Removal of Cu^{2+} from aqueous solution by chitosan-coated magnetic nanoparticles modified with α-ketoglutaric acid

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ABSTRACT

Chitosan-coated magnetic nanoparticles (CCMNPs), modified with a biodegradable and eco-friendly biologic reagent, α-ketoglutaric acid (α-KA), was used as a magnetic nanoadsorbent to remove toxic Cu^{2+} ions from aqueous solution. The prepared magnetic nanoadsorbents were characterized by FTIR, TEM, VSM, XRD, and EDS. Factors influencing the adsorption of Cu^{2+}, e.g., initial metal concentration, initial pH, contact time and adsorbent concentration were investigated. TEM images show that the dimension of multidispersed circular particles is about 30 nm and no marked aggregation occurs. VSM patterns indicate superparamagnetic properties of magnetic nanoadsorbents. EDS pictures confirm the presence of the Cu^{2+} on the surface of magnetic nanoadsorbents. Equilibrium studies show that Cu^{2+} adsorption data follow Langmuir model. The maximum adsorption capacity (q_{max}) for Cu^{2+} ions was estimated to be 96.15 mg/g, which was higher than that of pure CCMNPs. The desorption data show no significant desorption hysteresis occurred. In addition, the high stability and recovery capacity of the chitosan-coated magnetic nanoparticles modified with α-ketoglutaric acid (α-KA-CCMNPs) suggest that these novel magnetic nanoadsorbents have potential applications for removing Cu^{2+} from wastewater.

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1. Introduction

The environment and all the life forms on earth face a very serious threat from the heavy metal pollution due to rapid industrialization and the growth in the world population [1]. At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risk to human health [2]. Copper (Cu^{2+}), an abundant and naturally occurring element present in municipal wastewaters, is one of such heavy metals harmful to human health. If copper is ingested excessively in the human diet, it may result in vomit, cramps, convulsion, and even death. On the other hand, the lack of Cu^{2+} in animal diet may lead to anemia, diarrhea, and nervous disturbances [3]. Moreover, enzymes, whose activities depend on sulhydryl and amino groups [4], are strongly inhibited by Cu^{2+} ions which have high affinity for N and S containing donor ligands [5]. Therefore, it is of great practical interest to explore ways to effectively remove these heavy metal ions from the wastewaters before their discharge, and to possibly separate them for recovery and re-use.

Numerous technologies have been developed for the removal of Cu^{2+} from industrial wastewater, such as chemical precipita-

tion, ion exchange, liquid–liquid extraction and resins, cementation, electrodialysis, and biosorption [6,7]. Each method has been found to be limited for the cost, complexity and efficiency, as well as secondary wastes. For example, the electrolysis processes often take higher operational costs, and the chemical precipitation may generate secondary wastes [8,9]. Another example is that, remediation technologies of Cr(VI) from wastewater have been carried out from many years, but successive applications are limited [10]. Thus, among these various processes, biosorption, which uses cheap and non-pollutant adsorption materials, may be an alternative wastewater technology, in which technological, environmental and economic constraints are taken into consideration. And this method can avoid the generation of secondary waste, and the adsorption materials employed in this method can be recycled and used easily on an industrial scale.

The search for new adsorbents is an important factor in improving analytical sensitivity and precision in biosorption techniques [11]. However, traditional adsorbents show poor recovery of the target metal ions from large volumes of solution due to low binding capacity, diffusion limitations and the lack of active surface sites. Hence, it would be of great interest to develop a novel adsorbent with a large adsorptive surface area, low diffusion resistance, high adsorption capacity and fast separation for large volumes of solution [11]. Recently, magnetic separation techniques have attracted lots of attentions due to the specific char-

acteristics. Magnetic separation may become one of the promising ways for environment purification technique because it produces no contaminants, and has the capability of treating large amount of wastewater within a short time [12]. Moreover, this approach is particularly adapted when the condition of separation is complex, i.e., when polluted water contains solid residues which exclude their treatment in column with regards to the risks of filling [12]. Because these magnetic particles are superparamagnetic, that is, they do not become permanently magnetized without the external magnetic field. The superparamagnetic particles adsorbing target metal ions can be removed very quickly from a matrix using a magnetic field, and be reused without losing active sites. Therefore, magnetic separation has been gradually employed as a recovery and pollution-control process for many environmental and industrial processes. Nanometer-sized materials have also attracted substantial interest in the scientific community because of their special properties [13]. The relatively large surface area and highly active surface sites of nanoparticles enable them to possess higher adsorption capacity compared with the previous adsorbents. Thus, an adsorbent combining with magnetic separation techniques and nanometer-sized materials, which can be easily recovered or manipulated with an external magnetic field, can be used as an alternative large scale wastewater treatment procedure.

