



Effect of porogen solvent on the properties of nickel ion imprinted polymer materials prepared by inverse suspension polymerization

Walid Meouche^{a,1}, Katri Laatikainen^b, André Margaille^a, Timka Silvonen^{b,2}, Heli Siren^c, Tuomo Sainio^b, Isabelle Beurroies^d, Renaud Denoyel^d, Catherine Branger^{a,*}

^a University of Toulon, MAPIEM Laboratory, EA 4323, CS 60584, 83041 Toulon Cedex 9, France

^b Lappeenranta University of Technology, Laboratory of Industrial Chemistry, P.O. Box 20, FI-53851 Lappeenranta, Finland

^c University of Helsinki, Department of Chemistry, Laboratory of Analytical Chemistry, PO Box 55 (A.I. Virtasen aukio 1), FI-00014 University of Helsinki, Finland

^d Aix-Marseille University, CNRS, MADIREL UMR 7246, 13397 Marseille Cedex 20, France

ARTICLE INFO

Article history:

Received 28 September 2016

Received in revised form 6 December 2016

Accepted 18 December 2016

Available online 21 December 2016

Keywords:

Ion-imprinted polymer

Inverse suspension polymerization

Porogen

Nickel

Selective adsorption

ABSTRACT

Ion-imprinted polymers (IIPs) for nickel were synthesized by inverse suspension copolymerization of vinylbenzyl iminodiacetic acid (VbIDA) with ethyleneglycol dimethacrylate (EDMA) in the presence of nickel(II) ions with various porogen solvents to study their impact on the IIPs properties. They were prepared with mixtures of acetonitrile and dimethylsulfoxide (DMSO), 50/50%v/v, for IIP-A/D and 2-methoxyethanol and DMSO, 50/50%v/v, for IIP-M/D. The structure and properties of these polymers were compared with those of IIP-D previously prepared with pure DMSO as porogen solvent. Although IIP-A/D and IIP-M/D were less porous than IIP-D, they presented better nickel adsorption properties and selectivity towards Zn²⁺, Co²⁺ and Pb²⁺. This is assumed to be the result of the stabilization of the ligand-metal complex during the polymerization process. Moreover, the nickel binding capacities of the prepared IIPs in competitive conditions are remarkably high (184 μmol/g for IIP-D, 170 μmol/g for IIP-A/D and 174 μmol/g for IIP-M/D). The impact of the VbIDA chelating monomer was highlighted by comparing the adsorption properties of a copolymer of methyl methacrylate (MMA) and EDMA with NIP-D. It was proved that the methacrylic polymer matrix has low binding properties.

© 2016 Published by Elsevier Ltd.

1. Introduction

Because of its natural presence in the earth crust and its large consumption in the industry (refining, electroplating, and welding), pollution of the environment by nickel has become an unavoidable concern. The presence of nickel in water is due to direct leaching from rocks and sediments [1]. Nickel is responsible for various pathologies such as skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning, stimulation of neoplastic transformation and cancer of the respiratory tract [1,2]. Moreover, all nickel compounds, except the metallic form, have been classified as carcino-

* Corresponding author.

E-mail address: branger@univ-tln.fr (C. Branger).

¹ Present address: University of Balamand, Faculty of Sciences Department of Chemistry, Balamand Al Kurah, Lebanon.

² Present address: IND & PLM, Orion Oyj, Tengströminkatu 8, FI-20360 Turku, Finland.

genic to humans [3]. For these reasons, there is a constant need for the extraction and quantification of nickel, as well as of most heavy metals.

Solid-phase extraction is widely used either for decontamination or preconcentration before a quantification step. For metal ions, it is currently based on ion-exchange or chelating sorbents [4,5]. These materials proved to be very efficient, with large adsorption capacities, good mechanical properties and reusability. Nevertheless, they are not adapted if selectivity is desired, for instance to recover a metallic compound. Selective extraction of metal ions from aqueous solutions can be successfully achieved using ion-imprinted polymers (IIPs) [6–9]. These polymers are prepared in the presence of an ion playing the role of a template in order to create binding cavities after its removal. The rigidity of the polymer network and the stability of the recognition cavities are provided by a high crosslinking rate. Chelating or ion-exchange functions are usually introduced in the form of a functional comonomer. This can be classical commercial monomers such as acrylamide [10], acrylic acid [11], methacrylic acid [12] or 4-vinylpyridine [13,14] or home-made monomers based on ligands such as benzo-15-crown-5-acrylamide [15], N-methacryloyl-(L)-histidine [16,17] or N-(3-vinylbenzyl)-2-(aminomethyl)pyridine [18] for example.

