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RESEARCH PAPER

Carboxymethyl Chitosan-Fe₃O₄ Nanoparticles: Preparation and Adsorption Behavior toward Zn²⁺ Ions

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Abstract: A novel magnetic nanoadsorbent was prepared by the covalent binding of carboxymethyl chitosan (CMC) onto the surface of Fe_3O_4 magnetic nanoparticles, which was developed using a coprecipitating method. This nanoadsorbent was characterized by transmission electron microscopy (TEM) and X-ray diffraction patterns (XRD), etc. Moreover, the adsorption performance of the nanoadsorbent toward Zn^{2+} ions was investigated. The results showed that the mean diameter of the magnetic nanoadsorbent was 18 nm and the amount of CMC was about 5%. The nanoadsorbent showed high efficiency for the removal of Zn^{2+} ions. The adsorption rate was so rapid that the equilibrium was achieved within 2 min. The isotherm adsorption data obeyed the Langmuir model, with a maximum adsorption capacity of 20.4 $mg \cdot g^{-1}$ and an adsorption equilibrium constant of 0.0314 $L \cdot mg^{-1}$. The thermodynamic calculations indicated that the adsorption process was exothermic and that the enthalpy change was -5.68 $kJ \cdot mol^{-1}$.

Key Words: Nanoadsorbent; Carboxymethyl chitosan; Fe_3O_4; Zn^{2+} ions

New and innovative methods are of great importance for the development of technologies that can help deal with environmental problems. The application of magnetic nanoadsorbent technology to solve environmental problems is one method that has received considerable attention in recent years[1–5]. Magnetic nanoparticles can be used to adsorb contaminants from aqueous or gaseous effluents, and after the adsorption is completed, the nanoadsorbent can be separated from the medium by a simple magnetic process. Some examples of this technology are the use of magnetite particles to accelerate the coagulation of sewage, magnetite-coated functionalized polymers such as resin to remove radionuclides from milk, poly(oxy-2,6-dimethyl-1,4-phenylene) for the adsorption of organic dyes, and polymer-coated magnetic particles for the remediation of oil spills[1–4]. However, these materials have the inherent drawbacks, namely a small surface area, low adsorption capacity, or low adsorption rate, which limit their application.

Chitosan (CS) is an *N*-deacetylated derivative of chitin, a cationic polysaccharide composed of *β*-D-glucosamine and *N*-acetyl-*β*-D-glucosamine residues with a 1,4 linkage[6]. It is an environmentally benign nanoadsorbent characterized by a high content of hydroxyl and amine groups, which in turn explains its ability to uptake heavy metal ions through different mechanisms such as ion exchange or chelation processes.

CS microspheres have been widely used in the fields of agriculture, food, industry, and medicine, such as biomedicine, pharmacology, and biotechnology, because of its biocompatibility, biodegradability, and biological activities. It can be prepared using different methods such as chemical cross-linking and inverse phase microemulsion technology. Several studies have focused on the application of these magnetic microspheres in the biomedical field[7–9], but only few studies have focused on using them for metal adsorption.

In this study, magnetic carboxymethylated chitosan-bound Fe_3O_4 (CMC-Fe_3O_4) nanoparticles were prepared as an adsorbent for the removal of metal ions from aqueous solutions and Zn^{2+} ions were used as a model compound to investigate

the adsorption performance of CMC-Fe$_3$O$_4$. Because chitosan has no suitable functional groups to bind directly onto the surface of Fe$_3$O$_4$ particles, it was first carboxymethylated and then covalently bound onto Fe$_3$O$_4$ by carbodiimide activation. Similar methods for tailoring of CS and the corresponding reactions have been described in other studies[10,11]. The rapid adsorption of Zn^{2+} ions by CMC-Fe$_3$O$_4$ nanoparticles was due to the absence of internal diffusion resistance. The mechanical strength of CMC-Fe$_3$O$_4$ nanoparticles was enhanced because of the rigid Fe$_3$O$_4$ core being encapsulated by the CMC macromolecular shell.

1 Experimental

1.1 Feedstocks

Chitosan (M_w=1.3×10^5, deacetylating degree, 90%) was obtained from Zhengbang Bio-Technology Company (Nanchang, China). FeCl$_3$·6H$_2$O and FeCl$_2$·4H$_2$O were purchased from Fucheng Chemical Reagent Factory (Tianjin, China). Ammonium hydroxide (25%–28%, volume fraction) was supplied by Xinguang Chemical Reagent Factory (Nanchang, China). Zn(NO$_3$)$_2$ and ethanol were purchased from Shanghai Reagent Factory (Shanghai, China). Carbodiimides (CH$_2$N$_2$) were supplied by Sigma Chemical Co. (St. Louis, USA). Isopropanol and monochloroacetic acids were purchased from Damao Chemical Reagent Factory (Tianjin, China). All the chemicals were analytic grade reagents.