Numerous types of magnetic nanoparticles for heavy metals removal could be tailored by using functionalized natural or synthetic polymers to impart surface reactivity [1]. Hu et al. [14] employed δ-FeOOH-coated maghemite as adsorption material for the removal and recovery of Cr(VI) from wastewater, and Shashwat et al. [1] utilized gum Arabic modified magnetic to do that. And Kochen et al. [15] used magnetic polymer resin for the removal of actinides and other heavy metals from contaminated water. The removal of nickel ions from aqueous solution by magnetic alginate microcapsules was reported by Ngomsik et al. [16]. And Chang et al. [17] reported chitosan-bound Fe_3O_4 magnetic nanoparticles for removal of Cu^{2+} ions. Although there are reports on the effectiveness of the inorganic-coated or organic-coated magnetic particles on the removal of heavy metals [18,19], the chemical modification of these coated magnetic adsorbents and the potential effectiveness of these coated magnetic adsorbents modified with biologic reagent have not been discussed.

In this study, a novel magnetic nanoadsorbent for the removal of Cu^{2+} was firstly developed by the surface modification of chitosan-coated magnetic nanoparticles (CCMNPs) with α-ketoglutaric acid (α-KA), which is a natural, inexpensive, harmless and environmental friendly biologic reagent containing active functional groups like carboxyl groups. These magnetic nanoadsorbents were carefully characterized before investigating their adsorption capacity of Cu^{2+} through adsorption isotherms. Their adsorption capacity was demonstrated using Cu^{2+} ions, and compared with that of unmodified CCMNPs. The best adsorption conditions for Cu^{2+} from aqueous solution were determined at various initial ion concentration, initial pH, contact time and adsorbent concentration. The uptake stability of Cu^{2+} from aqueous solution and the regeneration of magnetic nanoadsorbents were carried out by adsorption and desorption process.

2. Materials and methods

2.1. Materials

$CuSO_4 \cdot 5H_2O$ ($M_w = 249.68$ g/mol, purity >99%) from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, were used as copper source. α-KA (99%), chitosan ($M_w = 6 \times 10^5$ with 80% deacetylation degree), ferric chloride 6-hydrate, ferrous chloride and sodium hydroxide (29.6%) were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Highly pure deionized

water (Shanghai Jingke Industrial Co., Ltd., SZ-93) obtained from a Labconco system (Shanghai Jingke Industrial Co., Ltd., China) was used throughout this work, and was used for the preparation of all of the solutions. All other chemicals were the analytic grade reagents commercially available, and used without further purification.

2.2. Preparation of maghemite nanoparticles

The maghemite nanoparticles were prepared by the existing method from Kang et al. [20]. Firstly, 6.7 g $FeCl_3 \cdot 6H_2O$ and 3.06 g $FeCl_2$ were dissolved in the 200 ml of deionized water under mechanical stirring, while the molar ratio of the Fe^{3+}/Fe^{2+} was fixed to 2:1. Then NaOH (5 M) solution was added dropwise into the above mixture with mechanical stirring until pH reached about 10. After an initial yellow solution, a brown precipitate was immediately formed. The brown precipitate was then heated at 80 °C for 30 min under vigorous stirring. Subsequently, the brown precipitate was isolated by an external magnetic field of 3000 G with the supernate decanted. To get the maghemite (γ-Fe_2O_3), freeze-dried brown precipitates were dispersed in 99% octyl ether. And the mixture was then heated to 250 °C under an air atmosphere, and maintained at this temperature for 2 h. The γ-Fe_2O_3 was collected via an external magnetic field after adding ethanol. To obtain the pure products, synthesized materials were rinsed with deionized water three times, and finally stored in 5 M NaOH solution for further use.

2.3. Preparation of CCMNPs

For coating magnetic nanoparticles with chitosan, 10 ml the above obtained maghemite solution and 1 ml Span-80 were dispersed in 50 ml chitosan solution (16%) which was prepared using 0.8 g chitosan dissolved in 25 wt% acetum solution under vigorous stirring of 2000 rpm. The reaction mixture was then sonicated in an ultrasonic cleaner (Shanghai Kudos Ultrasonic Instrument Co., Ltd., SK5200H) for 30 min. The coating process was carried out at 50 °C. The CCMNPs were recovered from the reaction mixture by placing the bottle on a permanent magnet with a surface magnetization of 3000 G. The prepared CCMNPs settled within 1–3 min, and then were washed with deionized water three times.

2.4. Surface modification of CCMNPs with α-KA

The α-KA-CCMNPs were produced according to the existing chemical method [21]. With mechanical stirring, 0.25 g α-KA was added to 5 ml acetic acid buffer (pH 5.6) which contained 100 mg CCMNPs. The pH of this mixture was adjusted to 4.5–5.0 using sodium hydroxide solution. Afterwards, sodium borohydride was added to the stirred mixture at 35 °C. The pH of the mixture solution was adjusted to 6.5–7.0 using hydrochloric acid solution, and the reaction was further stirred for 24 h. The reaction was terminated by 95% alcohol. The synthesized α-KA-CCMNPs were isolated, washed three to four times with ethanol and diethyl either, respectively. Subsequently, the products were dried in an oven. Finally, 53 mg α-KA-CCMNPs were obtained and characterized before their application.

2.5. Characterizations of the α-KA-CCMNPs

The dimension and morphology of CCMNPs and γ-Fe_2O_3 were observed by transmission electron microscopy (TEM) (Hitachi, H-800). The elemental information and structure of synthesized α-KA-CCMNPs were determined by an X-ray diffractometer (XRD) (Rigaku, D/max-2550PC) at ambient temperature. The instrument was equipped with a copper anode generating Cu$K\alpha$ radiation