

ION-IMPRINTED POLYMERS FOR SELECTIVE SEPARATION OF LANTHANUM(III) IN ENVIRONMENTAL SAMPLES

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Abstract. This study describes the selective recognition of La(III) in aqueous solutions in the presence of various lanthanide ions by ion imprinted polymers. Ion imprinted polymers (IIPs) were prepared by suspension polymerization. N-methacryloylamido folic acid (MAFol) was used as the functional monomer. The effects of different variables such as pH, time, and initial La(III) concentration on binding characteristics were investigated. Binding equilibrium time was achieved in 20 min. The maximum binding capacity was found to be 21.5 mg La(III) g⁻¹ polymer. Binding studies of La(III) in the presence of Th(IV), Ce(III), and Eu(III) ions were also carried out using La(III)-imprinted polymers. The imprinted polymers displayed high selectivity toward La(III) ions. The obtained binding order under competitive conditions was La(III) > Eu(III) > Ce(III) > Th(IV).

Keywords: *folic acid, Lanthanides, bastnasite ore, recognition*

Introduction

Extraction and preconcentration of rare-earth metals such as lanthanum have always been of interest over the past several decades, since they have been commonly used as micro-additives in functional materials such as high-temperature superconductors, secondary batteries, magnetic, luminescence, and laser materials (Morais and Ciminelli, 2004; Maestro and Huguenin, 1995).

Various techniques were proposed for extraction and preconcentration of rare-earth metals such as solvent extraction, precipitation, and ion-exchange chromatography (Jain et al., 2001; Dolak et al., 2011; Yener et al., 2017; Kim et al., 1997; Xiong et al., 2008; Dolak and Ziyadanoğulları, 2019; Fayazi et al., 2016; Dolak, 2021; Dolak and Keçili, 2022). However, these traditional processes have some disadvantages such as high consumption of solvent and energy and low selectivity, etc. Therefore, innovative technologies and processes with higher selectivity, fewer process steps, and lower time and energy requirements are needed.

Ion imprinting technology is a technique for the synthesis of selective adsorbents that possess binding groups in the porous polymeric structure that are adapted to the three-dimensional (3D) shape and functionalities of a target compound (Ensing and De Boer, 1999; Sellergren et al., 2001; Wei and Mizaikoff, 2007; Lasáková and Jandera, 2009). In the ion-imprinting process, the selectivity of a polymeric adsorbent is based on the specificity of the functional monomer, coordination geometry, coordination number of the target ions, and their charges and sizes (Baysal et al., 2018; Gao et al., 2015; Canpolat et al., 2022; Ye and Mosbach, 2001; Zhang et al., 2003). In recent years, several studies on removal of trace metal ions by ion imprinted polymers (IIPs) were reported (Dolak, 2018, 2019a, b; Lin et al., 2010; Buyuktiryaki et al., 2005; Bereli et al., 2012; Moussa et al., 2016; Keçili et al., 2018; He et al., 2007; Ersöz et al., 2004; Dolak et al., 2015; Say et al., 2003; Guo et al., 2014; Jiang and Kim, 2013; Singh et al., 2010; Najafi et al., 2013; Xiaogang et al., 2020; Shi et al., 2022).

In this study, IIPs display better selectivity compared to reported studies for the selective separation of La(III) ions from aqueous solutions and mineral bastnasite were prepared. For this purpose, N-methacryloylamido folic acid (MAFol) and ethylene glycol dimethacrylate (EDMA) were used as the new functional monomer and cross-linker, respectively. Structural characterization of the prepared polymers was carried out and their binding behavior toward target La(III) ions was analyzed and discussed. Parameters such as La(III) binding efficiency, contact time, pH and initial lanthanum concentration were examined and optimum conditions were determined. Optimum conditions determined at the end of the study were applied for the separation of La(III) in bastnasite ore containing rare earth elements found in Beylikahır region of Eskişehir province in Turkey.

Materials and methods

Materials

Folic acid, Lanthanum(III) nitrate hexahydrate, cerium(III) nitrate hexahydrate, thorium(IV) nitrate, europium(III) nitrate hexahydrate, benzotriazole, poly(vinylalcohol) (PVA) (MW 27000), 2,2'-azobis(isobutyronitrile) (AIBN), ethylene glycol dimethacrylate (EDMA), and HPLC-grade solvents were purchased from Sigma Aldrich. Distilled water was purified using an ultrapure water system with a reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead, Model D2731) followed by a NANO pure organic/colloid removal and ion exchange packed-bed system (Barnstead, Model D3804).

