Journal of Hazardous Materials 341 (2018) 355–364

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Preparation and adsorption characteristics of an ion-imprinted polymer for fast removal of Ni(II) ions from aqueous solution

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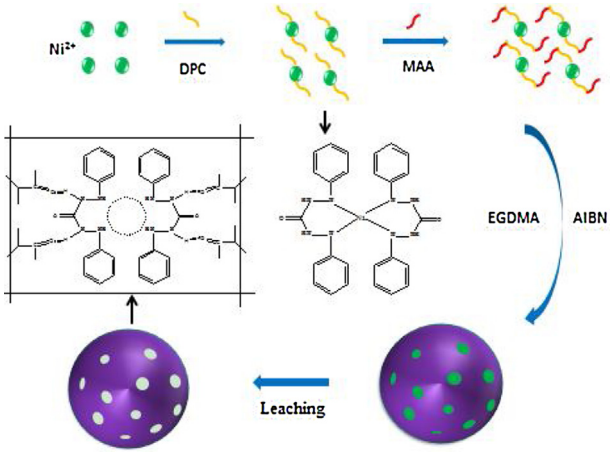
HIGHLIGHTS

- A novel Ni(II)-IIP was prepared by bulk polymerization.
- The prepared polymers have irregular shapes and three-dimension network structure.
- Ni(II) ion can be eluted successfully by HCl aqueous solution.
- Adsorption equilibrium was reached within 30 min.
- The maximum adsorption capacity is higher than other sorbents reported previously.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 February 2017
Received in revised form 17 May 2017
Accepted 6 June 2017
Available online 8 June 2017

Keywords:
Bulk polymerization
Ion-imprinted polymer
Ni(II)
Adsorption
Ligand

ABSTRACT

A novel Ni(II) ion-imprinted polymer (IIP) was synthesized by bulk polymerization for fast removal of Ni(II) ions from aqueous solution. Effects of preparation conditions on adsorption performance were investigated. Diphenylcarbazide (DPC) and N,N-azobisisobutyronitrile (AIBN) were used as ligand and initiator, respectively. Various monomers, solvents, cross-linking agents and molar ratios of template, monomer and cross-linking agent for polymerization were studied to obtain the largest adsorption capacity. The prepared Ni(II)-IIPs were characterized using Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX) and thermogravimetric analysis (TGA). The elution process has no influence on the three-dimension network structure observed on the surfaces of Ni(II)-IIPs. Ni(II) ions could be eluted from IIPs successfully with HCl solution. Effects of operating time, pH and initial concentration of Ni(II) in aqueous solution on adsorption performance were investigated too. The adsorption equilibrium was reached within 30 min. The maximum adsorption capacity of Ni(II)-IIPs was 86.3 mg g^{-1} at pH 7.0 with initial Ni(II) concentration of 500 mg L^{-1}. The adsorption by Ni(II)-IIPs followed a pseudo-second-order kinetic and Freundlich isotherm models. The selectivity coefficients for all Ni(II)/interfering ions are larger than one because of the imprinting effect. The Ni(II)-IIPs also showed high reusability and stability.

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http://dx.doi.org/10.1016/j.jhazmat.2017.06.010
0304-3894/

1. Introduction

Nickel is a trace element in human nutrition and mainly comes from vegetable, grain and kelp. As we all know, whether heavy metal will be harmful to human body is determined by its amount. Diseases, such as diabetes, liver cirrhosis and uremia, are caused by lack of nickel. However, too high amount of nickel is hazardous to human body, especially to the skin. Neurological disorder will be caused when people are in contact with nickel for a long time. In addition, nickel will lead to nose cancer and lung cancer too. Nowadays, nickel is widely used in electrical, mechanical, chemical and building industries. Moreover, nickel also plays a key role in mining, smelting, steel production and processing industries, resulting in the heavy metal pollutions in soil and water [1]. Heavy metal in water generally has two forms: particles and dissolved ions. The pollution degree is often determined based on dissolved heavy metals. Worldwide agencies have defined the maximum allowable concentration of heavy metals in the water emissions. China has also introduced a series of standards in heavy metal pollution prevention [2–5]. Therefore, it is urgent and necessary to enrich and separate Ni(II) ions from wastewaters.

Various conventional technologies have been used for removing nickel ion from wastewaters, such as chemical precipitation, membrane filtration [6,7], ion exchange [8,9], activated carbon adsorption [10,11] and electrolysis. However, these conventional technologies show lots of disadvantages, such as secondary pollution, just suitable for simply system, short service life, low processing capacity, high cost, low selectivity and highly energy-consuming. Therefore, a low-cost, economic and pollution-free technique with both high adsorption capacity and selectivity is badly in need of development.

