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Retention of Pb(II) by a Low-Cost Magnetic Composite Prepared by Environmentally-Friendly Plasma Technique

Xuemei Ren, Shitong Yang, Dadong Shao, and Xiaoli Tan

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A low-cost magnetic composite (gelatin/Fe₃O₄) is prepared by Fe₃O₄ nanoparticles treated with gelatin using an environmentally-friendly plasma technique, and is applied for the removal of toxic Pb(II) ions from aqueous solutions. Not only that it originates from cheap and abundant raw materials, the gelatin/Fe₃O₄ composite also has advantages in convenient magnetic separation from aqueous solution, which can hopefully reduce water treatment expenses. The batch experimental results indicate that the maximum adsorption capacity (q_{\max}) of Pb(II) on this gelatin/Fe₃O₄ composite is ~115 mg/g, higher than most of the other bare and modified magnetic materials, which is considered to be attributed to the strong interaction between Pb(II) and the abundant functional groups introduced by gelatin. When exposed to acidic solutions, the dissolution of the gelatin/Fe₃O₄ nanoparticles is minimal due to the protective character of the grafted gelatin layer on the Fe₃O₄ nanoparticles. The utilization of the plasma technique in the synthesis of magnetic composite agrees well with the tenet of green chemistry. It is promising that this gelatin/Fe₃O₄ composite would become an efficient and economic material for heavy metal ion removal in the practical environmental remediation.

Keywords gelatin/Fe₃O₄ composite; magnetic separation; Pb(II); surface modification

INTRODUCTION

Compared to the traditional microsized materials used in the recovery process (1–6), nanosized materials possess quite good performance due to high specific surface area and the absence of internal diffusion resistance (7,8). The application of nanomaterials in solving environmental problems has received considerable attention in recent years. However, the main disadvantage of the nanoparticles is that their sizes are too small to be recovered by the conventional filtration or centrifugation (9), limiting their application in large scale in real work. Recent research focused on the development of magnetic nanomaterials with enhanced adsorption capacity and easiness to

separate from large volumes of aqueous solutions. Numerous magnetic nanoadsorbents such as Fe₃O₄, MnFe₂O₄, MgFe₂O₄, ZnFe₂O₄, CuFe₂O₄, NiFe₂O₄, and CoFe₂O₄ were developed for the removal of heavy metal ions (10). However, bare magnetic nanoparticles are found to be susceptible to air oxidation (11), unstable at low pH (12,13), and easy to form aggregation in aqueous solutions (9). Therefore, it is necessary to coat a protective layer to ensure their chemical stability. The strategies for the protection of magnetic nanoparticles comprise grafting or coating with organic species (e.g., surfactants or polymers), or coating with an inorganic layer (e.g., silica or carbon) (12,14). It is important to note that in many cases the protecting polymer shells not only stabilize the nanoparticles, but also can be used for the functionalization of the nanoparticles. For example, chitosan-coated magnetic nanoparticles have wide-ranging application in the sequestration or removal of Cu²⁺ ions (15). Humic acid coated Fe₃O₄ nanoparticles were found to have an excellent ability for the removal of Hg(II), Pb(II), Cd(II), and Cu(II) ions from aqueous solutions (11). A series of NH₂-functionalized magnetic polymer nanomaterials with different amino groups showed different removal efficiency for Cr(VI) ions (16). Magnetic γ -Fe₂O₃ nanoparticles coated with poly-L-cysteine has larger sorption capacities than bare γ -Fe₂O₃ nanoparticles for As(III), Cu(II), Ni(II), and Zn(II) ions (17). As mentioned above, many works have been published on the use of bare and modified magnetic particles as adsorbents for various types of metal ion removal. However, the potential effectiveness of gelatin coated magnetic nanoparticles, which have been used as drug delivery (18,19), are still not available for the removal of metal ions. Especially, the research work on the use of plasma treatment introducing gelatin on the surface of Fe₃O₄ to improve the adsorption capacity and stability property of Fe₃O₄ and the application of modified Fe₃O₄ in the removal of metal ions from aqueous solution is still scarce.

Gelatin is a natural, harmless, and environmentally friendly polymer. The utilization of gelatin as heavy metal

