A designed magnetic CoFe$_2$O$_4$–hydroxyapatite core–shell nanocomposite for Zn(II) removal with high efficiency

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Abstract

In this study, magnetic CoFe$_2$O$_4$–hydroxyapatite core–shell nanoparticles have been synthesized by reverse microemulsion method and used as adsorbent to remove Zn(II) from aqueous solution. The synthesized products were studied by X-ray diffraction, Brunauer–Emmett–Teller surface area analysis, vibrating sample magnetometer and transmission electron microscopy. The effect of parameters, including adsorbent dosage, contact time, and zinc concentration on the adsorption properties were investigated. The results revealed that hydroxyapatite was coated on the CoFe$_2$O$_4$ surface and formed a core–shell structure. The adsorption of Zn(II) onto the nanoparticles increased sharply within 60 min and equilibrium condition can be obtained gradually. Adsorption data were well described by Freundlich model. The kinetic study illustrated that the adsorption of Zn(II) onto nanoparticles surface fits the pseudo-first-order model.

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1. Introduction

Removal of undesirable chemicals, heavy metals and biological contaminants from polluted water is a subject of interest and is a serious problem for many global organizations [1]. Many industrial facilities such as metal plating, petroleum refining, tanneries, batteries, mining operations, chemical plants, pigments, alloys and fertilizer discharge heavy metals via their waste effluents [2,3]. Zn(II) ions are frequently present in acid mine drainage wastewaters, which has received worldwide environmental attention [4]. Despite an essential micronutrient for life, zinc can also lead to depression, lethargy, increased thirst and neurologic symptoms beyond the maximum acceptable concentration in living organism [5]. Hence, it is essential to remove Zn (II) from wastewaters before entering into environment. Several methods were reported for removal and extraction of heavy metals from wastewaters, such as electrochemical treatment [6], chemical precipitation [7], ion-exchange [8], solvent extraction [9], membrane separation [10] and adsorption [11–13]. Among them, adsorption is found to be cheap, effective and easy to adapt and has been confirmed as one of the most promising technologies for removing heavy metals from wastewaters. To date, many adsorbents have been used for metal ions removal, such as zeolites [14], chitosan [15], organic resins [16], clay minerals [17], and even some industrial waste, like fly ash [18]. However, how to increase the removal efficiency and simplify the reuse and recovery process of the adsorbents still needs to be further studied. In order to solve the difficulties of recovery and reuse of treatment agents, magnetic composite materials have been put forward and drawn great attention. Magnetic materials offer advantages due to the easy recovery of the adsorbent under a magnetic field without filtration or centrifugation. For instance, Yuan et al. [19] synthesized magnetic Fe/carbon composites and showed that it could be separated by applying an external

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magnetic field instead of centrifugation or filtration, leading to lower cost and easier operation.

Hydroxyapatite (denoted as HAp) has attracted wide interest in modern material chemistry due to its outstanding biocompatibility, environmental friendly nature, and abundant in hydroxyl groups [20–22]. Up to date, nano-size HAp shows excellent potential in sewage treatment because of their high capacity for removing divalent heavy metal ions, good dispersibility and simple synthesis method [23–25].

Up to now, the use of CoFe$_2$O$_4$–HAp nanocomposite as an adsorbent for removal of Zn(II) has not been reported. Therefore, the aims of this study are: (1) to prepare magnetic CoFe$_2$O$_4$–HAp core–shell nanoparticles and, (2) to investigate the adsorption behavior of Zn(II) on the magnetic composites. The influence of various experimental parameters on Zn(II) adsorption and the optimum adsorption conditions were studied. Adsorption mechanisms, including dynamics and isotherms were also analyzed. The goal is to develop an efficient magnetic nanocomposites adsorbent with high adsorption capacity for Zn(II).

2. Experimental procedure

2.1. Materials

Co(NO$_3$)$_2$·6H$_2$O (Merck) and FeCl$_3$·6H$_2$O (Merck) were used as the precursors for the synthesis of core nanoparticles. The precursors for the preparation of the water in oil microemulsion were Brij 35 (polyoxyethylene(23)lauryl ether, Merck) as nonionic surfactant, n-hexan (C$_6$H$_{14}$, Merck) as an oil phase and n-butanol (C$_4$H$_9$OH, Merck) as a co-surfactant. Ca(NO$_3$)$_2$·4H$_2$O (Merck) and (NH$_4$)$_2$HPO$_4$ (Merck) were used as the precursors for the HAp shell layer. Zn(NO$_3$)$_2$·6H$_2$O (Merck) was utilized in this study as the heavy metal sources by dissolving zinc nitrate into the water.

