



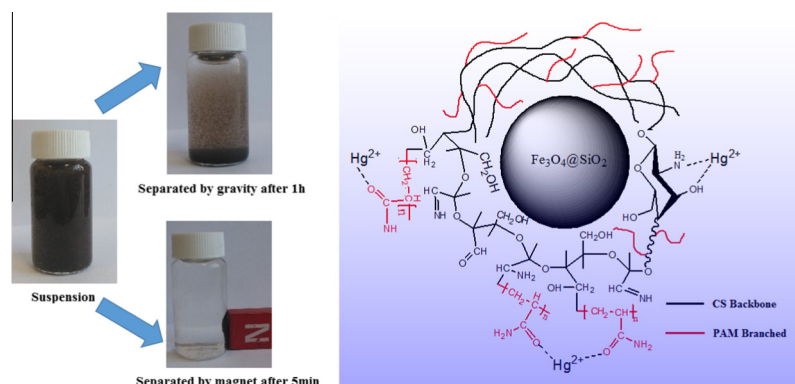
Preparation of chitosan-graft-polyacrylamide magnetic composite microspheres for enhanced selective removal of mercury ions from water [☆]



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GRAPHICAL ABSTRACT



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ABSTRACT

A novel magnetic composite microsphere based on polyacrylamide (PAM)-grafted chitosan and silica-coated Fe_3O_4 nanoparticles (CS-PAM-MCM) was successfully synthesized by a simple method. The molecular structure, surface morphology, and magnetic characteristics of the composite microsphere were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), vibrating-sample magnetometer (VSM), and scanning electron microscopy (SEM). The prepared CS-PAM-MCM was applied as an efficient adsorbent for the removal of copper(II), lead(II), and mercury(II) ions from aqueous solutions in respective single, binary, and ternary metal systems. Compared with chitosan magnetic composite microsphere (CS-MCM) without modification, CS-PAM-MCM showed improved adsorption capacity for each metal ion and highly selective adsorption for Hg from Pb and Cu. This improvement is attributed to the formation of stronger interactions between Hg and the amide groups of PAM branches for chelating effects. The adsorption isotherms of Hg/Cu and Hg/Pb binary metal systems onto CS-PAM-MCM are both well-described by extended and modified Langmuir models, indicating that the removal of the three aforementioned metal ions may follow a similar adsorption manner; that is, through a homogeneous monolayer chemisorption process. Furthermore, these magnetic adsorbents could be easily regenerated in EDTA aqueous solution and reused virtually without any adsorption capacity loss.

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1. Introduction

The rapid development of industries has led to increasing metal pollutions in water [1]. Given their toxicity and liquidity [2–4], metal ions, especially heavy metal ions, pose significant threat to humans and the environment. Copper, lead, and mercury are three common heavy metals with high toxicity that are widely presented in numerous industrial effluents, such as electroplating industries, nonferrous metals smelting, and mine tailing [5]. Among these metals, mercury can enter the human body through the food chain, causing damage to the cardiovascular system, kidney, and bones, and even death [6,7].

Considering the problems mentioned above, increasing attention has been given to the development of suitable methods for the efficient removal of heavy metal ions from waste water in recent years. Various techniques have been used for this aim, including chemical precipitation, coagulation, ion exchange, chemical reduction, membrane separation, biological treatment, solid phase extraction, and adsorption [8–11]. Among these methods, adsorption is an effective and versatile method that is capable of removing trace levels of heavy metal ions from dilute solutions [12]. Activated carbon is one of the most commonly used adsorbents that possesses strong adsorption ability [13]. However, activated carbon is considerably expensive and hardly renewable. Therefore, development of novel adsorbents with low cost and high performance remains as one of the hottest topics in adsorption.

Natural polymers, with advantages of extensive sources and low cost, have recently been receiving considerable attention [14–18]. Among these polymers, chitosan (CS), a chemical derivative obtained through alkaline deacetylation of chitin and found naturally in certain fungal cell walls, is one of the high-performance materials because of its hydrophilicity, biocompatibility, biodegradability, and antibacterial property [19]. This material has already been widely applied in the fields of food, medical drug, and agriculture [20,21]. Moreover, chitosan has been also considered as an ideal adsorbent because of the abundant free amino and hydroxyl groups on its backbone. Numerous metal ions could be easily bound to these groups because of its chelating effects, resulting in efficient removal [22,23].