Instruments

Fourier transform infrared spectroscopy (FT-IR) experiments were performed using a Perkin–Elmer Model Spectrum 400 spectrometer. Near-infrared (NIR) spectra were obtained using a Shimadzu Model UV-3600 ultraviolet–visible–near-infrared (UV-VIS-NIR) spectrophotometer. The specific surface areas of the synthesized polymers were determined by using a Nova Model 2200e surface area and pore size analyzer. Scanning electron microscopy (SEM) images were recorded using a FEI Quanta FEG 250 SCE system.

The analysis of the La(III) and the other interfering ions was performed using an Agilent 7700 Series inductively coupled plasma–mass spectroscopy (ICP-MS) system with the following parameters: RF power = 1600 W, sampling depth = 6 mm, analyzer pressure = 5.47×10^{-5} Pa, helium flow in the collision cell = 4.99 mL min⁻¹, and plasma temperature = 9876 K. The measurements were done with three replicates (95% confidence level).

Synthesis of N-methacryloylamido folic acid (MAFol)

The functional monomer MAFol was prepared according to the previously published method as described in the following (Dolak et al., 2015). Folic acid (1 equiv) was dissolved in 50 mL of deionized water. The pH was set to 9–10 with 1 M NaOH to obtain anionic folate in the solution. Then, a solution of methacryloyl benzotriazole in dioxane (15 mL) was added to the folate solution. This mixture was stirred for 30 min at room temperature. Completion of the reaction was monitored by thin layer chromatography (TLC). Dioxane then was evaporated under vacuum. At the end of the

reaction, 1H-benzotriazole was extracted with ethyl acetate (3×20 mL). Aqueous phase was acidified with 0.1 M HCl to adjust pH to 5–6. Finally, aqueous phase was evaporated under vacuum to get MAFol, a yellow microcrystal, in 85% yield. Synthesis of MAFol is schematically depicted in *Figure 1*.

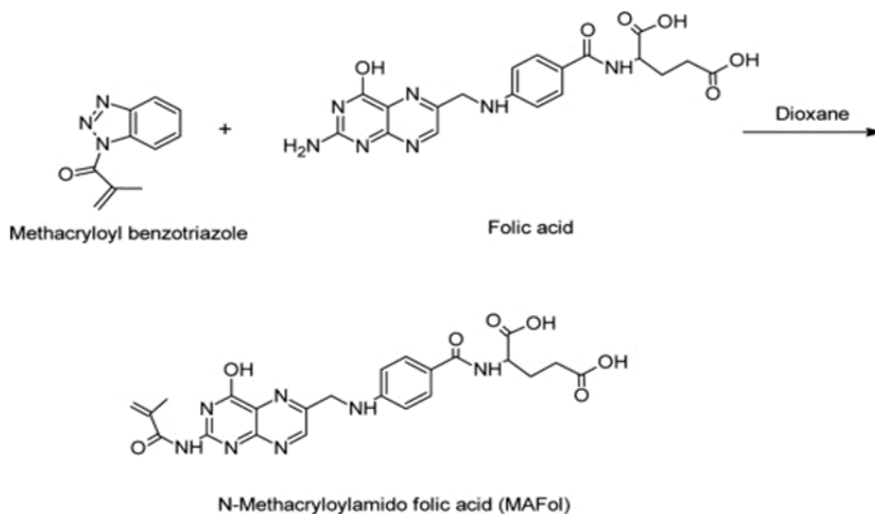


Figure 1. Synthesis of functional monomer *N*-methacryloylamido folic acid (MAFol)

Preparation of MAFol–La(III) complex monomer

For the synthesis of complex monomer MAFol–La(III), MAFol (0.50 g, 2.0 mmol) was dissolved in 15 mL of chloroform. Then, La(NO₃)₃·6H₂O (0.22 g, 1.0 mmol) was slowly added to this solution and allowed to stir at room temperature for 24 h. Finally, the complex monomer was filtered off, washed with ethanol, and dried in a vacuum oven at 50°C for 24 h.

