

Synthesis of ion imprinted polymers for selective recognition and separation of rare earth metals

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Abstract: Lanthanide-ion imprinted polymers (L-IIPs) were synthesized by stoichiometric amounts of rare earth ions and the cavities in the polymers were created for the corresponding lanthanide ions. The maximum sorption capacities were estimated to be 125.3, 126.5, 127.6, 128.2 and 129.1 mg/g for Pr, Nd, Sm, Eu and Gd, respectively at pH 6. In the selectivity study, the L-IIPs exhibited good selectivity to the specific rare earth ions in the presence of coexisting cations. The imprinting results were found to be excellent with some rare earth ions over other competitor rare earth ions with the same charges and close ionic radius.

Keywords: ion-imprinted polymers; rare earths; separation; adsorption; lanthanide-ions

Molecular imprinting technology (MIT) certainly described a molecular lock to match a molecular key for the creation of molecularly imprinted polymers (MIPs) with tailor-made binding sites complementary to the template molecules in shape, size and functional groups^[1]. MIPs have found a wide range of applications in various fields due to their unique features of structure predictability, recognition specificity and application universality^[1,2]. For excellency of MIT, a new pattern MIPs surge popularity for versatile applications, including sample pretreatment/chromatographic separation (solid phase extraction, column chromatography, etc.) and chemical/biological sensing (electrochemical sensing, fluorescence sensing, etc.)^[1]. Ion imprinting technology (IIT) targets to recognize ions while retains the unique virtues of molecular imprinting technology (MIT) such as structure predictability, recognition specificity and application versatility^[3]. Ion imprinted polymers (IIPs) are function with the special coordination or electrostatic interaction and IIPs are generally compatible with aqueous media advantageous over most molecularly imprinted polymers (MIPs). IIPs can be secure effective identification of water-soluble ions, especially heavy metals and radioactive elements^[3]. Typically, IIPs are stable and robust due to the polymeric nature formation from cross-linked materials^[4,5].

A multi-ion imprinted polymers (MIIPs) embedded in a sol-gel matrix using Hg²⁺, Cd²⁺, Ni²⁺ and Cu²⁺ as templates and 3-aminopropyltriethoxysilane as a functional

monomer, and the possible synergy mechanism was explored between dithizone coordination chemistry and multi-ion imprinting was reported by Fu et al.^[6]. The resultant MIIPs showed high binding capacity and fast dynamics, and the adsorption processes obeyed Langmuir isotherm and pseudo-second-order dynamic models. The MIIPs showed excellent selectivity toward the four target ions with high selectivity^[6]. A Pb²⁺ ion imprinted polymers (IIPs) was prepared with dual functional monomers of methacrylic acid and vinyl pyridine for selective solid-phase extraction of Pb²⁺ in water media^[7]. The IIPs exhibited good selectivity toward Pb²⁺ over other transition metal ions. The IIPs also showed rapid and effective enrichment of trace Pb²⁺ ions in complicated matrices^[7]. A functional monomer, 3-isocyanatopropyltriethoxysilane bearing thymine bases was synthesized for imprinting Hg²⁺ ion^[8]. Thus, a novel Hg²⁺ ionic imprinted polymers (IIPs) were prepared by sol-gel process and the Hg-IIPs exhibited excellent selectivity towards Hg²⁺ with high affinity over alkali and transition metal cations. The IIPs showed a rapid and high-effective enrichment method for trace Hg²⁺ in water samples^[8].

Lanthanides are widely used in various fields, such as functional materials, catalysts and semiconductor industry. Pure lanthanides are required for industrial uses, while the separation of lanthanides is one of the challenging tasks for chemists with traditionally used ion-exchange and liquid-liquid extraction separations, as

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lanthanides possess identical chemical and physical properties^[9–13]. Zhang et al.^[11] prepared an ion-imprinted silica gel sorbent with the surface-imprinting technique for selective extraction of dysprosium. Guo et al.^[14] synthesized and characterized IIPs materials for selective recognition of neodymium from a mixture of lanthanide ions. The adsorption capacity of the Nd-IIP was 35.18 mg/g. The largest selectivity coefficient for Nd in the presence of competitive ions such as La, Ce, Pr and Sm was over 110. Because, lanthanide and its compounds exhibit peculiar physical, chemical, and nuclear properties, the lanthanide elements play an important role in many fields of advanced materials science such as electronics, magnetism, metallurgy, phosphors, catalysts, glass, laser and ceramic technology^[15–19].