In order to favor the interactions with the liquid phase and to make the binding cavities accessible, imprinted polymers need to be porous materials. This is the reason why a solvent called “porogen” solvent is always used even when “bulk” polymerization is implemented. The role of this porogen agent for the elaboration of porous polymers has been intensively studied and is mainly related to its thermodynamic affinity with the monomers and the copolymer [19,20]. As far as imprinted polymers are concerned, the polarity of the porogen impacts the level of interactions between the template and the functional monomer. It is thus usually chosen in order to promote these interactions and therefore aprotic and low polar solvents are commonly preferred [8,21]. However for IIPs, the first requisite for the porogen, which is to dissolve the monomers, the initiator and the template, implies the use of protic and/or polar solvents because of the nature of the functional monomer and of the ion template. Although the impact of the porogen is well known, only few systematic studies have been carried out. Gladis and Rao used different porogens to synthesize IIPs for uranyl: 2-methoxyethanol, methanol, tetrahydrofuran (THF), acetic acid, dichloroethane, N,N-dimethylformamide (DMF) and toluene [22]. They showed that the selectivity varied with the polarity of the solvent with the best capacity and selectivity obtained with 2-methoxyethanol. More recently, Godlewska-Zylkiewicz et al. compared the performances of Pd(II)-IIPs prepared with chloroform, cyclohexanol and ethanol [23]. They concluded that the porogen did not significantly influence the analytical properties of the sorbent and they advise the application of polar porogen in case the IIP is planned to be used for the separation of analyte from aqueous samples.

In a previous work, we described a new route to synthesize IIPs in a bead format by inverse suspension polymerization [24]. As water is not used as the continuous phase, this method avoids the risk that the ion template leaves the suspension for the aqueous phase. In this preliminary work, IIPs for nickel were prepared with vinylbenzyl iminodiacetic acid (VbIDA) as the functional monomer and the very polar DMSO solvent was used to allow phase separation of the dispersed polymerization medium from the continuous non polar phase. In the present paper, we now investigate the role of the porogen on the IIPs properties. Moreover, the impact of interfering cations (Co^{2+} , Zn^{2+} and Pb^{2+}) on the adsorption kinetics of nickel was followed over a period of 24 h. Finally, a comparison was done with two reference materials: (i) a copolymer of methyl methacrylate (MMA) and ethyleneglycol dimethacrylate (EDMA) to evaluate the influence of the methacrylic polymer backbone and (ii) the commercial iminodiacetic acid (IDA) bearing Amberlite® IRC 748 to study the imprinting effect.

2. Experimental

2.1. Materials

Vinylbenzylchloride (90% technical grade), iminodiacetic acid (IDA), ethylene glycol dimethacrylate (EDMA) (98% technical grade), 2-methoxyethanol were used as received from Acros Organics. Dimethylsulfoxide (DMSO) and acetonitrile were used as received from Fischer Scientific (99% technical grade). Mineral oil ($d = 0.862$), azobis(isobutyronitrile) (AIBN), nickel (II) nitrate hexahydrate (99.9%, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate (>98%, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zinc(II) nitrate hexahydrate (>99%, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), lead(II) nitrate hexahydrate (>99%, $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), calcium nitrate tetrahydrate (>99%, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), tris(hydroxymethyl)aminomethane (TRIS) and 4-(2-pyridylazo) resorcinol (PAR) were used as received from Sigma Aldrich.

2.2. Instrumentation

FTIR spectroscopy was performed in transmission mode on KBr pellets (32 scans, resolution 4 cm^{-1}) on a Nicolet Nexus apparatus. Scanning electron microscopy (SEM) images were taken using a Philips XL30 microscope. A Shimadzu UV-2501 PC was used for absorbance measurements with one centimeter matched quartz cells. pH measurements were performed with a digital pH meter (Hanna Instruments, model HI 92240). Metal ion concentrations were determined by plasma emission spectroscopy (Iris Intrepid II XDL ICP-AES). All samples were analyzed at least twice and the duplicate determinations agreed within variation of 5%. The detection limit of the compounds with plasma emission spectroscopy was 0.1 mg/L .

Pore volume, surface area and pore size have been determined by N_2 adsorption at 77 K using an ASAP2010 from Micromeritics or a Bell Mini from Bell Japan. Prior to each experiment, samples were outgassed at 327 K under vacuum.

Download English Version:

<https://daneshyari.com/en/article/5159301>

Download Persian Version:

<https://daneshyari.com/article/5159301>

[Daneshyari.com](https://daneshyari.com)