1.2 Preparation of magnetic nanospheres

Fe$_3$O$_4$ nanoparticles were prepared using the coprecipitating method. FeCl$_3$·6H$_2$O and FeCl$_2$·4H$_2$O (molar ratio 2:1) were dissolved in water at a concentration of 0.3 mol·L^{-1} iron ions. Precipitation was achieved at 298 K by adding NH$_3$·H$_2$O with vigorous stirring and supersonic dispersion. The pH was maintained at approximately 10 during the reaction process. The reaction was continued at 353 K for 30 min. The product was separated by centrifugation and washed several times with water and ethanol, and finally dried in a vacuum oven at 343 K for 24 h. The reaction was as follows:

$$2Fe^{3+}+Fe^{2+}+8NH_3·H_2O→Fe_3O_4+4H_2O+8NH_4^+$$
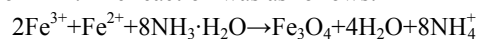
Carboxymethylated chitosan was prepared as follows: 5 g of chitosan was added to 75 mL of isopropanol, 125 mL of sodium hydroxide solution (40%) was then added slowly with stirring. The mixture was heated at 333 K to alkalize for 1 h. Then, 100 mL isopropanol containing 30 g monochloroacetic acid solution was added drop by drop in 1 h to the reaction mixture. After reacting for 4 h at 333 K, 250 mL of ethanol (70%) was added to terminate the reaction. The solid product obtained was filtered, washed with 70% and 90% ethanol until no Cl$^-$ was detected, and dried at 323 K.

Preparation of CMC-Fe$_3$O$_4$ nanoparticles was as follows: 200 mg of Fe$_3$O$_4$ nanoparticles were added to 4 mL of buffer A (0.003 mol·L^{-1} phosphate, pH=6, 0.1 mol·L^{-1} NaCl). Then,

1 mL of carbodiimide solution (0.025 g·L^{-1} in buffer A) was added. The mixture was reacted using supersonic dispersion for 10 min. Finally, 5 mL of CMC solution (50 g·L^{-1} in buffer A) was added and the reaction was continued for 60 min. The CMC-Fe$_3$O$_4$ nanoparticles were separated from the reaction mixture using a magnet. The magnetic particles were precipitated within 2 min and then washed with water and ethanol (90%). The NaCl electrolyte is a flocculating agent and could accelerate the separation of the magnetic particles in alkaline solutions.

1.3 Characterization of the samples

The morphology of the magnetic particles was characterized by TEM, using a JEM2010HT. TEM analysis was carried out by placing a drop of the ethanol-dispersed magnetic nanoparticle aqueous solution onto a copper grid and allowing the solution to evaporate in air at room temperature. Before sample withdrawal, it was sonicated for 30 min to obtain a better dispersion. XRD measurement was carried out on an XRD-2000 X-ray diffractometer (Cu K_α, λ=0.1542 nm). The size distribution was tested on a Malvern 4700 Laser Light-Scattering. The zeta potentials of Fe$_3$O$_4$ and CMC-Fe$_3$O$_4$ were measured on a Malvern 3000Hs Zetasizer.

1.4 Adsorption experiments

The adsorption of Zn^{2+} ions by CMC-Fe$_3$O$_4$ nanoparticles was investigated in aqueous solutions under conditions of pH=2–5 and temperature of 300–330 K. pH was adjusted by the addition of 0.1 mol·L^{-1} NaOH or 0.1 mol·L^{-1} HCl in Sφrensen buffer solution. A total of 210 mg of adsorbent was added to 10 mL of zinc nitrate solution. After adsorption for 2 min, the adsorbent was magnetically removed from the solution. The concentrations of Zn^{2+} ions were measured using an atomic absorption spectrometer. Unless otherwise specified, the absorption experiments were carried out in aqueous solution at pH=5.0 and temperature 300 K. The dose of the adsorbent was 21 g·L^{-1}. The amount of adsorbed Zn^{2+} ions was calculated as:

$$q = \frac{C_0 - C_e}{m} \times V$$

where q is the amount of Zn^{2+} ions adsorbed onto unit mass of the adsorbent (mg·g^{-1}); C_0 and C_e are the initial concentration and the equilibrium concentration (mg·L^{-1}) of Zn^{2+} ions, respectively; V is the volume (L) of the solution; and m is the mass (g) of the adsorbent.

2 Results and discussion

2.1 Characterization of Fe$_3$O$_4$ and CMC-Fe$_3$O$_4$ nanoparticles

The TEM micrographs for Fe$_3$O$_4$ and CMC-Fe$_3$O$_4$ nanoparticles are shown in Fig.1. It can be observed from the graphs that the nanoparticles were essentially monodispersed. The