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Full Length Article

Synthesis and application of ion imprinting polymer coated magnetic multi-walled carbon nanotubes for selective adsorption of nickel ion

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ABSTRACT

A novel nickel ion imprinted polymers (IIPs) based on multi-walled carbon nanotubes (MWCNTs) were synthesized inverse emulsion system, using chitosan(CS) and acrylic acid as the functional monomers, Ni (II) as the template, and N' N-methylene bis-acrylamide as the cross-linker. The chemical structure and morphological feature of the IIPs were characterized by scanning electron microscopy (SEM), Thermogravimetry (TG), X-ray diffraction (XRD), and Fourier transform infrared spectrometer (FTIR). The studies indicated that the gel layer was well grafted on the surface of MWCNTs. Studies on the adsorption ability of the IIPs, by atomic absorption spectrophotometry, demonstrated that IIPs possessed excellent adsorption and selective ability towards Ni (II), fitting to pseudo second-order kinetic isotherms and with a maximum capacity of 19.86 mg/g, and selectivity factor of 13.09 and 4.42. The electrochemical performance of ion imprinting carbon paste electrode (CPE/IIPs) was characterized by Cyclic voltammetry (CV). Studies have shown that CPE/IIPs showed excellent electrochemical performance.

1. Introduction

With fast development of industry, lots of heavy metal pollutants from metallurgy, coal chemical, electrolytic plating and pharmaceutical enterprises were discharged into environment every year. With great toxicity, heavy metal ions are prone to collection and expansion in the biological chain. The heavy metal ions into human body can not exist in the form of ions. By combining with the organic compositions in human body, metal complex or metal chelates were produced, harmful to human [1–5]. For instance, the cadmium rice, itaiitai disease, minamata disease in China, America, Canada, Japan and other industrial countries, all of which were evidence of damage on human from heavy metal pollution. Consequently, water pollution of heavy metal ions has already seriously done harm to ecological environment and human beings. Nowadays, the common heavy metals with toxicity include Hg, Ni, Cd, Cr, Pb, Cu, etc. [6–11].

Nickel ions are the necessary microelements for human body and participate in the metabolism of human protein and adjustment of hormone. Besides, nickel ion also plays a role in stimulating hematopoiesis function, promoting red blood cell regeneration and function the stability of labile factor during coagulation process. However, long-term intake of and exposure to nickel metal seriously impacted on the normal human metabolism, causing nickel dermatitis. Meanwhile, nickel also irritates to respiratory system, inducing hypercalcemia, as well as leads to occupational diseases [12–15].

In recent years, various methods in China have been adopted to process the heavy metal ions in waste water, such as physical treatment, sedimentation, chemical reduction, and biological techniques [16–19]. However, the heavy metal ions with low concentration, especially the trace heavy metal ions in water can not be effectively removed via traditional method, which serves as one of the major problems for water treatment. Ionic imprinting technique has advantages of high adsorption capacity, good selectivity, and reusability so that it can be a new-type adsorption method attracting extensive attention from many researchers [20,21].

The ionic imprinting technique has been seen a rapid development these years. Different ion imprinted polymers were successfully prepared. Based on the template of heavy metals, rare earth elements, etc., the new-type functional monomers have already been found. With increasingly in-depth searches and ripeness of the ionic imprinting technique, its preparation technology has been gradually improved. Ion imprinted polymers have been widely used in the fields of electrochemical sensor, chromatographic analysis, and solid-phase extraction. The general preparation process of ion imprinted polymers can be concluded as below [22–29]:

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1) Prepolymerization

The monomer- template ionic polymers were prepared through the interaction of functional groups between the template and functional monomers. Because the combination of template and functional monomers was formed by sequestration, the combination and rupture velocity of coordination bonding could be adjusted by changing relevant conditions.

2) Crosslinking

The prepolymerization products highly cross-linked and polymerized with the moderate cross-linking agent so as to prepare highly cross-linking rigid polymer and to keep the stability of polymer's structure and shape in following experiments.

3) Desorption

The proper eluent was used to make the polymer released from the template ions via desorption.

In this work, surface imprinting technique was adopted in this paper to make chitosan and acrylic polymer modified on the surface of carbon nanotube, and the nickel ion imprinted polymer was successfully prepared. Some approaches like SEM, TG, XRD and FTIR were used to characterize its chemical structure performance and appearance features. The adsoprtion capacity and selectivity behavior of the imprinted materials were also described and discussed.