Different kinds of metal ions coexist in real wastewater. Evidently, removing and separating the target metal ions in their individual pure form efficiently through the selectivity of certain adsorbents is significant for recycling use and avoiding secondary pollution [24,25]. However, most ordinary adsorbents, including chitosan, have no evident selectivity to certain individual heavy metal ions [26]. Accordingly, different kinds of effective functional groups have been introduced onto adsorbents by chemical modification to improve selectivity [27–30]. For mercury ion removal, Li et al. [29] reported that chitosan beads grafted with polyacrylamide prepared by surface-initiated atom transfer radical polymerization (ATRP) showed high selective removal of mercury ions over lead ions. However, the preparation method of ATRP is quite complicated and uneasy operation [31].

Many of adsorbents, including chitosan-based ones used as solid powders, could not be separated from water rapidly and easily after achieving adsorption equilibrium in practical applications because of their extremely small size. The magnetic separation technique has recently been proven to be an effective method to accelerate the process of separation and is widely applied in water treatment [30,32–34]. After being impregnated with magnetism, the separability of the adsorbents is greatly enhanced under external magnetic fields.

In this work, a novel polyacrylamide grafted chitosan magnetic composite microsphere (CS-PAM-MCM) was prepared through a simple method. FTIR, XRD, VSM, and SEM were conducted to

characterize the structure and magnetic property of the chitosan-based adsorbents. Aside from the fundamental adsorption behavior of CS-PAM-MCM for the removal of copper(II), lead(II), and mercury(II) ions from their respective single metal system, i.e., the effects of pH, adsorption equilibrium, and kinetics, the selective adsorption for Hg over Cu and Pb in binary and ternary metal systems were investigated systematically. Adsorption and selective adsorption mechanisms were also discussed in detail. In addition, chitosan magnetic composite microsphere (CS-MCM) without modification was prepared for comparison. Moreover, the recycling and reuse of chitosan-based adsorbents were conducted for its considerable importance in real applications.

2. Experimental

2.1. Materials

Chitosan with deacetylation degree of 90.5% and viscosity average molecular weight of $3.0 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ was purchased from Shandong Aokang Biological Co., Ltd., Acrylamide, ammonium iron(II) sulfate hexahydrate $((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O})$, iron(III) chloride hexahydrate $(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$, glutaraldehyde (GLA) solution (25%, w/w), cyclohexane, and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ were supplied by Sinopharm Chemical Reagent Co., Ltd., Span 80 (sorbitan monooleate) was obtained from Shenyu Chemical Reagent Co., Ltd., $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, hydrochloric acid (HCl), sodium hydrate (NaOH), acetic acid, and other reagents used in this work were obtained from Nanjing Chemical Reagent Co., Ltd. All chemicals are of analytical grade, and distilled water was used in all experiments.

2.2. Preparation of adsorbents

2.2.1. Preparation of Fe_3O_4 nanoparticles

Magnetic Fe_3O_4 nanoparticles were prepared by coprecipitation method. 3.14 g of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 4.32 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 20.0 cm^3 of 0.5% HCl aqueous solution, and the mixture was added into 200.0 cm^3 of $1.5 \text{ mol} \cdot \text{dm}^{-1}$ NaOH aqueous solution in a dropwise manner with vigorous stirring at 353 K and under N_2 atmosphere. Fe_3O_4 nanoparticles were obtained after washing with distilled water for several times.

To improve the acid duration of Fe_3O_4 , the magnetic nanoparticles were further coated by a layer of silica for protection [35,36]. Briefly, 30.0 cm^3 of $1.0 \text{ mol} \cdot \text{dm}^{-1}$ Na_2SiO_3 aqueous solution was added dropwise into 200.0 cm^3 of the Fe_3O_4 suspension (0.5 wt%) with vigorous stirring at 353 K under N_2 atmosphere. The silica-coated nanoparticles ($\text{Fe}_3\text{O}_4@ \text{SiO}_2$) were obtained at pH 6.0, which was adjusted using a HCl aqueous solution with $2.0 \text{ mol} \cdot \text{dm}^{-1}$. Finally, the resultant $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ was washed to neutral condition by distilled water and stored in water for further use.

2.2.2. Preparation and characterization of CS-MCM and CS-PAM-MCM

2.2.2.1. Preparation of CS-MCM. 1.6 g of chitosan powder and acetic acid was dissolved in 100.0 cm^3 of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ suspension (1.6 wt%) under vigorous stirring at 323 K. The mixture of chitosan and magnetic nanoparticles was then dispersed evenly in cyclohexane containing 2.0 cm^3 of Span 80, and the volume ratio of cyclohexane to the aforementioned aqueous mixture was 10:1. 4.0 cm^3 of glutaraldehyde (25.0 wt%) was then selected as crosslinker and added dropwise into the water-cyclohexane emulsion. After the crosslinking reaction, which was maintained at 318 K for 3 h, the mixture was neutralized by dilute NaOH aqueous solution to pH ≈ 8.0 . The product was then filtered and washed with

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