Preparation of La(III)-imprinted polymers

The La(III)-imprinted polymers were prepared by using suspension polymerization technique as described in the following (Dolak et al., 2015). Aqueous dispersion medium was prepared by dissolving 0.2 g of poly(vinyl alcohol) (PVA) in 50 mL of deionized water. Then, MAFol–La(III) complex was dissolved in 5.0 mL of dimethyl sulfoxide (DMSO) and this solution was mixed into the EDMA/toluene (2.0 mL/10.0 mL) mixture. Finally, the initiator AIBN (30 mg) was added. This solution was transferred into the dispersion medium placed in a glass polymerization reactor and purged with nitrogen for 5 min. The polymerization was initiated by placing the reactor in a thermostated water bath at 70°C for 6 h at a constant stirring rate of 600 rpm. The temperature was then increased to 90°C and held constant for the next 3 h. After polymerization, La(III)-imprinted microbeads were separated from the reaction medium and washed with ethanol and deionized water to remove unreacted initiator, monomer, and solvent. Removal of the template (La(III)) from the polymers was achieved by extraction with 5 M HNO₃ for 24 h. Schematic depiction of the prepared La(III)-imprinted polymer is shown in *Figure 2*. A nonimprinted polymer (NIP) was prepared in the same way as described above, but with the omission of the template.

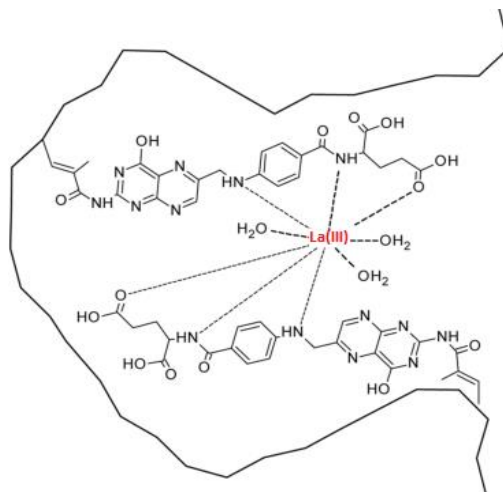


Figure 2. Schematic depiction of the prepared imprinted polymer toward La(III)

Characterization studies

The polymers were characterized by FT-IR, SEM, EDX, and swelling tests. For FT-IR spectra of the polymers, the dry polymer particles (ca.100 mg) were mixed with KBr (ca. 100 mg) and pressed into a tablet form, and the spectrum was then recorded.

For the SEM analysis of the polymers, polymer particles were deposited on the platinum surface and coated with gold (thickness of ~20 nm) to provide conductivity and protect from the beam damage. Then, the SEM images were obtained at magnifications of 5000×, and 13000×.

The swelling behavior of the polymers is an important parameter for the binding performance and thus, the swelling behavior of the prepared polymers was evaluated. To evaluate the swelling behavior of the polymers, NMR tubes were filled with dry polymer up to 1 cm and the polymer particles were allowed to equilibrate in the distilled water for 2 h. Afterward, the volume of the swollen polymer:

$$\text{Swelling Ratio (\%)} = V_{\text{swollen}} - V_{\text{dry}} / V_{\text{dry}} \quad (\text{Eq.1})$$

where V_{swollen} is the bed volume of swollen polymer and V_{dry} is the bed volume of dry polymer.

Effect of pH, time, and initial La(III) concentration

In order to investigate the effect of pH on binding, 2 mL solution of 10 ppm of La(III) in different pH values (varying between pH 2 to pH 9) was added to 25 mg of each polymer (IIP and NIP). The solution was stirred for 1 h and 1 mL aliquot of each mixture was taken and analyzed by ICP-MS. For the time effect, 2 mL solution of 10 ppm of La(III) in 10 mM NH_4Ac buffer, pH 6.5 was added to 25 mg of each polymer (IIP and NIP). The solution was stirred and aliquot of 1 mL of each mixture was taken at 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 min at the pH 6.5 and analyzed by ICP-MS. The effect of initial concentration was also investigated and for this purpose; 2 mL solution of different concentrations of La(III) in 10 mM NH_4Ac buffer, pH 6.5 was added to 25 mg of each polymer (IIP and NIP). The solution was stirred for 20 min and aliquot of 1 mL of each mixture was taken and analyzed by ICP-MS.

