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Fast and efficient removal of copper using sandwich-like graphene oxide composite imprinted materials

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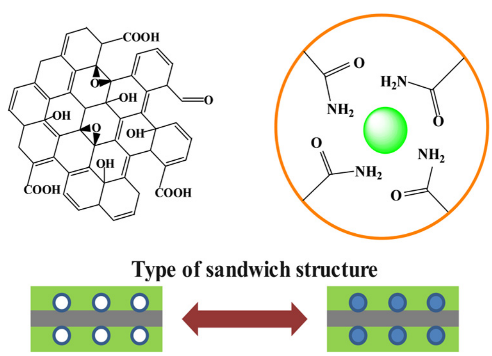
HIGHLIGHTS

- A sandwich-like graphene oxide composite copper imprinted polymer was prepared.
- Effect of solvents on polymerization and adsorption properties was investigated.
- Copper-imprinted polymer has fast adsorption kinetics and high adsorption capacity.
- Polymers have good specific identification for Cu(II) in presence of other ions.

GRAPHICAL ABSTRACT



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ABSTRACT

A sandwich-like ion-imprinted polymer (IIP) was prepared using functional graphene oxide (GO) as the support, acrylamide as the functional monomer, and ethylene glycol dimethacrylate as the crosslinking agent in the presence of copper ions with various solvents (porogen). The effect of solvent type on polymerization process and properties of polymers was investigated. Methanol/acetonitrile was considered as the best porogen, and almost no redundant secondary polymer particles were produced. This can be explained by the good thermodynamic compatibility and slow phase separation property of monomers and crosslinking agents in polymerization process. Fourier-transform infrared spectroscopy, Energy dispersive X-ray spectroscopy, thermogravimetric analysis, and scanning electron microscopy were used to confirm the prepared IIP. The effects of pH, initial concentration of the Cu(II) aqueous solution, and contact time on adsorption behavior were investigated. Adsorption by prepared IIP was fast (adsorption equilibrium was reached within 15 min) and followed pseudo-second-order kinetic and Freundlich isotherm models. The IIP showed a good imprinted factor and the maximum adsorption capacity was up to 132.77 mg g^{-1}, which is higher than that of IIP prepared by bulk polymerization, owing to the large surface area of GO and surface imprinted technology. The selectivity factors for Cu/Zn, Cu/Ni, Cu/Co, and Cu/Cd were 36.33, 8.44, 77.3, and 8.5, respectively. The polymer showed a widely application prospect for recovery of Cu ions from aqueous solutions.

1. Introduction

Rapid industrial development in China has led to concern regarding the environmental impact of the discharge of increasing amount of industrial wastewater. In particular, industrial wastew-

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ater containing heavy-metal ions, such as copper, zinc, and lead, is one of the sources of severe pollution. Such wastewater is toxic and the complex compositions change rapidly. Copper ion is a common toxic contaminant in wastewater, and excessive amounts of Cu(II) are harmful to the environment and living organisms [1]. Various techniques have been developed for removal of copper ions from wastewater [2,3], e.g., chemical precipitation [4], adsorption [5], ion exchange [6], membrane filtration [7], and electrochemical treatment [8]. Among these methods, adsorption is deemed to be the most widely used and economically feasible alternative due to high efficiency and low cost. Various adsorbents, such as active carbon, molecular sieves, resins, and bio-adsorbents, are widely used for the treatment of wastewater containing heavy metals [9]. However, most of the adsorption materials are non-selective and show a low adsorption capacity and slow adsorption kinetic. Therefore, development of high selective adsorbents for fast removal of heavy metal ions has become the current research hot.

Ion-imprinting technology (IIT) is attracting increasing attention because of its structure predictability, recognition specificity, and universal applicability [10,11]. It is widely used in many fields including separation, catalysis, and detection. Ion-imprinted polymers (IIPs) are prepared by copolymerization of functional monomers and cross-linkers in presence of a target ion based on specific coordinative or electrostatic interactions. Removal of the template ion with an eluent results in the formation of three-dimensional specific recognition cavities in the polymer matrix [12,13]. However, some problems such as incomplete removal of template and slow mass transfer property restrict the use of traditional IIPs [10,14,15]. The surface imprinting technique, which makes binding sites locate on the adsorbent surface or in a thin surface layer, overcomes these problems and gives highly efficient removal performance of template ions, low mass-transfer resistance, and good accessibility [16,17]. Li et al. [18] used a surface-imprinting technique with activated carbon as the support to prepare a polymer for selective solid-phase extraction of Cu(II); the maximum static adsorption capacities of the ion-imprinted and non-imprinted adsorbents were 26.71 and 6.86 $mg\,g^{-1}$, respectively. Yan [19] synthesized a Pb(II)-IIP using a surface-imprinting technique; the fast kinetics and the satisfied adsorption capacity were obtained.