2.2. Sample preparation

The CoFe$_2$O$_4$–hydroxyapatite core–shell nanoparticles (HAp–20 wt% CoFe$_2$O$_4$) were synthesized via reverse microemulsion method. In this work, 5 g surfactant was dissolved in 100 mL n-hexan and 10 mL n-butanol and stirred to obtain a transparent solution. The solution was divided into four parts (A, B, C and D). Aqueous solutions of FeCl$_3$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O were added to part A. Aqueous solutions of Ca(NO$_3$)$_2$·4H$_2$O (0.5 mol/L) and (NH$_4$)$_2$HPO$_4$ (0.3 mol/L) were added to part B and C, respectively. The fourth microemulsion solution (part D) was prepared in the same manner except the metal salt aqueous solution was replaced by NH$_4$OH solution. The last part (D) was added drop-wise to part A and stirred for 30 min to form a precipitate of parts A and D under the condition of pH=9. The CoFe$_2$O$_4$–HAp core–shell particles were obtained by adding the calcium nitrate microemulsion (Part B) and ammonium dihydrogen phosphate microemulsion (Part C) to the A+D mixture. The mixture was stirred for 30 min and aged for an additional 24 h. Then the mixture was centrifuged and the precipitate was washed with ethanol and water two times and dried at 100 °C for 24 h. The powders were then calcined at 700 °C under air atmosphere for 2 h. The whole procedure for the preparation of the nanoparticles is schematically described in Fig. 1.

2.3. Characterization

X-ray diffraction (XRD) analyses of the samples were performed by using a Philips X’pert model with CuKα radiation. The morphology of the samples was investigated using a JEM-100CX transmission electron microscope (TEM). Magnetic measurements of the samples were performed by a vibrating sample magnetometer (VSM) (TM-XYZTB-SIH). BET analysis on surface area and porosity of the samples was measured using a Micromeritics ASAP 2020. Zn(II) concentration in the solutions...
was determined by a Perkin-Elmer Analyst 700 atomic absorption spectrophotometer.

2.4. Batch adsorption experiments

All of the synthetic solutions were prepared by diluting Zn(II) solution (1000 ± 1 mg/L) obtained by dissolving Zn(NO$_3$)$_2$ · 6H$_2$O in water at room temperature. In order to determine the optimum Zn(II) adsorption conditions, batch adsorption experiments were carried out with a proper amount of CoFe$_2$O$_4$–HAp nanoparticles and 10 mL of different concentration of Zn(II) solutions. The effect of CoFe$_2$O$_4$–HAp dosage on the adsorption capacity was tested in the range of 0.5–2 mg (room temperature (RT) and natural pH). The effect of contact time was studied in the range of 0–120 min and Zn(II) concentration was studied in the range of 16–131 mg/L. At the end of the adsorption process, adsorbent was separated from the solution through magnetic separation. All experiments were carried out two times, and only the average values were reported. The maximum errors were less than 4%. The removal efficiency (R) of Zn(II) was calculated from the following equation:

\[
R = \frac{C_0 - C_t}{C_0} \times 100
\]

(1)

where \(C_0\) is the initial concentration of the Zn(II) and \(C_t\) is the concentration of the Zn(II) at time \(t\). The adsorption capacity at equilibrium (\(q_e\) (mg/g)) was calculated from the difference between initial concentration and final equilibrium concentration, according to the following formula:

\[
q_e = \frac{C_0 - C_e}{m} \times V
\]

(2)

where \(C_e\) is the equilibrium concentration of Zn(II) in solution (mg/L), \(V\) is the volume of solution (L), and \(m\) is the adsorbent mass (g).