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ion carrier should enhance the adsorption capacity of heavy metal ions due to its abundant active functional groups like carboxylate and amine groups (9,20). Plasma-induced treatment is an environmentally friendly method to introduce functional groups to a material surface without altering the material bulk properties (21). The excited species, radicals, electrons, ions, and UV light within the plasma strongly interact with the surfaces of material and create active sites for binding of functional groups. Compared to other chemical modified methods, the plasma treatment method has the advantages of shorter reaction time, nonpolluting process, and providing a wide range of different functional groups depending on plasma parameters such as power, used gases, treatment time, and pressure (22,23). In this work, gelatin is introduced on Fe_3O_4 (denoted as gelatin/ Fe_3O_4) by using N_2 plasma induced treatment. Then, Fourier transforms infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and potentiometric titrations are used to characterize the derived gelatin/ Fe_3O_4 composites. Finally, gelatin/ Fe_3O_4 is used to remove heavy metal ions from large volumes of aqueous solutions to evaluate the application of the synthesized gelatin/ Fe_3O_4 in environmental pollution cleanup. Pb(II) is chosen as a representative bivalent metal ion, because it is ubiquitous in the environment and is hazardous at high levels (24–28). A mechanism of Pb(II) interaction with gelatin/ Fe_3O_4 is proposed based on modeling the experimental data using diffuse-layer model (DLM) with the aid of FITEQL 3.1.

MATERIALS AND METHODS

Material and Adsorbent Preparation

All chemicals used in the experiments were of analytical purity and purchased from Guoyao Chemical Reagent Corporation (China). Milli-Q water obtained from a Direct-Q water purification system (Millipore Corporation, America) was used in all experiments. Analytical-grade lead nitrate was employed to prepare the Pb(II) stock solution, which was further diluted with Milli-Q water to the required concentrations ($60 \text{ mg} \cdot \text{L}^{-1}$) in the adsorption measurements.

The magnetite nanoparticles were prepared by the conventional coprecipitation method (29). Briefly, 10.81 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 3.97 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 100 mL water and heated to 70°C , then 10 mL of ammonium hydroxide (25%) was added rapidly and sequentially under a nitrogen flow (45 mL/min) with vigorous stirring. The mixture was stirred at 70°C for 1 h and then cooled to room temperature. The precipitate was collected by filtration and rinsed with Milli-Q water. The sample was dried in oven at 60°C for 48 h, and thus the as-prepared Fe_3O_4 was obtained. The plasma treatment of the as-prepared Fe_3O_4 nanoparticles was performed in

a custom-built grafting reactor for 40 min under continuous stirring. The scheme of the plasma reactor set-up was described in the previous study (30). N_2 was used as the plasma forming gas. The purpose of plasma treatment is to make the surface of Fe_3O_4 active, so the gelatin can react with Fe_3O_4 directly without using any additional chemicals. The plasma treatment conditions were N_2 plasma of 38 Pa, discharge power of 109 W, and voltage of 880 V. After Fe_3O_4 were treated with N_2 plasma, 100 mL 3.4 g/L gelatin solution was injected into the grafting reactor and Fe_3O_4 were grafted with gelatin at 80°C for 24 h under continuous stirring. The derived samples were repeatedly washed with Milli-Q water thoroughly to remove the residual amount of the physical adsorbed gelatin. At last, the sample was dried in an oven at 80°C for 48 h, and thus gelatin/ Fe_3O_4 nanoparticles were obtained.

Characterization

Fe_3O_4 and gelatin/ Fe_3O_4 were characterized by FT-IR spectroscopy and TGA. The FT-IR measurements of Fe_3O_4 and gelatin/ Fe_3O_4 samples were carried out by using a Perkin-Elmer 100 spectrometer (America) in KBr pellet at room temperature. The TGA measurements were carried out by using a Shimadzu TGA-50 thermogravimetric analyzer (Japan) from room temperature to 800°C at the heating rate of $10^\circ\text{C}/\text{min}$ with a nitrogen flow rate of 100 mL/min. The potentiometric titrations of the samples were performed at $20 \pm 1^\circ\text{C}$ with a Mettler Toledo DL50 titration apparatus (Switzerland) under Ar gas conditions, using NaClO_4 as background electrolyte, and NaOH as titration solution. Briefly, the potentiometric titration of adsorbent suspension (2.5 g/L) in 0.01 mol/L NaClO_4 solutions was carried out in a 100 mL Teflon vessel under argon gas condition at $T = 20 \pm 1^\circ\text{C}$. Before beginning the titration, the pH values of suspensions were quickly lowered to approximately 3.0 by addition of 1.4721 mol/L HClO_4 and purged with argon for at least two hours to exclude $\text{CO}_2(\text{g})$. Then, the titration was carried out from pH ~ 3 to ~ 11 by using 0.1972 mol/L NaOH. The equilibrium value was taken when showing a drift less than 0.03 mV per second.

Batch Experiments

The adsorption experiments of Pb(II) on Fe_3O_4 and gelatin/ Fe_3O_4 were carried out in polyethylene tubes at $T = 20 \pm 1^\circ\text{C}$ by using batch technique. The stock suspensions of Fe_3O_4 or gelatin/ Fe_3O_4 and the stock solutions of Pb(II) and NaClO_4 were added in polyethylene test tubes to achieve the desired concentrations of different components. The desired pH values of the suspensions in each tube were adjusted by adding a negligible amount of 0.1 or 0.01 mol/L HClO_4 or NaOH. The use of strong acid and base (HClO_4 or NaOH) could get the desired pH of suspension quickly without obvious changing of the solution volume. After the

suspensions were shaken at a constant speed of 120 rpm for 24 h to achieve adsorption equilibration, the solid phase was separated from the solution by using a permanent magnet. The concentration of Pb(II) was determined by spectrophotometry (722, Shanghai) at wavelength 616 nm by using Pb(II)-Chlorophosphonazo(III) complex. The detection limit of this analytical method is 0.10 mg/L. All the experimental data were the average of duplicate determinations and the relative errors were about 5%.