Graphene oxide (GO) with a large surface area and numerous oxygen atoms is a promising material for heavy-metal removal. However, the direct use of GO as an adsorbent for heavy-metal ions is impractical [20]. GO tends to aggregate in a layer-by-layer mode because of strong interplanar interactions, which is not favorable for regeneration of adsorbent [21]. In addition, GO is also unstable at high temperature. For better practical applications, it is therefore necessary to modify GO or prepare GO composite materials to improve the stability of GO [22,23].

Due to the unique surface properties of GO, modified or functionalized GO can be used as a solid support for IIPs. The large specific surface area and two-dimensional nanosheet structure of GO are expected to give a high adsorption capacity and fast mass transfer property. Liu et al. [24] synthesized a novel GO-based cadmium-imprinted polymer with a high adsorption capacity and fast adsorption kinetics. Pan et al. [25] prepared a GO-based molecularly imprinted polymer for fast recognition and capture of luteolin. Although many GO-based polymers have been prepared, the effect of solvent type on polymerization has not been studied.

In this study, novel copper-ion-imprinted polymers based on functionalized GO were synthesized using a surface-imprinting technique with acrylamide (AM) as the functional monomer. The combination of IIP and GO using a surface-imprinting technique provides selective performance with fast mass transfer property and also can solve some problems associated with practical applications of GO. For surface-imprinting techniques, the solvent type affects the inner structure of the IIP and polymer-gel production. Various polymerization solvents were used to avoid polymer-gel production. The imprinted polymer was characterized using Fourier-transfer infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Energy Dispersive X-ray spectroscopy (EDX). The effects of initial pH, initial Cu(II) concentrations, and contact time on the adsorption behavior of copper were investigated. The thermodynamics and kinetics of the adsorption process were also studied to explore the adsorption mechanism. The reusability of the prepared adsorbent was also investigated.

2. Experimental

2.1. Materials and analysis

GO was purchased from Nanjing JCNANO Co., Ltd. Ethylene glycol dimethacrylate (EGDMA), acrylamide (AM), 3-(Trimethoxysilyl) propyl methacrylate (MPS) and azodiisobutyronitrile (AIBN) were obtained from China National Pharmaceutical Group Corp. All other chemicals were analytical grade and purchased from Beijing Chemical Factory. Copper (II) aqueous solutions were prepared using $Cu(NO_3)_2{\cdot}3H_2O$. Deionized water was used to prepare all solutions. UV–vis spectroscopy (UV-1800, Shimadzu, Japan) was used to determine the Cu(II) concentrations in aqueous solutions. A pH-meter (UB-7, Denver, USA) was used to measure the pH of aqueous solutions.

2.2. Characterization

FT-IR spectra (FT-IR 8000, Shimadzu, Japan) of the IIPs were recorded before and after elution. GO-IIP was mixed with KBr and pressed into pellets. The particle morphology was examined using SEM (S-4700, Hitachi, Japan). TGA was performed on a TG thermal analyzer (TG209C, Netzsch, Germany) in a dynamic N_2 atmosphere from 25 to 800 °C. EDX (S-4700 SEM-EDS, Hitachi, Japan) was used to detect copper in the IIP before and after elution. N_2 adsorption–desorption measurements were carried out using a Belsorp-Max surface area and pore size analyzer. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volume and pore size distribution were calculated using the Barrett–Joyner–Halenda (BJH) model.

2.3. Preparation process of the imprinted polymer

2.3.1. Modification of GO

In a typical procedure, a certain amount of GO was dispersed in methanol and the mixture was ultrasonicated for 60 min. 3-(Trimethoxysilyl) propyl methacrylate (4 mL) and $NH_3{\cdot}H_2O$ (3 mL) were then added to the above mixture. The reaction was continued with stirring for 24 h at 60 °C. After that, the modified GO (GO-MPS) was separated by high-speed centrifugation and then washed several times with absolute ethanol and dried under vacuum.

2.3.2. Preparation of Cu(II)-imprinted polymer with GO as support (GO-IIP)

GO-IIP was prepared by precipitation polymerization using surface IIT. $Cu(NO_3)_2{\cdot}3H_2O$ (0.1 mmol) and AM (0.4 mmol) were added to methanol/acetonitrile. The solution was stirred mechanically for 1 h to enable self-assembly of Cu(II) and AM. GO-MPS was dispersed in the mixture ultrasonically and then EGDMA (2 mmol) was added. The above mixture was purged with N_2 and then AIBN was added to the system. The mixture was polymerized in an oil