Molecular imprinting as a kind of special technology is realized by the specific identification. A molecularly imprinted polymer is generally prepared by mixing the template molecules with functional monomers first. Then the cross-linking agents and initiators are added for polymerization. Next, the template molecules are removed with a physical or chemical method. Finally, a molecularly imprinted polymer with full of space cavities which match well with the target molecules is completely prepared [12,13]. Mosbach et al. [14]. successfully synthesized the theophylline imprinted polymer for the first time, which opened the door of molecular imprinting technique. Ion imprinting can be seen as a branch of molecular imprinting and plays an important role in the recovery of metal ions and treatment of wastewaters [15]. Various methods, such as bulk polymerization [16], precipitation polymerization [17], sol-gel polymerization [18,19], suspension polymerization [20] and surface imprinted technique [21–23], have been used for the preparation of ion imprinted polymers. In the last century, Nishide et al. [24]. synthesized the first ion-imprinted polymer (IIP) with 4-vinylpyridine (4-VP) as the ligand, which showed good selectivity for target ions. Since then, ion imprinting technology attracted great attention of many scholars in the world. Kato et al. [25]. used vinyl imidazole and VP as the monomers and divinylbenzene (DVB) as the cross-linking agent for self-assembly. Yan et al. [26]. successfully obtained a Pb(II)-IIP using a surface-imprinting technique, which showed good adsorption performance for lead ion in the water. IM et al. [27]. prepared the organic-inorganic hybrid silica gel with amine, amide and sulphur on its surface. This prepared polymer could efficiently separate the mixture of copper, zinc and cadmium ions.

In this work, Ni(II)-IIP was synthesized by bulk polymerization with DPC as ligand and AIBN as initiator for removal of Ni(II) ions from aqueous solution. Effects of DPC and AIBN dosages on adsorption performance were studied. Adsorption behaviors with various functional monomers, cross-linking agents and solvents were also investigated. The prepared IIPs were characterized using SEM, FT-IR, EDX and TGA. In addition, effects of adsorption conditions, such as adsorption time, pH and initial Ni(II) concentration, on adsorption capacity were studied too. Na^+, K^+, Mg^{2+}, Al^{3+}, Ca^{2+} and Ba^{2+} were selected as interfering ions to investigate the selectivity of Ni(II)-IIPs for Ni(II) ions. Finally, the reusability and stability of Ni(II)-IIPs were studied.

2. Material and methods

2.1. Reagents

Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Beijing J&K Scientific Ltd. AIBN, methanol, chloroform, sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), magnesium nitrate ($Mg(NO_3)_2$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Beijing Chemical Plant. DPC was obtained from Tianjin FuChen Chemical Reagent Factory. Nickel nitrate ($Ni(NO_3)_2$) and calcium nitrate ($Ca(NO_3)_2$) were purchased from Guangdong Xilong Chemical Co., Ltd. Dimethylglyoxime, acrylamide (AM), 2-vinyl pyridine (2-VP), 4-vinyl pyridine (4-VP), 1-vinyl imidazole (VI), pentaerythritol triacrylate (PETA) and 1,1,1-trimethylol propane triacrylate (TMPTA) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the above reagents are analytical reagents and used without further purification.

2.2. Preparation of Ni(II)-IIP

As shown in Fig. 1, Ni(II)-IIP was synthesized through thermally induced free radical polymerization. First, DPC and Ni(II) ion were dissolved in methanol/chloroform mixed solvent which was stirred for 30 min. Then MAA was added with continuous stirring for 3 h to form a Ni(II)/DPC/MAA complex. Certain amounts of EGDMA and AIBN were added to the well-mixed solution with stirring for 20 min at room temperature. Finally, nitrogen gas was passed through the reaction chamber for 10 min to remove the oxygen. The mole ratio of Ni(II) ion, DPC, MAA and EGDMA was 1:2:6:30 and the addition amount of AIBN was 100 mg. The prepared solution was distributed into several sample bottles, which were sealed and placed in a 60 °C water bath for 24 h to complete the polymerization reaction. Then the obtained polymers were grounded into powder and then washed with methanol to remove the unreacted monomers, cross-linking agents and other ingredients. Then the treated polymers were washed with 1.0 $mol \cdot L^{-1}$ hydrochloric acid to elute Ni^{2+} and rinsed with deionized water. Finally, the wet polymer powders were placed in a 50 °C drying oven and then 62–200 μm dry polymer particles were sieved for adsorption study.

2.3. Characterization of Ni(II)-IIP

Fourier transform infrared spectra of polymers were carried out on a Nicolet 8700 attenuated total refection Fourier transform infrared spectrometer (Fisher Scientific, USA). The morphologies of particles were observed using a JSM-7800F scanning electron microscope (JEOL, Japan). The thermogravimetric analysis of IIPs was carried out on a TG209C thermal analyzer (Netzsch, Germany). The determination of the presence of nickel in IIPs was carried out on a S-4700 SEM/EDS energy dispersive X-ray diffractometer (Hitachi, Japan).

2.4. Adsorption procedure

Batch experiments were carried out to investigate the adsorption performances of Ni(II) ions from aqueous solution. Ni(II)-IIPs were synthesized with various monomers, crosslinking agents, solvents and various amounts of ligand and initiator. Then Ni(II)-IIPs