The amount of Pb(II) adsorbed on Fe₃O₄ or gelatin/Fe₃O₄ was calculated from the difference between the initial concentration (C_0 (mg/L)) and the equilibrium one (C_e (mg/L)) ($\text{Adsorption\%} = (C_0 - C_e)/C_0 \times 100\%$, and $q = (C_0 - C_e)/m_{\text{adsorbent}} \times V$, where q (mg/g) is the amount of Pb(II) adsorbed on the solid phase, V (L) is the volume of the suspension, and $m_{\text{adsorbent}}$ (g) is the mass of the adsorbent).

RESULTS AND DISCUSSION

Characterization

Figure 1a presents the FT-IR spectra of gelatin, Fe₃O₄, and gelatin/Fe₃O₄. The spectrum of pure gelatin exhibits O-H and N-H stretching at $\sim 3420 \text{ cm}^{-1}$, C=O stretching at $\sim 1650 \text{ cm}^{-1}$ for the amide I, and N-H deformation at $\sim 1530 \text{ cm}^{-1}$ for the amide II (18,31). The peaks at ~ 610 and 448 cm^{-1} are the characteristic peaks for Fe₃O₄ (32). All these characteristic bands are present in the spectrum of gelatin/Fe₃O₄, suggesting that gelatin has been successfully coated on Fe₃O₄.

The amount of gelatin coated on Fe₃O₄ is estimated from the TGA analysis of Fe₃O₄ and gelatin/Fe₃O₄ (Fig. 1b) (33). The weight loss which occurs at 17–100°C is due to the loss of physically adsorbed water on the surface of the nanoparticles. For Fe₃O₄, the weight loss between 100–450°C is related to further water loss and dehydroxylation (34). The weight loss of gelatin/Fe₃O₄ observed around 100 to 250°C is due to further water loss. The weight loss of gelatin/Fe₃O₄ in the third part between 250 to 450°C is $\sim 5.1\%$ due to the decomposition of gelatin. For pure gelatin, the TGA curve shows maximum weight loss between 250 to 450°C, with 29% of residue left after the thermal degradation (31). The wt% of grafted gelatin in gelatin/Fe₃O₄ is calculated to be $\sim 7.2\%$.

Stability of the Adsorbents in Acidic Conditions

The stability of gelatin/Fe₃O₄ and Fe₃O₄ nanoparticles is investigated by exposing the materials to different acidic solutions with pH varying from 1.5 to 4.0 for 24 h. Figure 2a shows that the colors of the left bottle (Fe₃O₄) in each picture become deeper due to the dissolution of the Fe₃O₄ and the right one (gelatin/

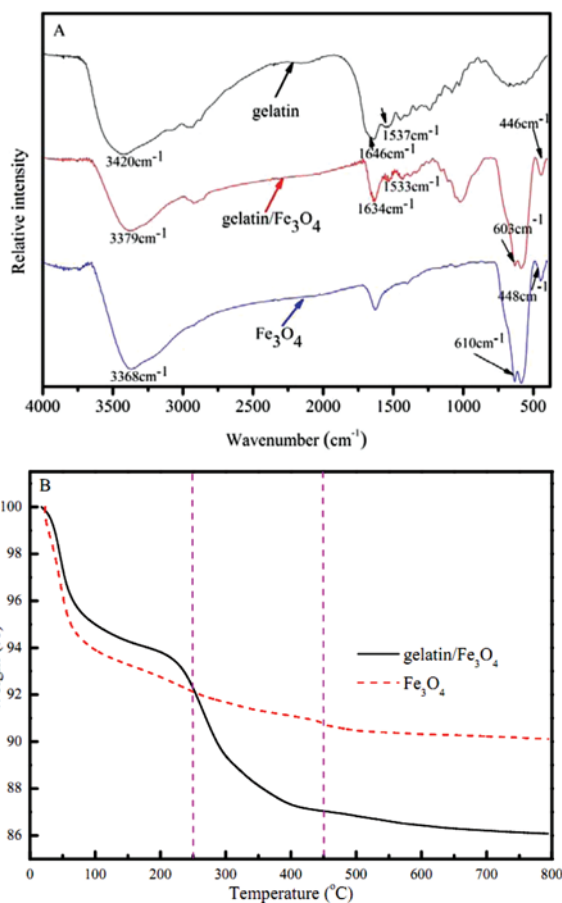


FIG. 1. FT-IR spectra of gelatin, Fe₃O₄ and gelatin/Fe₃O₄ (A) and TGA curves of Fe₃O₄ and gelatin/Fe₃O₄ (B). (Color figure available online)

