Preparation of novel cobalt ferrite/chitosan grafted with graphene composite as effective adsorbents for mercury ions

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ABSTRACT

In this study, a novel, amino-functionalized magnetic composite of CoFe$_2$O$_4$-chitosan-graphene (MCGS) had been successfully synthesized. The crystal phase, surface morphology and structure of the MCGS were investigated by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), zeta potential measurement, and Brunauer–Emmett–Teller (BET) surface area. The adsorptive characteristics of the MCGS which was intended for removal of Hg(II) from aqueous solutions were deeply studied. The results showed that the adsorption efficiency increased with the increasing of pH and reached the highest point at pH 7.0. The Hg(II) adsorption kinetics on MCGS was consistent with the pseudo second-order process. Langmuir and Freundlich isotherm models were employed to analyze the experimental data, and the Langmuir model was fitted better with a maximum adsorption capacity of 361.0 mg/g at pH 7.0 and 323 K. Thermodynamic studies illustrated that the adsorption process was endothermic and spontaneous.

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1. Introduction

Removal of heavy metals, such as mercury, lead, cadmium and arsenic, from natural water has attracted considerable attention for their adverse effects on the environment and human health [1]. Among the heavy metals ions, Hg(II) which was released into the environment is a worldwide concern due to its toxic and bioaccumulation. Hg(II) can bind with organic and inorganic materials and form various composites, which limit the quality of water [2]. Consequently, the removal of Hg(II) from contaminated water is necessary. In the past few years, Hg(II) has been removed by conventional methods such as ion exchange, precipitation, membrane processes [3–5] and so on. Compared with conventional methods, adsorption is a highly efficient and relatively simple approach [6,7].

Recently, numerous approaches have been studied for the development of cheaper and more effective polysaccharide adsorbents, such as chitosan, starch, cellulose and alginate [8,9]. Chitosan (CS), derived from the deacetylation of chitin, is abundant, low cost, highly reactive, nontoxic and multifunctional [10]. Particularly, it exhibits a higher adsorption capacity due to the presence of large amounts of amino groups (–NH$_2$) [11].

Graphene is an emerging form of carbon materials with hexagonally, sp^2-hybridized and a one-atom-thick layer structure [12]. It has attracted enormous scientific attentions due to its peculiar properties such as extraordinary electronic [13], mechanical properties [14], and high thermal conductivity [15]. The large theoretical specific surface area (theoretical surface area of 2630 m^2/g) ensures an excellent adsorption capacity of graphene [16,17].

Over the past decades, magnetic nanoparticles have attracted intensive attention of many researchers because of their excellent physical and chemical properties compared with conventional bulk materials, such as superparamagnetism, high surface area, large surface-to-volume ratio, easy separation by external magnetic fields, and strong adsorption capacity [18–21]. Liu's group prepared rhodamine hydrazide to modify Fe$_3$O$_4$ microspheres and studied its adsorption of Hg(II) [22]. Chen's group prepared a novel magnetic Fe$_3$O$_4$/ZnCr-LDH material which was formed via a two-step microwave hydrothermal procedure. It was shown that 99% of heavy metal ions (Fe(II), Fe(III), Cr(III), and Zn(II)) could be effectively removed from aqueous solutions through magnetic nanoparticles [23].

Ferrites of the type MFe$_2$O$_4$ (M = Zn, Mg, Co, Cu etc.) are magnetic materials with cubic spinel structure, which have been extensively used in various technological applications in the past decades [24,25]. Among ferrites, CoFe$_2$O$_4$ is an interesting magnetic material due to its moderate saturation magnetization, excellent chemical stability and mechanical hardness [26]. Until now, little work has been done on preparation of CoFe$_2$O$_4$-chitosan-graphene (MCGS) composites and their applications in heavy metal ions removal from water.

According to the Hard–Soft Acid–base (HSAB) theory [27], mercury ion is classified as a soft acid, which tends to form very strong bonds with –CN, –RS, –SH and –NH$_2$ groups. Thus, it could be reasonably assumed that grafting amino-containing ligands on MCGS surface would obtain a serial of new amino-functionalized MCGS with high adsorption

capacity to Hg(II) to achieve the rapid adsorption and separation of Hg(II) from aqueous solution (as shown in Scheme 1).

In this work, MCGS was prepared firstly and the application for adsorption of Hg(II) from aqueous solution was investigated. The adsorption process, including the adsorbent dose, pH value of the solution and the adsorption contact time, was also optimized. Moreover, Hg(II) adsorption isotherm was measured and discussed. The MCGS adsorption capacity was over 360.0 mg/g in 50 mL of solution containing 20 mg/L of Hg(II).

2. Experimental

2.1. Materials

All chemicals, obtained from Sinopharm Chemical Reagent Beijing Co. Ltd., China, were of analytical reagent grade or better quality. Ultra-pure water (EASY-pure LF, Barnstead International, Dubuque, IA, USA) was used throughout the experiments. The aqueous solution of Hg(II) (20 mg/L) was prepared using $HgCl_2$. The pH values were carefully adjusted by adding an appropriate volume of HCl or NaOH solution and monitored by pH meter.

