Effect of template ion–ligand complex stoichiometry on selectivity of ion-imprinted polymers

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ABSTRACT

In order to highlight the importance of the complex stoichiometry during ion imprinted polymer (IIP) synthesis, we investigated the effect of the complex structure on IIPs selectivity by adjusting the complex stoichiometry before polymerization. 2-(aminomethyl)pyridine monomer (amp) was chosen as a functionalized ligand for nickel(II) ions and a polymerizable vinylbenzyl derivative (Vbamp) was prepared. Complex formation was studied by varying the nickel/Vbamp ratio and recording absorption spectra of the complexes at the polymerization conditions. Using a least-squares minimization scheme, the complex species distribution was successfully established. From these results, it was possible to choose the metal/ligand stoichiometry in the complex (1:1; 1:2 or 1:3) by adjusting the initial metal/ligand ratio. IIPs were then prepared by inverse suspension copolymerization of Vbamp with ethyleneglycol dimethacrylate (EDMA). Highly porous particles with good nickel binding capacity and good Ni/Zn selectivity even at acidic conditions were obtained. Equilibrium uptake of Ni(II) at pH 7 ranged from 0.12 to 0.2 mmol g^{-1} and relative selective coefficient was as high as 260 for the IIP prepared using the Ni(Vbamp)$_2$ complex.

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1. Introduction

Ion exchange and adsorption are safe and environmentally acceptable technologies for the recovery of valuable metals from either dilute or concentrated aqueous solutions. Industrial applications such as hydrometallurgy require selective, fast, inexpensive and stable ion-exchangers and adsorbents. Furthermore, it is also essential that the separation material can be regenerated using minimum amount of chemicals and energy. One type of ion exchangers and adsorbents are solid chelating separation materials, in which chelating ligands have been attached to solid matrix. These ligands act as donors of electrons and form coordinative bonds with metal cation acting as the central atom in metal chelates and complexes [1]. Thus, metal selectivity of such materials depends mainly on the ligand selectivity [2,3]. Although several commercial chelating materials have been available since the 1970s [4,5], there are still many applications for which sufficiently selective commercial ion exchangers or adsorbents are not found

from the markets. Thus, development of new highly selective ion exchangers and adsorbents remains a very challenging topic.

Imprinting technology is one solution for the preparation of separation materials with high selectivity. Synthetic imprinted polymers include in their network selective recognition sites prepared using a template (usually a molecule or an ion) incorporated in the polymer matrix during the polymerization process. Subsequent removal of the template is necessary for recognition to occur in the spaces created by the template [6]. Consequently, imprinted polymers present remarkable recognition properties that can be compared to those of natural biological receptors such as antibodies [7,8], molecularly imprinted polymers (MIPs) and ion-imprinted polymers (IIPs) were described for the first time in the same period, 1972 [9,10] and 1976 [11] respectively, but real development in imprinted materials has taken place more recently [11]. The main difference between MIP and IIP techniques is that MIPs generally interact via hydrogen bonds or van der Waals interactions with the template molecules, whereas IIPs form coordinative complexes with the template metal ions. Consequently, IIPs can be considered as chelating resins with improved selectivity due to the introduction of an imprinting effect during their preparation.

Four approaches have been used for the preparation of IIPs; co-polymerization of a ligand carrying a polymerizable functionality,

trapping of a ligand (without such a functionality), crosslinking of linear polymer chains and surface imprinting (which can involve chemical immobilization or trapping procedure) [12,13]. In all cases, the key step is the formation of the complex between the ligand and the metal ion. The complex can be isolated before polymerization but this requires an additional step in the IIP synthesis. For this reason, it can be more convenient to just mix the ligand and the metal ion to form the complex in the pre-polymerization medium before the polymer formation. Because of its simplicity, absorption spectroscopy is most commonly used to verify the complex structure before polymerization [14–20]. Continuous variation analysis originally introduced by Job [21] and ligand titration are normally used to produce the spectral data. In many cases, however, highly selective chelating ligands form more than one complex with the template metal ion and advanced chemometric methodology is needed to analyze the overlapping spectra. Least-squares (LS) minimization [22] is one of the methods that enable calculation of complex species distribution from the spectral data [23].

The objective of the present study is to investigate the effect of the template–ligand complex structure on IIP selectivity by adjusting the complex distribution before polymerization. For that purpose, absorption spectra were recorded at different metal/ligand ratios and the complex species distributions were obtained by analyzing the spectral data with a least-squares (LS) minimization scheme [22]. From these results, it was possible to choose the metal/ligand stoichiometry in the complex (1:1; 1:2 or 1:3) by simply adjusting the initial metal/ligand ratio in the polymerization mixture. To the best of our knowledge, such a route has never been investigated till now. It offers the advantage to control the complex stoichiometry in a very easy fashion without tedious isolation of the complex. As the complex stoichiometry might influence the selectivity of the binding sites of the IIPs, such an approach is expected to enhance the performance of the prepared IIPs.

Using this strategy, nickel-selective IIPs were prepared with 2-(aminomethyl)pyridine (amp) as the ligand. Amp is known to form complexes with nickel even at mildly acidic conditions [29]. Furthermore, stability constants of different Ni–amp and Zn–amp complexes indicate selective binding of nickel over zinc [30]. Amp was functionalized with a vinylbenzyl group (Vbamp) in order to be used as the functional monomer during the IIPs synthesis via the chemical immobilization route. Other nickel-selective chelating materials have been developed mainly for analytical applications such as selective separation and pre-concentration of nickel from aqueous solutions [24–28] Some of these materials were used to remove nickel from zinc solutions [24,25,28]. Although they had good selectivity, they suffered from low uptake capacity which prevented their use for industrial purpose. The aim of this work is to enhance selectivity while reaching high binding capacity.