Fe₃O₄) is almost colorless with decreasing pH values, suggesting that gelatin/Fe₃O₄ is stable whereas the Fe₃O₄ is partly dissolved in solution when they are exposed to acidic solutions. Figure 2a also shows that it is possible to remove magnetic gelatin/Fe₃O₄ from water by an external magnet (N40, 25 × 25 mm). The stable gelatin/Fe₃O₄ nanoparticles can be easily and quickly (<1 minute) separated from aqueous solutions by using magnetic separation techniques in our experiments.

The iron ions leaching to the solution are measured with an atomic absorption spectrometer (Perkin-Elmer AA800, America) and the results are shown in Fig. 2b. At pH 1.08 ± 0.02 , the aqueous dispersed gelatin/Fe₃O₄ (3.6 g/L) gives a free concentration of 1.26 mg/L iron ions, whereas the free iron ions in the aqueous dispersion of Fe₃O₄ nanoparticles (3.6 g/L) are 125.6 mg/L, which is almost 100-fold of that of gelatin/Fe₃O₄, suggesting that the grafted gelatin markedly improves the stability of gelatin/Fe₃O₄ nanoparticles under acidic conditions.

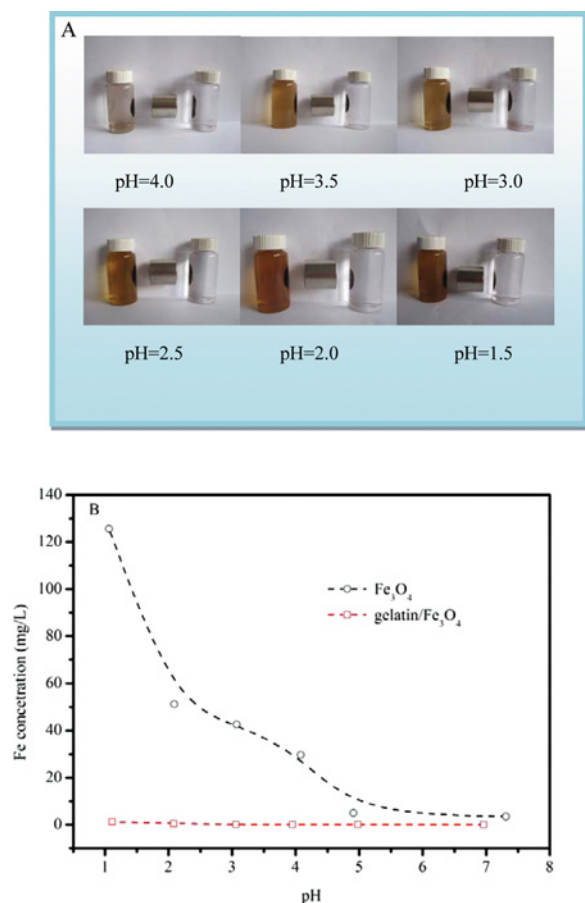


FIG. 2. The stability of Fe₃O₄ and gelatin/Fe₃O₄ in acidic solutions. (A) Digital photograph of the Fe₃O₄ (the left ones) and gelatin/Fe₃O₄ (the right ones) suspensions after magnetic separation using an external magnet at pH values varying from 1.5 to 4.0; (B) Concentration of Fe released from Fe₃O₄ and gelatin/Fe₃O₄ to solution at pH values varying from 1.0 to 7.5. (Color figure available online)

The Batch Experiments

Effect of pH and Ionic Strength

pH can influence the speciation of Pb(II) ions and the surface properties of gelatin/Fe₃O₄. It is one of the most important parameters affecting the adsorption process of Pb(II) ions on gelatin/Fe₃O₄ and on Fe₃O₄ (35). The adsorption of Pb(II) on gelatin/Fe₃O₄ and on Fe₃O₄ are studied over a pH range of 4.0–9.0. Figure 3a shows the pH effect on the adsorption of Pb(II) on gelatin/Fe₃O₄ and on Fe₃O₄ in 0.001 and 0.01 mol/L NaClO₄, respectively. The removal percentage of Pb(II) on gelatin/Fe₃O₄ is higher than that on Fe₃O₄ at pH < 6.5. The functional amine and carboxyl groups of gelatin have lone pairs of electrons from nitrogen and oxygen, which primarily act as active sites for the formation of gelatin-Pb(II) complexes, and thereby enhances the adsorption of Pb(II) on gelatin/Fe₃O₄. The surface modification of Fe₃O₄ not only can protect magnetic nanoparticles from the erosion of acidic solution, but also can

provide lots of functional groups, which markedly promote the adsorption of Pb(II) on gelatin/Fe₃O₄.