Batch rebinding studies

Batch rebinding experiments for La(III) were carried out using 25 mg of polymer (IIP and NIP) placed in high-performance liquid chromatography (HPLC) vials. Two milliliters of a solution of 10 ppm of La(III) in 10 mM NH₄Ac buffer, pH 6.5 was added to the polymers. The mixtures were then stirred for 1 h. The polymers were allowed to settle for a while and 1 mL of the collected aliquots of the sample was taken and analyzed by ICP-MS.

Selectivity and reusability studies

The experiments for the specificity of the polymers toward La(III) were carried out by the competitive binding studies in the presence of La(III)–Ce(III), La(III)–Th(IV), and La(III)–Eu(III) ion pairs. Two milliliters of a solution of 10 ppm mixture containing ion pairs in 10 mM NH₄Ac buffer, pH 6.5 was added to 25 mg polymer. The solutions were stirred for 20 min, and 1 mL of the collected aliquots was taken and analyzed by ICP-MS.

The distribution coefficient of La(III) ions between the IIP particles and aqueous solution was determined using the following equation:

$$K_d = (C_i - C_f / C_f) \times (V/m) \quad (\text{Eq.2})$$

where K_d is the distribution coefficient, C_i and C_f are the initial and final solution concentrations, respectively, V is the volume of solution (mL), and m is the mass of IIP (g).

The selectivity coefficient (k) in the presence of potentially interfering ions and relative selectivity coefficient (k') for La(III) ions can be obtained from equilibrium binding data, according to the following equations:

$$k = K_{\text{La(III)}} / K_{\text{(interfering ion)}} \quad (\text{Eq.3})$$

$$k' = K_{\text{(imprinted)}} / K_{\text{(nonimprinted)}} \quad (\text{Eq.4})$$

where $K_{\text{La(III)}}$ and $K_{\text{(interfering ion)}}$ are the distribution ratios of La(III) ions and potentially interfering ions, respectively.

For the reusability experiments, La(III) ion binding and elution experiments were repeated 12 times, using the same polymer. After each cycle, polymers were washed with 1 M NaOH for regeneration.

Extraction studies from real samples

La(III) is commercially extracted from bastnasite ore by ion exchange and solvent extraction techniques. Therefore, bastnasite ore was chosen as the real sample for the extraction of La(III) in the presence of other lanthanides. Microwave-assisted leaching of 1 g of the powdered bastnasite ore was carried out using concentrated HNO₃ and H₂SO₄. Then, pH of the solution was adjusted to 6.5, using acetic acid and sodium acetate. One hundred milliliters (100 mL) of deionized water was then added to this solution.

To evaluate the binding properties of the polymers toward La(III), 25 mg of each polymer (IIP and NIP) were placed in HPLC vials and 2 mL of mineral bastnasite

solution was added to the polymers. The mixtures were then stirred for 30 min. The polymers were allowed to settle for a while, and 1 mL of the collected aliquots of the sample was taken and analyzed by ICP-MS.

Results

Characterization studies

FT-IR spectroscopy was also used for the characterization of MAFol–La(III) complex. Main characteristic absorption bands of MAFol monomer due to O–H stretching ($\sim 3228\text{ cm}^{-1}$), COO[−] group stretching ($\sim 1690\text{ cm}^{-1}$), N–H stretching (1606 and 1510 cm^{-1}) and C–H bendings (1406 and 1334 cm^{-1}) were observed in the FT-IR spectra, as shown in *Figure 3a*.

The prepared polymers were also characterized by FT-IR spectroscopy. All polymers exhibited very similar FT-IR patterns, indicating the similarity of the polymer backbone structure as can be seen in *Figure 3b*. In the FT-IR spectra, absorption peaks due to COO[−] group stretching ($\sim 1650\text{ cm}^{-1}$), C–H stretching ($\sim 2900\text{ cm}^{-1}$) from the functional monomer, and C–O stretching ($\sim 1000\text{ cm}^{-1}$) from the cross-linker EDMA were observed.