2. Material and methods

2.1. Apparatus and reagents

Multi-walled carbon nanotubes (MWCNTs, 20–30 nm) were obtained in Beijing Bo Yu high-tech new material technology Co., Ltd. (China). Low molecular weight Chitosan(CS, powder) with 80–90% degree of deacetylation, N, N-methylene double acrylamide (MBA), acrylic acid (AA), ammonium persulfate, sodium bisulfite, acetic acid, nickel chloride, sodium tartrate, ammonia (25%), ammonium chloride, butyl ketone oxime, graphite, sodium hydroxide and ethylenediamine tetraacetic acid disodium salt (EDTA-Na) were purchased in Tianjin Da Mao chemical reagent factory Co., Ltd. (China). All the chemicals used in this work were of analytical grade. Double distilled water was used in the all experiments.

2.2. Instrumentations

SEM images were obtained by using a field emission SEM (Hitachi, S-4800). TEM image was obtained by using transmission electron microscopy FT-IR spectra of samples were recorded with KBr pellet in the range of 500–4500 cm^{-1}. XRD patterns were recorded by a D/MAX2500PC X-ray diffraction spectrometer (Bruker, German) at a scan rate of 2θ from 10 to 90°. The electrochemical measurements were carried out using a CHI760E electrochemical workstation (CHI Instruments Co., Shanghai, China). A KCl calomel electrode as reference electrode and platinum wire electrode as counter electrode were used as the reference and auxiliary electrodes, respectively (Leichi, China). Adsorption capacity was obtained by using Atomic absorption spectrophotometer (HITACHI, Japan).

2.3. Preparation of oxidized multi-walled carbon nanotubes

The MWCNTs were oxidized by nitration mixture. The first step was to modify the MWCNTs with carboxyl functional groups. 500 mg raw multi-walled carbon nanotubes were added to 70 ml nitration mixture solution (VH_2SO_4:$VHNO_3$ = 3:1) under stirring at 70 °C. And mixture solution was diluted by adding 500 ml distill water at room temperature. Next, the mixed solution was separated by the microporous membranes of 50 uM. Finally, the obtained products were dried under vacuum environment and 70 °C.

2.4. Preparation of magnetic multi-walled carbon nanotubes particles

The magnetic carbon nanotubes (Fe_3O_4/MWCNTs-COOH) were fabricated by the way of coprecipitation. A certain proportion of Multi-wall carbon nanotubes, $FeSO_4{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ were added into the flask with four necks, and appropriate amount of water was added as well. In the environment of nitrogen as protective gas, isothermal stirring was performed and temperature increased to 50 °C and the $NH_3{\cdot}H_2O$ was added into the solution under quick stirring. Finally, the magnetic carbon nanotubes were prepared.

2.5. The preparation of ion imprinted polymers

The carbon nanotube-based ion imprinted materials were prepared by modifying the chitosan and acrylic acid on the surface of carbon nanotubes by inverse suspension polymerization. 300 mg magnetic carbon nanotubes, 300 mg chitosan, 2 ml $Ni(Cl)_2$ (0.1 mol/L), and 4 ml acrylic acid were dissolved in 2% aqueous acetic acid. And the mixture solution was sonicated for 30mins. Then 50 ml liquid paraffin and 2 ml span-80 were added into the solution. With rapid and even agitation, the solution became the water-in oil emulsion. Then the ammonium persulfate and sodium bisulfate as initiators and N, N − methylene double acrylamide as cross-linking agent were added. After the completion of the 8-h reaction under return flow agitation and nitrogen environment, the mixture was cooled down to room temperature, the ethanol added for emulsification, and the magnetic composite material separated with a permanent magnet. Finally, 20 ml EDTA (0.1 mol/L) solution was used to soak the product to remove nickel ions, and after vacuum drying to constant weight, the carbon nanotube-based imprinted polymers (IIPs) were obtained. The preparation process of nickel ion imprinted polymers was showed in Scheme 1.

Excluding adding nickel ion solution in the preparation of non-ion imprinted materials, its other used agents are the same as those used in the preparation of ion imprinted materials. Besides, all their adding order, reaction duration, and preparation procedure stay the same.

2.6. Adsorption experiment

Adsorption kinetics could be used to describe the adsorption rate of Ni(II) imprinted polymer. 50 mg IIPs were added to 50 mg/L of nickel ion aqueous solution at 30 °C. The experiments were carried out at 0–30 mins to research the adsorption kinetics. The effect of pH on the adsorption process was evaluated in the pH range from 2 to 8 for 30 min. 50 mg IIPs were added to 10–60 mg/L of nickel ion aqueous solution for 30 min at 30 °C. 50 mg carbon nanotubes were added into 20 ml mixture solution (20 mg/L, ion concentration ratio is 1:1:1) of Ni (II), Pb (II) and Cu (II) for adsorption. The ion concentration of the solution after adsorption was measured by atomic adsorption spectrometry (aas).

The adsorption capacity and removal efficiency were calculated according to the equations as follows [30,31]:

$$q_e = \frac{(C_e - C_0)V}{m} \quad (1)$$

$$\eta\% = \frac{C_e - C_0}{C_0} \times 100\% \quad (2)$$