It can also be seen from Fig. 3a that no obvious effect of ionic strength on Pb(II) adsorption is observed at pH > 6.5. The ionic strength independent adsorption at pH > 6.5 suggests that inner-sphere surface complexation/chemical adsorption are the main mechanism of Pb(II) adsorption on Fe₃O₄ and on gelatin/Fe₃O₄. However, the adsorption of Pb(II) is obviously affected by ionic strength at pH < 6.5. At pH < 6.5, the adsorption curve in 0.01 mol/L NaClO₄ exhibits a shift to lower pH as compared to that in 0.001 mol/L NaClO₄ systems, suggesting the adsorption increases with increasing ionic strength. The results are similar to Co(II) sorption on gibbsite (36) and Cu(II) sorption on rutile (37). Girvin et al. (36) attributed this apparent effect as an evidence for outer-sphere surface complexation. Yang et al. (37) credited the observed shift to the changes in the electrostatic interactions as the ionic strength increased below the pH_{ZPC}. Similar results were also observed by Wiesner et al. (38).

In order to further announce the effect of ionic strength on the adsorption of Pb(II) on Fe₃O₄ and on gelatin/Fe₃O₄, the effect of NaClO₄ concentrations on Pb(II) adsorption is investigated and the results are shown in Fig. 3b. The adsorption percentages of Pb(II) on Fe₃O₄ and gelatin/Fe₃O₄ increase with increasing NaClO₄ concentrations in the range of 0.0–0.2 mol/L. The effects may be attributed to the changes in the electric potential

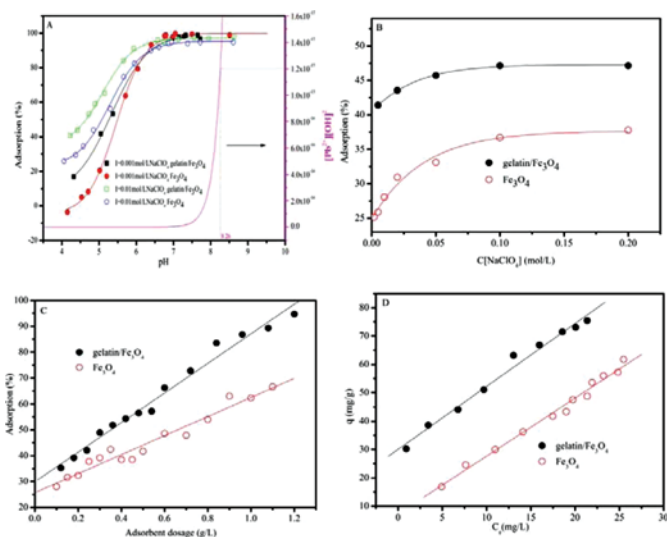


FIG. 3. Removal of Pb(II) from solution to Fe₃O₄ and gelatin/Fe₃O₄. T = 20 ± 1°C, equilibrium time of 24 h. (A) Effect of pH and ionic strength. C[Pb²⁺]_(initial) = 30.0 mg/L, m/V = 0.60 g/L; (B) Effect of NaClO₄ concentration. pH = 5.0 ± 0.1, C[Pb²⁺]_(initial) = 30.0 mg/L, m/V = 0.60 g/L; (C) Effect of adsorbent dosage. pH = 5.0 ± 0.1, C[NaClO₄] = 0.01 mol/L, C[Pb²⁺]_(initial) = 30.0 mg/L; (D) Adsorption isotherms. pH = 5.0 ± 0.1, C[NaClO₄] = 0.01 mol/L, m/V = 0.60 g/L. (Color figure available online)

in the interface, which decreases the electrostatic repulsion between the charged surface and Pb(II) ions and favors the interaction of Pb(II) with the solid particles (39). López-Ramón et al. (40) studied the adsorption of metal ions on activated carbons at variable ionic strengths, and they reported that the electrostatic interactions can be reduced by increasing ionic strength of the solution due to a screening effect of the surface charge produced by the salt added. When the electrostatic interaction between solid surface and metal ion is repulsive, or the surface concentration is sufficiently high, an increase in the ionic strength will increase the adsorption.

The effect of ionic strength on the adsorption of Pb(II) on gelatin/Fe₃O₄ can also be partly attributed to the decrease of water molecules adsorbed on gelatin surface. With the salt concentration increasing, water molecules available to interact with the charged part of the gelatin may decrease because some of them are attracted by the ions of the salt (41), and thereby more adsorption sites will be provided for Pb(II) adsorption.

