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Adsorption of copper ions by ion-imprinted simultaneous interpenetrating network hydrogel: Thermodynamics, morphology and mechanism

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ABSTRACT

Cu(II) ion-imprinted hydrogel [Cu(II)-IIH] with interpenetrating polymer network (IPN) structure was prepared and its application to adsorb Cu(II) ions from aqueous solution was studied. The Cu(II)-IIH was prepared by UV-initiated simultaneous free radical/cationic hybrid polymerization. The adsorption capacity of the Cu(II)-IIH increased with the initial pH value of the solution, but decreased as the temperature rose from 303 to 323 K. Thermodynamic parameters such as the Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the Cu(II) ions adsorption were evaluated. It was suggested that the adsorption was a spontaneous, exothermic process with further decrease in the degree of freedom at the solid-solution interface due to the negative ΔS° value. The morphology study indicated that the copper adsorption caused significant changes to the hydrogel structure. Finally the adsorption mechanism was studied by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The results indicated that copper adsorption was mainly through interactions with the amide and ether groups.

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Introduction

Environmental contamination by toxic metal ions in aquatic ecosystems has been increasing with industrial growth and development in recent years [1]. Among all toxic metals, copper could cause serious environmental problems because it is widely used in paints and pigments, paper and pulp, fertilizer manufacturing, copper polishing, etc. Excessive uptake of copper can cause a lot of serious health problems such as damage of liver and kidney, anemia, immunotoxicity, etc. [2,3]. Therefore, in order to protect human health and the environment, it is very important to remove or minimize excess of copper in industrial effluents before discharging it into surface water, as well as into groundwater.

Compared with the conventional physicochemical technologies, the adsorption is demonstrated to be promising for heavy metal removal because of its low cost, high adsorption efficiency for low concentration metal ions [4,5]. It is based on utilization of various sorbents, such as agricultural wastes, biomass, clays, hydroxyapatite, silica gels and zeolites, as well as natural and synthetic polymers [6–8]. Nowadays, a special attention has been given to hydrogels which possess ionic functional groups that can absorb and trap metal ions from wastewater [9–11]. Compared with conventional solid sorbents, the main advantages of hydrogels are desired tailored swelling and mechanical properties, easy handling and reusability [11].

Taking into account all the hydrogel adsorbents reported in the literature, the hydrogels based on ion imprinting technology have received considerable attention [12]. Ion-imprinted hydrogels are a class of materials with predetermined selectivity for analytical separation. In the process of ion imprinting, a functional monomer and a crosslinker are polymerized in the presence of a template ion. Then the template is extracted leaving sites which are complementary in both shape and chemical functionality to those of the template [13]. This hydrogel then becomes capable of selectively adsorbing the template species. Such an imprinted polymer shows an affinity for the template ion over other coexisting metal ions.

To develop an adsorption process by using the ion-imprinted hydrogels for industrial applications, it is desirable to better understand the metal uptake process. Advanced instruments such as X-ray photoelectron spectroscopy (XPS) and Fourier transform

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infrared (FTIR) spectroscopy can provide good tools to achieve the goal because they can provide insight into environmental processes at the molecular level [14,15].

In our previous study [16], simultaneous interpenetrating network technique was employed to prepare Cu(II) ion-imprinted hydrogel [Cu(II)-IIH] with improved mechanical strength. The adsorption kinetics and isotherm, selective adsorption ability and reusability were investigated. The present work was in continuation to our previous study. In the current report, the Cu(II)-IIH was characterized using thermogravimetric analysis (TGA) and scanning electron microscopy/energy dispersive X-ray (SEM/EDX). Several factors affecting the sorption of Cu(II) ions, such as pH, initial concentration and temperature were investigated. Finally the adsorption mechanism was better elucidated via FTIR in combination of XPS.

Experimental

Materials

Acrylamide (AAm), ethylene glycol dimethacrylate (EGDMA) and triethylene glycol divinyl ether (DVE-3) were purchased from Sigma–Aldrich Chemicals and used without further purification. Free radical photoinitiator (Darocur 1173 from Ciba Specialty Chemicals) and a diaryliodonium hexauorophosphate salt (DAI from Ciba Specialty Chemicals) were respectively used to initiate the free radical and cationic polymerization. Copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$)] was purchased from Shanghai Chemical Reagents Co., and was heated in order to remove crystal water before used.