2.2. Preparation of MCGS

GO was synthesized using the modified Hummers method through oxidation of graphite powder [28]. The preparation process of MCGS was as follows: 1% (w/v) of chitosan solution was prepared by dissolving 0.3 g of chitosan in 30 mL of 2.0 (v/v) acetic acid aqueous solutions under ultrasonic stirring for 2 h at room temperature. Subsequently, 0.15 g of magnetic nanosized $CoFe_2O_4$ was added into the colloidal solution and the reaction system continued to be stirred for 1.5 h. Some paraffin oil and span-80 were slowly dispersed in the prepared mixture under stirring. After 0.5 h of emulsification, 3 mL of glutaraldehyde was added to cross-link the chitosan. Then, 0.3 g of GO was added and the mixed system was stirred continuously for 90 min in a water bath at 50 °C. The pH of the reaction system was adjusted to 9–10 using 1 mol/L NaOH and the mixture was kept in a water bath for a further 60 min at 80 ± 0.2 °C. Black products were washed with petroleum ether, ethanol and distilled water in turn until pH was around 7. Then, the precipitate was dispersed in a 250 mL round-bottom flask at 80 °C. Then a certain amount of hydrazine hydrate was added to reduce GO. After reaction for 4 h, the product was washed with ethanol and distilled water, and separated using a magnet.

2.3. Characterization of MCGS

FTIR spectra were recorded in the spectral range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum One FTIR spectrometer (Perkin-Elmer, United States) at room temperature. The structure of MCGS was investigated on (Philips X'Pert Pro Super X-ray) diffractometer with a Cu Kα radiation (λ = 1.5418 Å). Zeta potential was measured using a Malvern zetameter (Zetasizer 2000). Surface area measurements were performed on Micromeritics ASAP 2020 system.

2.4. Adsorption experiments

Batch adsorption studies were carried out in a series of Erlenmeyer flasks containing 50 mL of Hg(II) solution in certain concentrations with a fixed amount of MCGS. Thereafter the MCGS with adsorbed Hg(II) was separated from the mixture with a hand-held magnet. The residual Hg(II) in the solution was determined with a UV–vis spectrophotometer (Lambda 35 UV/VIS Spectrometer, Perkin Elmer). The adsorption capacity (q, mg/g) and the removal percentage (R, %) were calculated using the following equations:

$$q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \tag{2}$$

where q (mg/g) is the amount of Hg(II) adsorbed per unit amount of adsorbents, C_0 (mg/L) is the initial concentration of Hg(II), C_e is the concentration of Hg(II) at equilibrium, V (L) is the volume of adsorbates, m (g) is the mass of adsorbents, % is the removal efficiency of Hg(II), and C_t (mg/L) is the concentration of Hg(II) at any time.

2.4.1. Blank samples

For batch adsorption experiments, blank samples (containing only distilled water and the corresponding MCGS) were prepared and monitored for the duration of the experiment as a control.

2.4.2. Effect of adsorbent dose

The adsorption of Hg(II) was studied using MCGS (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 mg) in 100 mL Erlenmeyer flasks containing 50 mL aqueous solution of 20 mg/L Hg(II). The batch adsorption experiments were carried out under shaking at 150 rpm at room temperature for 5 h and then the samples were separated using a magnet.

2.4.3. Effect of pH

The adsorption experiments were performed at 303 K for 5 h by equilibrating 6 mg adsorbents with 50 mL of 20 mg/g Hg(II) solution in a shaker. 0.1 mol/L NaOH or 0.1 mol/L HCl stock solutions were used to adjust the solution pH. The pH of the solution was varied in the range of 2.0–7.0.
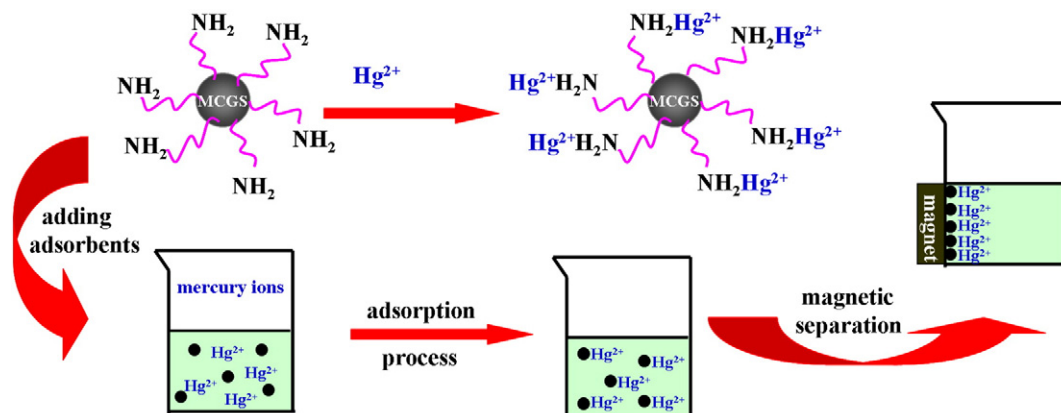
Scheme 1. Diagram of the process of adsorption and magnetic separation of Hg(II) on MCGS.