Effect of Adsorbent Dosage

The amount of adsorbent used in the removal of heavy metal ions from wastewater is one of critical factors affecting the application of adsorbent in heavy metal ion elimination. The less the amount of adsorbent is used, the lower is the cost needed under the effective removal percentage uncertainties. The removal percentages of Pb(II) on Fe₃O₄ and on gelatin/Fe₃O₄ are studied by varying the adsorbent dosage ranging from 0.1 to 1.2 g/L at pH 5.0 (Fig. 3c). The removal percentage increases with increasing adsorbent dose. With increasing adsorbent doses, more surface sites and surface functional groups are available to bind Pb(II) on adsorbent surfaces, and thereby results in more Pb(II) ions to be removed from aqueous solution (42). With the increase of the adsorbent dosage from 0.1 to 1.2 g/L, the adsorption of Pb(II) on gelatin/Fe₃O₄ increases from ~35% to ~95%, whereas the adsorption of Pb(II) on Fe₃O₄ increases from ~28% to ~67% under the same experimental conditions. The results show that the adsorption efficiency of gelatin/Fe₃O₄ is higher than that of Fe₃O₄ under the same adsorbent dose. This is very important in the application of gelatin/Fe₃O₄ in the removal of Pb(II) from wastewaters in real work.

Adsorption Isotherms

The adsorption isotherms of Pb(II) on Fe₃O₄ and gelatin/Fe₃O₄ are carried out in the concentration range of 10.0–44.0 mg/L at pH 5.0. The results are shown in Fig. 3d. It is clear that the adsorption amounts of Pb(II) on gelatin/Fe₃O₄ are higher than that on Fe₃O₄. The high adsorption capacity of gelatin/Fe₃O₄ is attributed to the

strong affinity of amine and carboxyl groups introduced by gelatin towards Pb(II) ions. The amine and carboxyl groups can act as efficient anchor for Pb(II) ions, and thereby obviously increases the adsorption capacity of gelatin/Fe₃O₄.

The adsorption isotherms are analyzed with Langmuir (29) and Freundlich (43) models. The Langmuir and Freundlich adsorption isotherms are expressed as follow (44):

$$\frac{C_e}{q} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (1)$$

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where C_e is the equilibrium concentration of Pb(II) in supernatant after centrifugation, q is the amount of Pb(II) adsorbed on the adsorbent, q_{max} is the maximum adsorption capacity, and K_L is the Langmuir constant. K_F and n are Freundlich constants.

The relative parameters for Pb(II) adsorption on Fe₃O₄ and gelatin/Fe₃O₄ are listed in Table 1. From the correlation coefficients, it can be seen that the Langmuir model fits the adsorption data better than the Freundlich model. According to the Langmuir model simulation, the maximum adsorption capacities (q_{max}) of Pb(II) on gelatin/Fe₃O₄ is ~115 mg/g. The maximum Pb(II) adsorption capacities of various magnetic adsorbents are given in Table 2 for comparison. The complete monolayer adsorption capacity of gelatin/Fe₃O₄ for Pb(II) is higher than that of other magnetic adsorbents such as iron oxide (43), chitosan/magnetite nanocomposite (45), Poly-L-cysteine coated γ -Fe₂O₃ (17). The relatively high adsorption capacity of gelatin/Fe₃O₄ indicates that gelatin/Fe₃O₄ would be a suitable and promising material in the preconcentration and solidification of heavy metal ions from large volumes of aqueous solutions in environmental pollution cleanup.

TABLE 1.
Langmuir and Freundlich parameters of Pb(II) adsorption on Fe₃O₄ and gelatin/Fe₃O₄

		Fe ₃ O ₄	gelatin/ Fe ₃ O ₄
Langmuir model	q_{max} (mg/g)	95.238	114.942
	K_L (L/mg)	0.044	0.089
	R^2	0.987	0.993
Freundlich model	n	0.752	0.474
	K_F (mg ¹⁻ⁿ · L ⁿ · g ⁻¹)	5.076	17.865
	R^2	0.989	0.987

TABLE 2
Comparison of Pb(II) adsorption by various magnetic adsorbents

Adsorbent	q_{max} (mg/g)	Conditions	Reference
Fe ₃ O ₄ @SiO ₂ -NH ₂	76.66	pH 6.2; T 298 K	(29)
HA coated Fe ₃ O ₄	92.4	pH 6.0; T 293 K	(11)
Poly-L-cysteine coated γ -Fe ₂ O ₃	14.71	pH 7.0; room temperature	(17)
γ -Fe ₂ O ₃	18.65	pH 7.0; room temperature	(17)
Iron oxide	36.0	pH 5.5; T 298 K	(43)
Chitosan/magnetite nanocomposite	63.33	pH 6.0; room temperature	(45)
gelatin/Fe ₃ O ₄	114.92	pH 5.0; T 293 K	This work

