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Ion imprinted polymeric nanoparticles for selective separation and sensitive determination of zinc ions in different matrices

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HIGHLIGHTS

- Synthesis of nano-sized ion imprinted polymers for separation of zinc ions.
- Characterization studies of Zn-IIP by FT-IR, SEM, XRD and colorimetry.
- Highly selective and sensitive determination of Zn^{2+} in complex matrices.
- Rapid kinetics of adsorption and desorption of Zn^{2+} ion on the resulting IIPs.

GRAPHICAL ABSTRACT

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ABSTRACT

Preparation of Zn^{2+} ion-imprinted polymer (Zn-IIP) nanoparticles is presented in this report. The Zn-IIP nanoparticles are prepared by dissolving stoichiometric amounts of zinc nitrate and selected chelating ligand, 3,5,7,20,40-pentahydroxyflavone, in 15 mL ethanol-acetonitrile (2:1; v/v) mixture as a porogen solvent in the presence of ethylene glycol-dimethacrylate (EGDMA) as cross-linking, methacrylic acid (MAA) as functional monomer, and 2,2-azobisisobutyronitrile (AIBN) as initiator. After polymerization, Cavities in the polymer particles corresponding to the Zn^{2+} ions were created by leaching the polymer in HCl aqueous solution. The synthesized IIPs were characterized by scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, fluorescence spectroscopy and thermal analysis techniques. Also, the pH range for rebinding of Zn^{2+} ion on the IIP and equilibrium binding time were optimized, using flame atomic absorption spectrometry. In selectivity study, it was found that imprinting results increased affinity of the material toward Zn^{2+} ion over other competitor metal ions with the same charge and close ionic radius. The prepared IIPs were repeatedly used and regenerated for six times without any significant decrease in polymer binding affinities. Finally, the prepared sorbent was successfully applied to the selective recognition and determination of zinc ion in different real samples.

Introduction

Zinc ion (Zn^{2+}), as the second abundant transition metal, in human body plays very important roles in cellular metabolism, gene expression, apoptosis, neurotransmission, and so forth [1]. Zinc deficiency effects may be severe. They range from impaired neuro-

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psychological functions and wound healing to growth retardation, immune disorders and dermatitis. On the other hand, zinc could be toxic when exposures exceed physiological needs. After single or short-term exposure to water and beverages containing zinc at concentrations between 1.0 and 2.5 mg L^{-1} poisoning incidents with symptoms of gastrointestinal distress, nausea and diarrhea may be observed [1]. Therefore, due to the biological and environmental impact of zinc ion, introducing an efficient method for selective separation, purification and determination of Zn^{2+} ion in complex matrices is of continuing interest.

A high degree of selectivity is particularly desirable when a single compound is extracted from a complex matrix [2]. Recently, novel materials called ion imprinted polymers (IIPs) have been attracted much attention as a highly selective sorbents for the solid phase extraction in order to concentrate and clean-up samples prior to analysis [3,4]. IIPs show very interesting characteristics such as high selectivity, low cost, high surface area, durability and reusability [5]. A variety IIPs have been previously reported for separation and determination of copper [6], selenium [7], uranyl [8,9], mercury [3,10], cesium [11] potassium [12] and nickel [13] ions. Three steps are involved in the ion-imprinting process: (i) complexation of template (i.e., metal ions) to a suitable ligand, (ii) polymerization of this complex and (iii) removal of template after polymerization. After ion imprinting polymerization, the imprinted metal ion is removed from the polymeric particles by leaching with a mineral acid which caused leaving the cavities or "imprinted sites" in the polymeric particles that are complementary in shape and size of the imprinted metal ion. This imprinted polymeric material shows an affinity for the template ion over other structurally related compounds [6]. The high selectivity of IIPs can be explained by the polymer memory effects toward the metal ion interaction with a specific ligand, coordination geometry, metal ion coordination number, charge and size [14]. Morin (i.e. 3,5,7,20,40-pentahydroxyflavone) has been widely used as a complexing reagent in the extraction of different metal ions in both spectrophotometric and fluorimetric methods [15].

In this research, we report a simple and efficient synthetic method for preparation of ion imprinted polymeric nanoparticles for fast and selective extraction, preconcentration and determination of zinc ion in aqueous solutions. In the bulk polymerization process, morin, methacrylic acid (MAA), ethyleneglycoldimethacrylate (EGDMA) and 2,2′-azobisisobutyronitrile (AIBN) are used as Zn^{2+} ion selective complexing reagent, functional monomer, cross-linker and free radical initiator, respectively. The polymeric nanoparticles have been characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), colorimetry, thermal gravimetry (TG) and differential thermal analysis (DTA) techniques. After removal of Zn^{2+} ion from the polymeric network, the prepared Zn-IIP nanoparticle was applied for uptake of zinc ion from aqueous solutions, as solid phase extractor. Flame atomic absorption spectrometry (FAAS), as a standard technique, was applied for quantitative analysis of zinc containing aqueous solutions in all experiments.