3. Results and discussion

3.1. Characterization of the CoFe$_2$O$_4$–HAp core–shell nanoparticles

X-ray diffraction analysis of the sample is shown in Fig. 2(a). The clear and well-defined main peaks at 2\(\theta\) = 22.84, 25.87, 28.89, 31.74, 32.27, 32.86, 34.04, 35.42, 50.43, 54.46, 64.94 are related to HAp (JCPDS No. 073-0293) [26]. In addition the peaks at 2\(\theta\) = 30.13, 35.76, 37.71, 54.01, 55.13, 57.08, 62.63 are related to CoFe$_2$O$_4$ (JCPDS No. 01-1121) [27]. These results confirm the formation of CoFe$_2$O$_4$–HAp composite. XRD crystallite size of the samples (\(d\)) can be estimated from XRD patterns by substituting the value of the fullwidth at half maximum (FWHM) of broadened characteristic peaks to Scherrer’s formula:

\[
d = \frac{0.94}{\text{FWHM} \cos(\theta)}
\]

(3)

where \(\lambda\) is the X-ray wavelength and \(\theta\) is the Bragg angle. The average crystallite sizes HAp and CoFe$_2$O$_4$ were 36 and 31 nm, respectively.

The magnetization measurements show that the specific saturation magnetization (\(M_s\)) is 7.8 emu/g under a maximum magnetic field of ± 10 kOe (Fig. 2(b)). The lower saturation magnetization of the synthesized composite in comparison with the pure cobalt ferrite reported in literature can be attributed to the lower weight fraction of the cobalt ferrite in the composite (20 wt%) [28,29].

Fig. 3 shows the TEM images of CoFe$_2$O$_4$–HAp nanoparticles. As can be seen the particles are relatively spherical in shape and appear to be monodisperse. As known, in the microemulsion method, particles are formed in the internal structure of the nanoreactors, which is determined by water to surfactant ratio. At high oil concentration, small water droplets (nanoreactors) are formed within a continuous oil phase when a surfactant is added [30–32]. Therefore, the size of droplets determines the particle size, depending on the kind and amount of the surfactant [33]. In addition, the particle growth is limited by the dimensions of the nanoreactors. The homogeneity in size distribution was probably attributed to the w/o nanoreactors and the soft template of the surfactants. The results clearly reveal that a hydroxyapatite nanoshell was formed on the CoFe$_2$O$_4$ nanoparticles.
Fig. 4 presents the N$_2$ adsorption–desorption isotherm and pore size distribution of the nanocomposite. The sample exhibits typical type IV isotherm according to the IUPAC classification, typical for mesoporous materials [34]. Such hysteresis is usually assigned to the mesoporous structure due to capillary condensation of N$_2$ in mesopores. In addition, the sample exhibited sharp peaks in pore size distribution curve, indicating their uniform mesoporous structure. The textural properties of the samples obtained from Fig. 4(a and b) shows that the surface area, pore volume and the mean pore diameter of powders are 42 m$^2$/g, 0.1 cm$^3$/g and 2.7 nm, respectively.

3.2. Determination of the optimum Zn(II) adsorption conditions

The optimum adsorption conditions, including adsorbent dosage, contact time and Zn(II) concentration were investigated in this work.

3.2.1. Influence of dosage on the removal efficiency of Zn(II)

Fig. 5 indicates that as the amount of the adsorbent increased, the removal efficiency of Zn(II) increased rapidly. This was due to the active sites which are enhanced with an increase amount of CoFe$_2$O$_4$–HAp nanoparticles. When the adsorbent dosage is 1 mg, the removal efficiency reach to steady state, where the percentage of Zn(II) removal efficiency approached equilibrium with the value of (76)% . Consequently of 1 mg dosage was selected as the optimum value.

3.2.2. Influence of reaction time on the removal efficiency of Zn(II)

The effect of contact time on removal of Zn(II) was studied, and the results are shown in Fig. 6. Large amounts of Zn(II) were removed in the first 30 min and reached equilibrium gradually. After the equilibrium, adsorption efficiency was not increased significantly. So, 60 min was used as the optimal contact time. The rapid adsorption at the initial contact time may be due to the abundant availability of active sites on the composite surface. With increasing contact time, these sites are gradually occupied,
therefore the adsorption becomes less efficient [35]. A rapid kinetic is important for composite to treat the practical wastewater, ensuring high efficiency and economy.