Interaction Mechanisms of Pb(II) with Fe₃O₄ and Gelatin/Fe₃O₄

The hydroxyl groups, the abundant surface functional groups participating in the reactions on solid surfaces, are amphoteric and reactive. The following protonation and deprotonation reactions are expected to occur at solid surfaces at different pH values:



where $\equiv XOH$ represents a singly protonated site. Fe₃O₄ and gelatin/Fe₃O₄ are characterized using potentiometric titration to achieve the surface properties. Figure 4a shows the titration curves of Fe₃O₄ and gelatin/Fe₃O₄. As can be seen from Fig. 4a, the pH value jump of gelatin/Fe₃O₄ is softer than that of Fe₃O₄, suggesting that the buffer capacities of gelatin/Fe₃O₄ are higher than that of Fe₃O₄. The content of the functional group on gelatin/Fe₃O₄ is higher than that on Fe₃O₄ surfaces, which is also confirmed from the curves of TOTH vs. pH (Fig. 4b) (TOTH, the total concentration of protons consumed in the titration process (46)). The different site concentrations calculated with the aid of FITEQL 3.1 as a function of pH are shown in Fig. 4c. The site densities of Fe₃O₄ calculated from the titration curve are 2.98×10^{-4} mol/g for $\equiv XOH$ (-OH functional groups). The consecutive acidity constants as pK_a are optimized to be: $pK_{XO^-} = 5.638$ and $pK_{XOH_2^+} = -2.616$. The site densities of gelatin/Fe₃O₄ are 1.96×10^{-4} mol/g for $\equiv XOH$ (-OH functional groups) and 8.15×10^{-4} mol/g for $\equiv YOH$ (-NH₂ functional groups). The consecutive acidity constants as pK_a are optimized to be: $pK_{XO^-} = 5.720$, $pK_{XOH_2^+} = -3.689$, and $pK_{YO^-} = 8.131$. It reveals that the site densities of gelatin/Fe₃O₄ are much higher than that of Fe₃O₄.

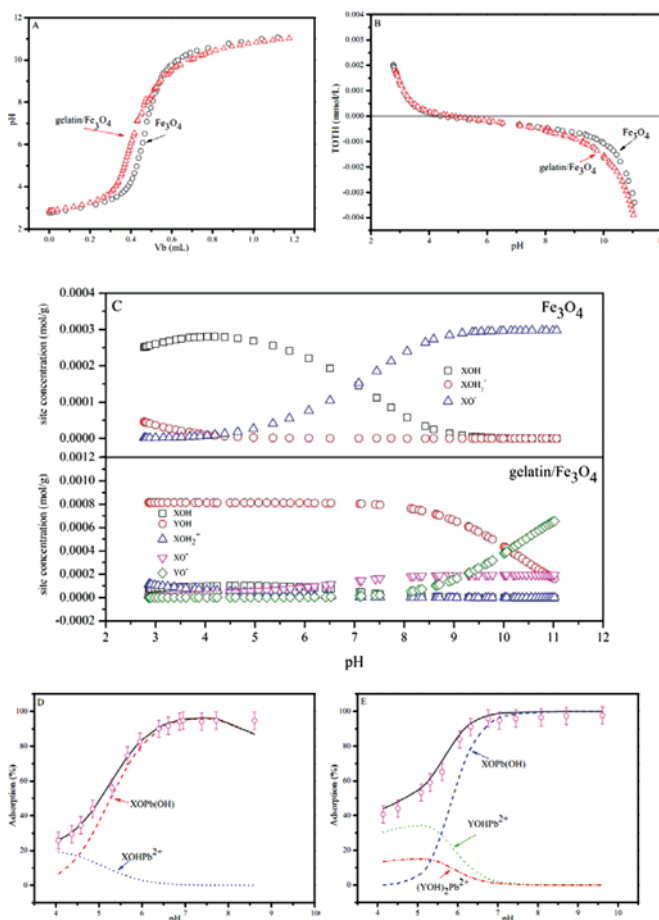


FIG. 4. (A) Potentiometric titration curves of Fe₃O₄ and gelatin/Fe₃O₄ suspension. $V_0 = 40$ mL, $T = 20 \pm 1^\circ\text{C}$, $C[\text{NaClO}_4] = 0.01$ mol/L, $C[\text{NaOH}] = 0.1972$ mol/L, $m = 0.1$ g; (B) TOTH curves as a function of pH simulated with DLM; (C) Surface site distribution of Fe₃O₄ and gelatin/Fe₃O₄ as a function of pH simulated by DLM with the aid of FITEQL 3.1 code; (D) Surface species of Pb(II) adsorption on Fe₃O₄ as a function of pH; (E) Surface species of Pb(II) adsorption on gelatin/Fe₃O₄ as a function of pH. $T = 20 \pm 1^\circ\text{C}$, $C[\text{Pb}^{2+}]_{\text{initial}} = 30.0$ mg/L, $m/V = 0.60$ g/L. (Color figure available online)

