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A novel magnetic and hydrophilic ion-imprinted polymer as a selective sorbent for the removal of cobalt ions from industrial wastewater

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ABSTRACT

A novel magnetic cobalt ion-imprinted polymer (Co(II)-IIP) was prepared by precipitation polymerization using 1-vinylimidazole as a functional monomer. The relative selectivity coefficients of Co(II)-IIP for Co(II)/Cu(II), Co(II)/Cd(II), Co(II)/Zn(II), and Co(II)/Pb(II) were 19.99, 50.28, 11.02, and 7.56, respectively. The experimental datas fit well with the Langmuir adsorption isotherm. The max Co-adsorption capacity obtained from the Langmuir isotherm is 23.09 mg/g for Co(II)-IIP. D-R model suggests that chemisorption is the dominant adsorption mechanism. The kinetics studies indicated that the adsorption process closely correlated with a pseudo-second-order model. Co(II)-IIP can be reused more than four times, which demonstrate it have strong performance stability. TLC plates experimental verified that the imprinted material have good hydrophilic property. In addition, Co(II)-IIP can remove Co(II) ion with higher 96% from wasterwater, which confirms it is good adsorbents for the removal of Co(II).

1. Introduction

Cobalt, which is heavily used in industrial applications, especially in magnetic and stainless steels, electronics, porcelain, and radioisotope therapy, is now commonly found in industrial wastewater [1]. The damage from the low and media level radioactivity of cobalt undoubtedly creates a threat to human health [2]. Actually, it can produce a variety of undesirable effects such as vomiting, asthma, nausea, heart failure, and liver and thyroid damage in human beings [3,4].

Presently, there are many treatment technologies for the removal of cobalt, such as precipitation [5], ion exchange [6], biological technology [7], and adsorption [8]. Among them, adsorption is a commonly method used for treating industrial wastewater. Compared with other methods, the adsorption method has high efficiency, operational flexibility, and reversibility. However, traditional adsorbents have high costs, poor mechanical properties, weak selectivity, poor adsorption capacities, and low recycling rates, which hinder their large-scale use in industrial applications. Therefore, it is necessary and important to find a new adsorbent with high selectivity, large adsorption capacity, and good reusability.

Recent studies show that ion imprinting has excellent potential for metal ion adsorbents. Ion imprinting is an easy and promising separation method for the rapid preparation of organic polymeric and inorganic network-structured materials that selectively bind a template ion [9–11]. Furthermore, it has been successfully employed for the determination of many analytes such as Co(II) [12,13], Cr(VI) [14], Cu(II) [15], Li(I) [16], Cd(II) [17–19], Pb(II) [20–22], Ni(II) [23,24], and Ag(I) [25]. However, most traditional imprinting techniques suffer from low hydrophilicity, because most of the imprinted sites are synthesized from imprinted polymer functional monomers with low hydrophilicity in organic solvent environments. Several examples show the good hydrophilicity achieved with IIPs prepared using functional monomers, such as 4-vinylpyridine [26], methacrylic acid [27], which exhibit good hydrophilic properties. However, the effects of these attempts are not very obvious. To the best of our knowledge, 1-vinylimidazole was used as a functional monomer to significantly improve the hydrophilicity of the material. It may have additional hydrophilic groups that allow for the formation of hydrogen bonds in the water because it has one more nitrogen atom than 4-vinylpyridine. As far as we know, this functional monomer was applied to Co(II)-IIP for the first time in this study.

Traditional ionic imprinting techniques are based on 3D polymer networks and the templates are embedded deep inside the polymer matrices. Surface ion imprinting technique can overcome these drawbacks due to complete removal of templates, good accessibility to the target species. Our group [28] successfully

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synthesized Cu (II) ion-imprinted polymer on the surface of Fe_3O_4 particles by a surface imprinting technique combined with a sol-gel process. The magnetic ion-imprinted polymer could reduce complicated post-processing, which needs to filter and centrifugal. Therefore, it is necessary to develop new magnetic Co ion-imprinted polymer.

The main object of this study was to synthesize ion-imprinted polymers that exhibit a better hydrophilicity and magnetism, and a higher selectivity for Co(II). The structural characteristics of Co(II)-IIP were studied by Fourier transmission infrared spectra (FT-IR), scanning electron microscope (SEM), thermogravimetric analysis (TGA)and thin layer chromatography plate(TLC). The adsorption behaviors of Co(II)-IIP adsorbents toward Co(II) in aqueous solution were also investigated.

2. Experimental

2.1. Chemicals

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and ethyleneglycol dimethacrylate (EGDMA) were supplied by Xilong Chemical Co, Ltd. (Guangdong, China). N,N-dimethyl formamide (DMF), 2,2-azobisisobutyronitrile(AIBN) and 1-vinylimidazole were bought from Aladdin Chemistry Co., Ltd (Shanghai, China). Tetraethyl orthosilicate (TEOS), isopropanol, and ammonia solution (28%) were supplied by Pure Crystal Shanghai Reagent Co., Ltd. (Shanghai, China). Ferric chloride ($FeCl_3{\cdot}6H_2O$) and ferrous sulfate ($FeSO_4{\cdot}7H_2O$) were obtained from Shenyang Chemical Industry Corporation (Shenyang, China). Water was purified through a Milli-Q water system (Bedford, USA). All other chemicals were of analytical reagent grade.