Preparation of Cu(II) ion-imprinted hydrogel [Cu(II)-IIH]

The Cu(II)-IIH was prepared according to our previous report [16]. Briefly, a mixture of 0.96 g AAm, 1.44 g DVE-3, and 1.86 g Cu $(NO_3)_2$ were first dissolved in ethanol. Then, 0.048 g crosslinker EGDMA, 0.0192 g free radical photoinitiator, and 0.0288 g cationic photoinitiator were added. The mixture was introduced between two glass plates and cured under a high-pressure mercury lamp for 1 h. Subsequently, the film was treated with 1.0 mol/L HCl to completely leach Cu(II) ions. At last, the hydrogel was washed to neutralization, and dried at 60 °C under vacuum, resulting in the desired Cu(II)-IIH.

Adsorption capacity study

Adsorption study was carried out in magnetically stirred, thermostated cylindrical glass vessels in batch conditions. The sample was added into the heavy metal ion solution to determine the metal ion adsorption capacity of the samples under non-competitive conditions. The pH of the metal feed solutions was adjusted before the sample was applied for the adsorption process. Amount of the residual metal ion in the solution was determined using an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) after 24 h [11]. Amount of adsorbed metal ion (Q, mmol/g) was calculated from the following equation:

$$Q = \frac{(C_0 - C)V}{m}$$

where C_0 (mmol/L) and C (mmol/L) were the metal ion concentrations before and after adsorption respectively. V (L) was the volume of the solution added and m (g) was the mass of the xerogel.

Thermogravimetric analysis

The thermal stability was evaluated by thermogravimetry using a TA Instruments TGA 2950 thermogravimetric analyzer in the temperature range of 30–800 °C, at a scanning rate of 10 °C/min.

Surface morphology study

SEM/EDX was used to investigate the cross-section morphology of the prepared hydrogels. Measurements were taken on a FEI QUANTA 200 scanning electron microscope. Before SEM measurements, hydrogels were lyophilized. Then the freeze-dried samples were fractured carefully in liquid nitrogen, and then fixed on tubs with sputter coated with gold before observation.

Adsorption mechanism study

FTIR spectra were recorded on a Bruker Vector 22 FT spectrometer in the range 4000–400 cm^{-1}. XPS spectra were recorded by a Perkin-Elmer PHI 550 ESCA/SAM spectrometer using Mg Kα X-ray source.

Results and discussion

Preparation of Cu(II) ion-imprinted hydrogel [Cu(II)-IIH]

Free radical/cationic hybrid polymerization was usually employed to prepare simultaneous interpenetrating polymer network (IPN) materials [17,18]. In the present work, template Cu(II) ions firstly coordinated to the $-NH_2$ from acrylamide (AAm) and —O— from triethylene glycol divinyl ether (DVE-3). Then the Cu(II)-IIH was synthesized by UV-initiated free radical/cationic hybrid polymerization of complexes Cu(II)/AAm and Cu(II)/DVE-3 with EGDMA as a crosslinker. In the polymerization system, Cu(II)/AAm polymerized by free radical mechanism, and Cu(II)/DVE-3 polymerized by cationic mechanism simultaneously. Finally Cu(II) ions were leached from the hydrogel leaving behind some cavities with predetermined orientation and special size of templates. The obtained Cu(II)-IIH consisted of two polymer networks. One was poly(acrylamide) (PAAm), and the other was poly(triethylene glycol divinyl ether) poly(DVE-3). The proposed preparation process was shown in Fig. 1.

Adsorption equilibrium study

Effect of pH on adsorption

Metal ion sorption on sorbent is influenced by pH value due to the competition between the metal ions and H^+ for active sorption sites, so the pH value is one of the most important factors affecting the sorption of Cu(II) ions from aqueous solutions. As shown in Fig. 2, the removal percentage of metal ions increased sharply along with the increase of the pH value. That was to say, the adsorption capacity of the Cu(II)-IIH to Cu(II) ions in weak acidic solution was higher than that in strong acidic solution. The reason could be explained that, under strong acidic conditions, the Cu(II)-IIH surface was completely covered with H^+, and Cu(II) ions could not compete with them for adsorption sites [19]. However, with the increase of pH value, the competition from H^+ decreased and Cu(II) ions could be adsorbed on the adsorbent quite easily. The similar results were obtained by other researchers as reported elsewhere [20,21]. Experiments were not carried out at pH values above 5.0 due to the fact that Cu(II) ions precipitation occurred at higher pH values. In order to avoid the formation of precipitation in the aqueous solution, the pH of 5.0 was selected as the initial pH value of Cu(II) ions solution for subsequent adsorption experiment.

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