The rare earth elements are required in beneficial way to be separated for the industrial applications and the purification of these elements has attracted considerable attention with the increasing demand for high-purity rare earth elements^[20]. However, the separation and recovery of rare earth elements are difficult because of the similarity of their chemical properties such as the same valence and close ion radii^[21,22], especially for the separation of those light rare earth elements from each other (for example; La, Ce, Pr, Nd and Pm). The selective separation of mixed RE metals meets severe challenges, and the conventional methods have some problems with operation, including lack of selectivity, tight separable conditions, remain of organic material, and restriction on separable rare earth elements^[19,23].

Therefore, new materials need to be developed to overcome the limitation for the separation and purification of rare earth elements. Selective recognition of Nd³⁺ in aqueous solutions in the presence of various lanthanide ions by molecularly imprinted polymers was reported recently^[24]. The maximum binding capacity was found to be 14.6 mg Nd³⁺ g⁻¹ at 30 min equilibrium time and the binding studies of Nd in the presence of Ce, La and Eu ions were also carried out by Nd-IIPs. Europium(III)-imprinted polymer nanoparticles were synthesized by suspension polymerization^[25]. Carbon paste electrodes, impregnated with the ion-imprinted polymer (IIP) were used in the solutions containing different kinds of lanthanide ions. The electrode showed high selectivity for Eu³⁺ even in the presence of other lanthanide ions^[25]. The surface imprinting technique was used to prepare a straw-supported ion imprinted polymer sorbent by combining with activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP). The maximum sorption amount was 125 mg/g with a fast sorption rate (several minutes). Authors claimed that the imprinted sorbent could be repeatedly used for ten times without any significant loss in the initial binding affinity^[26]. Yan et al.^[27] synthesized a Ce(III)-IIP grafted on Fe₃O₄ nanoparticles supported by SBA-15

mesopores microreactor via RAFT polymerization for selective removal of Ce(III) from aqueous solutions. The competitive adsorption studies showed that Ce(III)-IIP owned the advantages of selectivity towards Ce(III) compared with NIP even in the presence of other metal ions.

In this study, simple and highly effective IIPs materials were synthesized for selective recognition and separation of five lanthanide ions (Pr, Nd, Sm, Eu and Gd) from their neighbouring lanthanide cations, which were close atomic radii with imprinted lanthanide ions. The L-IIPs polymers were used for competitive extraction media with good selectivity of lanthanide ions.

1 Experimental

1.1 Materials

(E)-3-(3-(4-fluorophenyl)-1-isopropyl-1H-indol-2-yl)acrylaldehyde (Molbase), 4-amino-4H-1,2,4-triazole-3-thiol (Apollo Scientific), acetic acid (Sigma), 4-vinylpyridine (Aldrich), sodium hydroxide (Aldrich), hydrochloric acid, ethylene glycol-dimethylacrylate (EGDMA) (Aldrich), 2,2-azobisisobutyronitrile (AIBN) (Aldrich), europium (III) chloride (Sigma-Aldrich), gadolinium (III) chloride (Sigma-Aldrich), neodymium (III) chloride (Sigma-Aldrich), praseodymium (III) chloride (Sigma-Aldrich), samarium (III) chloride (Aldrich-Aldrich) were used as receivers. Acetone and dichloro-methane were refluxed over phosphorus pentoxide (Merck) and dimethyl formamide (DMF) were also reflux over calcium hydride (Fluka) to obtain dry DMF and all solvents distilled out before use. Other solvents and chemicals were used without further purification.

1.2 Instruments

The characterizations of L-IIPs were performed to study the behaviours of different L-IIPs products. The structures of the compounds were confirmed by the spectroscopic method. IR spectra were recorded with a Perkin Elmer (670) FT-IR spectrometer. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded with a Bruker (DMX500) spectrometer. FE-SEM measurement was performed with JEOL (JSM-7800F) to study the morphology of L-IIPs. Sputter coating was applied for an ultra-thin coating of platinum metal onto a specimen. The absorbance measurements were performed by solid state UV-vis NIR spectrophotometer (UV-2600 Shimadzu). Metal ion concentrations were analysed by ICP-MS (Agilent 7500 series). Therefore, an Agilent (7500) instrument was used at the operating conditions: plasma gas flow rate: 15 L/min; auxiliary gas flow rate: 1.0 L/min; Cooling water flow rate (RF/TP): 2.0 L/min; ICP RF Power: 1200 W; Interface pressure: 350 Pa; Cooling water flow rate (WC/IF): 1.8 L/min and analyzer pressure: 3×10⁻⁴ Pa (no gas mode).

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