below 0.05%, whereas the leaching of Fe increased slightly from 0.07 to 0.21% with the time prolonged from 0.5–12 days. During the studied time interval of 0.5–12 days, the leaching of HA decreased from 3.5 to 0.33%. This decreasing of HA in solution phase may be attributed to the aggregation of Fe₃O₄/HA with time, which gave rise to the adsorption of the previously desorbed HA back to the Fe₃O₄/HA aggregations. The low leaching of HA agreed with ref 31, in which the negligible desorption of natural organic matter from iron oxide was observed within 63 days.

Implications for Heavy Metal Remediation. This study revealed that, compared to Fe₃O₄ nanoparticles, the as-prepared Fe₃O₄/HA exhibited remarkable enhancement of material stability and heavy metal removal efficiency. In particular, by coating with HA the aggregation of Fe₃O₄/HA in aqueous suspensions are effectively reduced and the magnetivity of Fe₃O₄/HA are maintained, while the removal efficiencies for Hg(II) and Cu(II) significantly increased at low pH. The as-prepared Fe₃O₄/HA nanoparticles are very cheap and environmentally friendly as their main component, Fe₃O₄ and HA, are abundant and have no adverse effect on the environment. The synthesis procedure is simple and cost-effective. Furthermore, the Fe₃O₄/HA with adsorbed heavy metals can be simply recovered from water with magnetic separations at very low magnetic field gradients, which can hopefully reduce water treatment expenses. It is expected that the as-prepared Fe₃O₄/HA has wide applicability in the removal of heavy metals from various waters.

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Supporting Information Available

Procedure of batch metal sorption (Figure S1); characterization of Fe₃O₄/HA and Fe₃O₄ including UV–vis spectra (Figure S2), XPS (Figure S3), pH of zero point charge (Figure S4), magnetization (Figure S5), TEM (Figure S6), and laser particle size analysis (Figure S7); sorption kinetics (Figure S8), effect of salinity on metal removal (Figure S8), adsorption isotherms of heavy metals (Figure S10), and effect of time on the leaching of Fe, HA and heavy metals from Fe₃O₄/HA laden with heavy metals (Table S1) are shown. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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