2.2. Instruments and analytical methods

The infrared (IR) spectroscopy measurements were recorded with a Bruker (Ettlingen, Germany) Vertex 70 FTIR spectrophotometer. A ContrAA 700 (Analytik Jena, Germany) flame atom absorption spectrophotometry (FAAS) was used for the determination of the cobalt ions. The morphologies of Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2-IIP were observed using a scanning electron microscope (SEM, Japan, Shimadzu). A WF-4000C microwave synthesizer was used for heating (Preekem Shanghai, China). Thermogravimetric analysis (TGA) was carried out using a DSC/DTA-TG (STA 449C Jupiter Netzsch, Germany). X-ray powder diffraction (XRD) measurements were carried out with a Bruker D8 diffractometer (Bruker, Germany).

2.3. Preparation of Co(II)-imprinted polymer (Co(II)-IIP)

2.3.1. Preparation of Fe_3O_4 particles

Fe_3O_4 particles were prepared according to the method described by our previous research [29]. a solution containing 13.5 g $FeCl_3$ and 6.95 g $FeSO_4$ was prepared with deoxygenated (nitrogen-purged) water. Then 40 mL 28% $NH_3{\cdot}H_2O$ was slowly added into the solution with vigorous agitation; the as-obtained mixture was aged (under vigorous agitation) at 90°C for 1 h. Finally, the precipitate was collected using a magnet and washed three times with methyl alcohol and distilled water, consecutively.

2.3.2. Preparation of Fe_3O_4@SiO_2

First, 5.00 g magnetite nanoparticles were dispersed in a mixture of 250 mL isopropyl alcohol and 20 mL ultrapure water under ultrasonic vibration for 30 min, and then 10 mL 25 wt% ammonia aqueous solution and TEOS (33 mL) were added in sequence. The mixture was subjected to continuous stirring at room temperature (RT) for 12 h. Finally, the precipitate was collected using a magnet and washed four times with methyl alcohol and distilled water, consecutively.

2.3.3. Preparation of Co(II)-imprinted polymers (Co(II)-IIP)

As shown in Fig. 1, ion-imprinted polymer materials by precipitation polymerization were prepared.

In the first step, under heating conditions, 1.46 g $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in 30 mL DMF and 50 mL of methanol, then purged with nitrogen (10 min), and the mixed solution was added with 0.906 mL 1-vinylimidazole. Finally, the mixture was stirred for 3 h in reflux (60°C) conditions. In the second step, 4.00 g Fe_3O_4@SiO_2 and 9.91 g EGDMA were added to 100 mL of methanol, and ultrasonically mixed for 20 min. The suspension and 0.1 g AIBN were added to was added to the mixed solution of first step, the

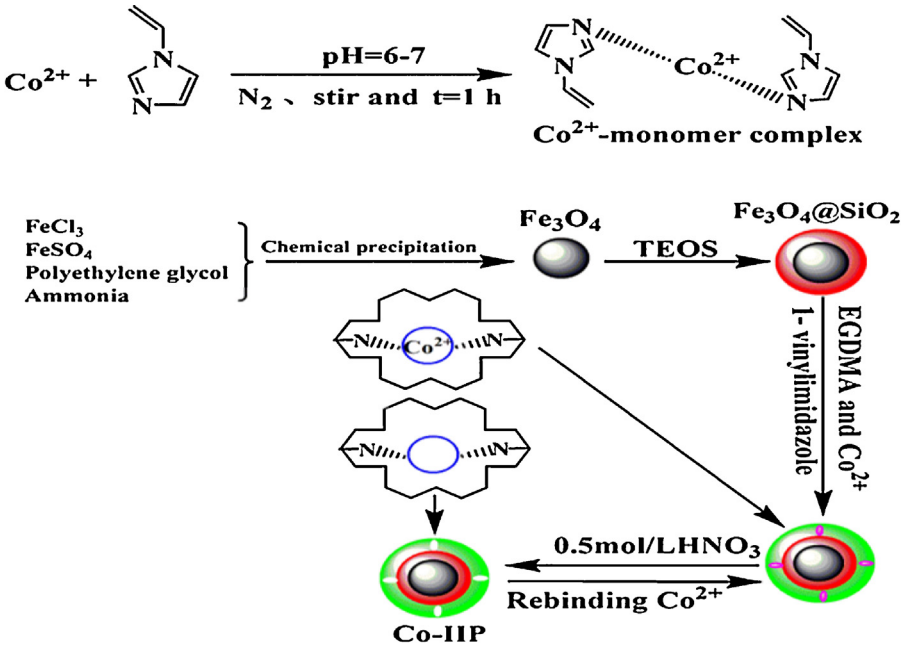

Fig. 1. synthesis rout for Co(II)-IIP.