Various surface complexation models have been developed to simulate metal ion adsorption. The constant capacitance model (CCM), the diffuse-layer model (DLM) and the triple-layer model (TLM) are the commonly used models (47). In this study, the adsorption data are fitted using the DLM with the aid of FITEQL 3.1 code, and the results are shown in Fig. 4d and 4e. For Fe₃O₄, $\equiv XOH$ is the dominating surface species at low pH. With increasing pH, $\equiv XO^-$ becomes the dominating species. Thus, the general adsorption reaction of Pb(II) on Fe₃O₄ can be described by the following equation:



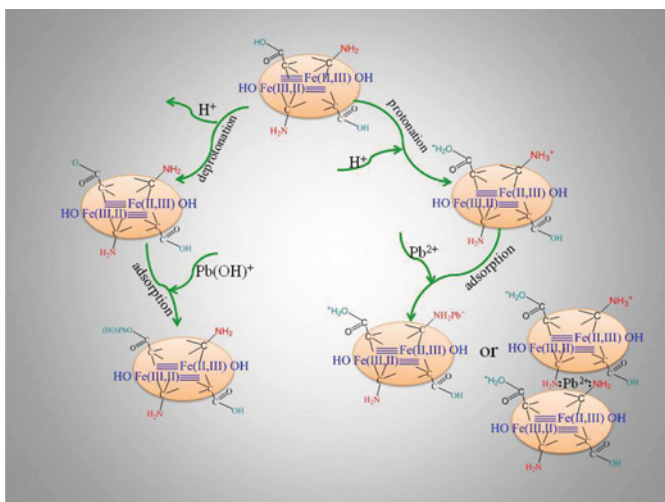
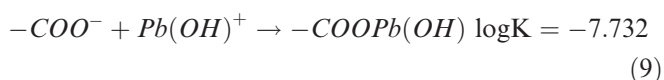
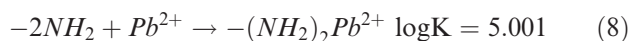
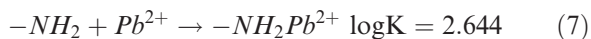


FIG. 5. Schematic diagram of Pb(II) interaction with gelatin/Fe₃O₄. (Color figure available online)



The uptake of Pb(II) by Fe₃O₄ is proposed to take place through different reaction mechanisms, including surface adsorption and electrostatic interaction. It is proposed that the reaction between Pb²⁺ and protons of surface hydroxyl groups could take place. The precipitation constant of Pb(OH)₂(s) is 1.2×10^{-15} (48). From the precipitation curve of Pb(II) at the concentration of 30 mg/L (Fig. 3a), one can see that Pb(II) begins to form precipitation at pH ~8.3 if no Pb(II) is adsorbed. However, ~90% Pb(II) is adsorbed at pH ~6.5, the precipitation of Pb(OH)₂ can be negligible at pH < 8.3. Furthermore, the replacement of Fe²⁺ in the lattice structure of magnetite with Pb²⁺ ions in solution is also suggested to take place as one of Pb(II) removal mechanisms (49).

As for Fe₃O₄-g-gelatin, the amine and carboxyl groups of gelatin are responsible for Pb(II) binding. On the basis of the adsorption data simulated using DLM with the aid of FITEQL 3.1 code, the change in the adsorption characteristics with solution pH may be more clearly explained by the following equations, which depict the major characteristic reactions at the surfaces of gelatin/Fe₃O₄:



Equations (7) and (8) show the formation of surface complexes of Pb²⁺ ions with the amine groups at low pH

values. At high pH values, the removal of Pb(II) by gelatin/Fe₃O₄ is mainly dominated by Eq. (9). From the above description, the complicated adsorption mechanisms are proposed by a conceptual model as shown in Fig. 5.

CONCLUSIONS

In this paper, we present an easy and environmentally friendly method to modify Fe₃O₄ with gelatin by using N₂ induced plasma technique. The feasibility of gelatin/Fe₃O₄ nanoparticles as a magnetic material for the preconcentration of Pb(II) ions from aqueous solutions is studied. The gelatin/Fe₃O₄ has remarkable stability in acidic solutions and relatively high adsorption capacity for Pb(II) ions. By introducing gelatin, the stability of Fe₃O₄ in acidic aqueous suspensions is effectively improved and the magnetic property of Fe₃O₄ is maintained, while the removal percentage of Pb(II) is increased. The gelatin/Fe₃O₄ nanoparticles are very cheap because of the abundant Fe₃O₄ and gelatin. Furthermore, the gelatin/Fe₃O₄ with adsorbed heavy metals can be simply recovered from solution with magnetic separations at very low magnetic field gradients, which can hopefully reduce water treatment expenses. It is expected that gelatin/Fe₃O₄ can be applied in the removal of heavy metal ions from acidic aqueous solution in real work.

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