The complex formation was therefore studied with Vbamp by varying the Ni(II)/Vbamp ratio and the anion (nitrate or perchlorate). Ni-selective IIP particles were prepared by inverse suspension polymerization with initial Nickel/Vbamp ratios corresponding to 1:1, 1:2 and 1:3 Ni/Vbamp complexes. The effect of this complex stoichiometry on the Ni(II)/Zn(II) selectivity was investigated at pH 4 and 7 in sulfate media. As has been shown in our previous studies, chelating adsorbents are potential also for purification of concentrated $ZnSO_4$ solutions, although only removal of copper has been found useful adsorbent so far [29].

2. Experimental

2.1. Materials

The chemicals 2-(aminomethyl)pyridine (2-picolylamine, 99%, Sigma-Aldrich), 3-vinylbenzaldehyde (97%, Sigma-Aldrich), NaBH₄ (99.99%, Sigma-Aldrich), toluene (99.9%, Sigma-Aldrich), ethanol (99.8%, Fluka), diethyl ether (99.9%, inhibitor free, Sigma-Aldrich), and $MgSO_4$ (99.5%, anhydrous, Sigma-Aldrich) were reagent grade and used without further purification.

Mineral oil (heavy, Sigma-Aldrich), 2,2-azobis(2-methylpropionitrile) (AIBN) (98%, Sigma-Aldrich), methanol (99.9%, Sigma-Aldrich), 2-methoxyethanol (99.9%, Sigma-Aldrich), $Ni(NO_3)_2 \cdot 6H_2O$ (98.5%, Sigma-Aldrich), $Ni(ClO_4)_2 \cdot 6H_2O$ (98%, Sigma-Aldrich), and chloroform (99.9%, Sigma-Aldrich) were reagent grade chemicals and used in the polymerization of non-imprinted and nickel-imprinted polymers. Ethylene glycol dimethacrylate (EDMA) (98%, Acros) used in the polymerization was washed with 10% NaOH (99.9%, Sigma-Aldrich), dried on $MgSO_4$ and distilled to remove inhibitors.

$Zn(NO_3)_2 \cdot 6H_2O$ (98%, Sigma-Aldrich), $ZnSO_4 \cdot 7H_2O$ (99%, Sigma-Aldrich), $NiSO_4 \cdot 6H_2O$ (99%, Fluka), HNO_3 (69%, Sigma-Aldrich), KNO_3 (99%, Sigma-Aldrich), $Na_2SO_4 \cdot 10H_2O$ (99%, Sigma-Aldrich) were used in binding experiments. Aqueous solutions were prepared, using deionized water (conductivity less than 0.1 $\mu S\ cm^{-1}$).

2.2. Instrumentation

^{1}H and ^{13}C NMR spectra were obtained using a Bruker AVANCE 400 MHz Ultrashield spectrometer using DMSO-d_6 as solvent.

BET surface area, BJH pore volume and pore size were measured using N_2 adsorption (Micromeritics Gemini V). Particles were analyzed using scanning electron microscopy (SEM, JEOL JSM-5800).

The absorption spectra of the Ni–Vbamp complexes were measured at 25 and 80 °C with UV–vis spectrophotometers (Agilent 8453, Jasco V670) equipped with a thermostated cuvette holder. Quartz cuvette with a light path of 1 cm was used. The concentrations of the sample solutions are estimated to be correct within 2%. The accuracy of the spectra was tested by repeating a measurement 4 times over a period of hours. The average absolute difference in the wavelength range 400–1000 nm was 0.001 absorbance unit. Stability constants were estimated using the HypSpec program based on least-squares minimization scheme [22]. Detailed description of the calculations can be found from Refs. [22,23].

FTIR spectra were obtained using the standard KBr pellet method (Perkin–Elmer Frontier FTIR). Number of scans was 64 and resolution was 4 cm^{-1}.

Total amount of N, C and H in the polymers was determined by elemental analysis according to DIN 51732. 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 5%.

2.3. Synthesis of 1-(pyridin-2-yl)-N-(3-vinylbenzyl)methanamine (Vbamp)

1-(Pyridin-2-yl)-N-(3-vinylbenzyl)methanamine (Vbamp) was synthesized according to well-known Schiff base reaction and reduction of the corresponding imine. 1.0 g of 3-vinylbenzaldehyde (7.6 mmol) and 0.98 g of 2-(aminomethyl)pyridine (9.1 mmol) were dissolved in 40 mL of toluene. The solution was refluxed for 30 min and water was removed using a Dean-Stark apparatus. Remaining toluene was evaporated and the crude product was dissolved in 200 mL of ethanol and dried with anhydrous $MgSO_4$. After removal of ethanol, a light yellow viscous liquid was obtained. This crude imine compound ((1-pyridin-2-yl)-N-(3-vinylbenzylidene)methanamine) was reduced without further purification. It was dissolved in 200 mL of dried ethanol. 2.86 g of NaBH₄ (75.6 mmol) was added and the reaction mixture was refluxed for 2.5 h under nitrogen. 15 mL of water was then added and the mixture was left at 4 °C overnight. The precipitate was filtered off and the solution was evaporated to 25 mL before addition of 25 mL of diethyl ether. The mixed solution was washed four times with water and the organic phase was dried with