Experimental

Materials

MAA, EGDMA, AIBN, and morin were obtained from Aldrich (Milwaukee, WI, USA). All of used solvents (e.g. acetonitrile, methanol, ethanol) and acids were of the highest purity available from Merck (Darmstadt, Germany) and used as received. Reagent grade $Zn(NO_3)_2.6H_2O$ and nitrate or chloride salts of other cations were purchased from Merck (Darmstadt, Germany) and used without any further purification. All solutions of metal ions were prepared with double distillated water.

Apparatus

Determination of zinc ion was carried out with a Shimadzu AA-670 atomic absorption spectrometer equipped with a Zn-hollow cathode lamp (HCL) and a deuterium background corrector, at respective wavelengths using an air–acetylene flame. The instrumental parameters were adjusted according to the manufacturer's recommendations as following conditions: central HCL wavelength: 213.9 nm; spectral bandwidth: 0.5 nm; Lamp current: 5.0 mA; Flow rate of air and acetylene gas: 8.0 and 1.7 L min^{-1}, respectively.

A digital pH meter, Metrohm model 632, equipped with a combined glass calomel electrode was used for the pH adjustments. The surface morphology of the polymeric beads was examined using scanning electron microscopy. SEM images were recorded on a Philips XL30 series instrument using a gold film for loading the dried particles on the instrument. Gold films were prepared by a sputter coater model SCD005 made by BAL-TEC (Switzerland). Agilent 7200 spectrophotometer and JASCO FP-6200 spectrofluorometer were used for recording the UV–Vis and fluorescence emission spectra at the temperature of 25.0 ± 0.1 °C. The FT-IR spectra (4000–500 cm^{-1}) were recorded on a Shimadzu FT-IR 8300 spectrophotometer. TG and DTA investigations were carried out using a Stanton Redcroft, STA-780 series with an alumina crucible, applying heating rate of 10 °C min^{-1} in a temperature range of 50–600 °C, under air atmosphere with the flow rate of 50 mL min^{-1} [16]. The sample mass used was about 3.0 mg.

Preparation of ion and non-ion imprinted polymeric nanoparticles

The Zn-IIP nanoparticles were prepared by thermal polymerization technique according to the previous reports [10,12]. The procedure of the Zn-IIP preparation is described in Scheme 1. For this purpose, 1.0 mmol of morin was added into 15.0 mL of ethanol/acetonitrile mixture (2/1; v/v) as porogen solvent, and then treated with 1.0 mmol of $Zn(NO_3)_2{\cdot}6H_2O$, as imprint metal ion, at room temperature under continuous stirring for 1 h. At the end of this process, the formed yellow complex was appeared. The Job's method, spectrophotometric and fluorescence techniques were used to confirmed the complex formation between Zn^{2+} ion and morin. In the polymerization procedure, MAA (6.0 mmol), EGDMA (20.0 mmol) and 0.30 mmol of AIBN were added as functional monomer, cross-linker and free radical initiator, respectively, to the initial solution and stirred at room temperature. The polymerization mixture was purged with N_2 gas for 10 min to remove its molecular oxygen, which traps the radicals and retards the polymerization. Then, the reaction vial was sealed and heated in an oil bath at 60 °C for 24 h under magnetic stirring at 400 rpm to complete the thermal polymerization. After polymerization process, the imprinted ion, (i.e. Zn^{2+} ion) was leached from the above synthesized polymer material via double stirring with 50 mL of HCl (50%; v/v) during about 18 h [11]. To evaluate the ion imprinted recognition properties of Zn-IIP, non- ion imprinted polymers (NIP) based on the Morin–MAA–EGDMA polymeric matrix were prepared as a control under the same procedure, but only in the absence of Zn^{2+} ion as template ion.

Sorption/desorption procedure

The sorption and desorption of the Zn^{2+} ions on the IIP and NIP nanoparticles in aqueous solutions were studied by batch experiments as follows: an aliquot of zinc solution (e.g. 25.0 mL of 0.10 μg mL^{-1}) was treated with 30.0 mg of polymeric nanoparticles at desired pH. The pH of the suspensions was maintained to 7.0 by adding sodium hydroxide or hydrochloric acid. The suspension was stirred for pre-selected periods of time using a magnetic