3.2.3. Influence of initial zinc ion concentration on the removal efficiency of Zn(II)

The initial zinc ion concentration of the solution is another important parameter that affects the adsorption of Zn(II) ions. As shown in Fig. 7 the percentage of Zn(II) removal increased from 50 to 76% with the increase in initial zinc ion concentration from 16 to 32 mg/L (0.25–0.5 mmol/L). This might be attributed to the fact that, the effective contact between zinc ions and absorbent are enhanced with an increase in initial zinc ion concentration. However, with further increase in concentration there is a decrease in efficiency of the Zn(II) removal. This effect can be explained by reduction in active sites on the surface of absorbent which leads to a decrease in the percentage of metal ion removal [36].

3.3. Adsorption kinetics

In order to examine the mechanism of adsorption, the pseudo-first-order kinetic and pseudo-second-order kinetic model were tested. The linear form of the pseudo-first-order and pseudo-second-order kinetic models is given by:

\[
\log \left( \frac{q_e}{q_t} \right) = \log \frac{q_e}{k_1 t} - \frac{k_1}{2.303} t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

where \( q_e \) and \( q_t \) are the Zn(II) adsorption capacities for absorbent at equilibrium and at any time \( t \), respectively; \( k_1 \) and \( k_2 \) are the rate constants of pseudo-first-order and pseudo-second-order kinetic model. The validity of each kinetic model is checked by the fitness of the straight lines (Fig. 8). It was found that the pseudo-first-order kinetic model presents a better fit to all of the experimental data according to \( R^2 \). The assumption behind the pseudo-first-order model was that the rate-limiting step might be physical absorption involving Van der Waals Force through electrostatic interaction between atoms, molecules and surfaces. It should be noted that adsorption mechanism of metal ions by an absorbent is complicated. For a solid/liquid sorption process or the design of adsorption systems, it is helpful to elaborate the underlying adsorption mechanism by analyzing the rate controlling steps, such as mass transport and reaction processes. In general, adsorption reaction may be considered the following steps [37]: (i) the migration and diffusion of metal ions from the boundary film to the external surface of the absorbent (film diffusion); (ii) transfer of metal ions into the intraparticle active sites (particle diffusion); (iii) adsorption of metal ions at the active sites of absorbent.

3.4. Adsorption isotherms

Adsorption isotherms are of importance in the design of adsorption systems because they can reflect the surface
characteristics of the adsorbent at a micro level as well as the adsorption characteristics of adsorption capacity at a macro level. The adsorption isotherm is based on the assumption that every adsorption site is equivalent and independent of whether or not adjacent sites are occupied. In this study, the Langmuir (Eq. (6)) and Freundlich (Eq. (7)) isotherms are adopted to describe the adsorption behaviors of Zn(II) onto nanoparticles.

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} k_L + \frac{1}{q_{\text{max}}} C_e
\]

\[
\log q_e = \log k_f + \frac{1}{n} \log c_e
\]

where \(q_{\text{max}}\) is the maximal sorption capacity at equilibrium (mg/g); \(k_L\) is Langmuir constant related to the affinity of the binding sites and energy of adsorption (L/mg); \(k_f\) is Freundlich constant (L/mg), which indicates the relative adsorption capacity of the adsorbent; \(n\) is the heterogeneity factor and is known as Freundlich coefficient. Adsorption equilibrium data have been fitted by Langmuir and Freundlich and the linear fitting results were shown in Fig. 9. As can be seen, the Langmuir isotherm model yielded a better fit with higher \(R^2\) values compared to the Freundlich model. As it is known, the Freundlich adsorption isotherm can be used successfully for modeling the equilibrium data in metal-surface systems. This model supposes that the removal of metal ions occurs on a heterogeneous surface by multilayer adsorption.

4. Conclusion

Novel magnetic CoFe\(_2\)O\(_4\)–hydroxyapatite core–shell nanoparticles were synthesized by reverse microemulsion method and were used as an adsorbent for the removal of Zn(II) from aqueous solution. The BET characterization showed that the specific surface area, pore volume, and pore diameter of nanoparticles were 42 m\(^2\)/g, 0.1 cm\(^3\)/g, and 2.7 nm, respectively. The adsorbent showed high adsorption capacity for Zn(II) and could be easily separated from aqueous solution by the application of an external magnetic field. The isotherm adsorption data fit well with the Freundlich model, and the kinetic data fit well with the pseudo-first-order model.

References