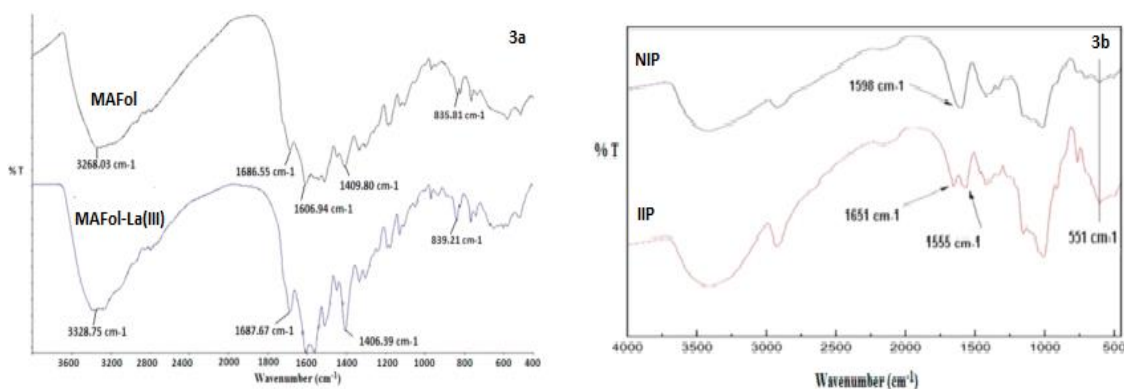


Figure 3. (a) FT-IR spectra of MAFol and MAFol–La(III) complex. (b) FT-IR spectra of La(III)-imprinted polymer IIP (bottom trace) and NIP (top trace)

SEM images of La(III) imprinted polymers are shown in *Figure 4a*. As can be seen from the figure, the polymeric particles are spherical and porous.

The specific surface areas of the prepared IIP and NIP were found to be $219\text{ m}^2\text{ g}^{-1}$ and $107\text{ m}^2\text{ g}^{-1}$, respectively. From this data, it can be concluded that the surface area of the polymer significantly increased by imprinting of La(III) ions.

The energy-dispersive X-ray analysis (EDX) was also performed to identify the elemental composition of the La(III)–MIP and La(III)–NIP. The EDX spectra are given in *Figure 4a*. The absence of La(III) in the EDX spectrum confirms the complete removal of La(III) ions from the polymeric structure, as can be seen from *Figure 4b*.

Swelling experiments were carried out using distilled water. The equilibrium swelling ratios of the La(III)-imprinted polymer and its corresponding NIP are 40.7% and 18.4%, respectively.

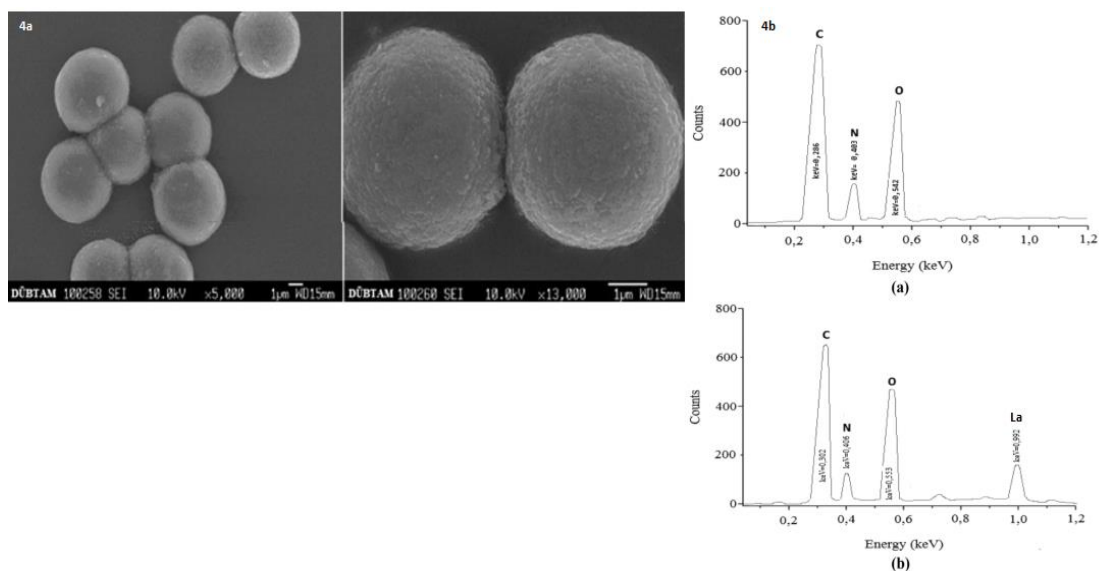


Figure 4. (a) SEM images of the La(III)-imprinted polymer. (b) SEM-EDX spectra of (a) NIP and (b) IIP

Binding behavior of the polymers

Effect of pH, time, and initial La(III) concentration

One of the most crucial parameters that affects the binding of metal ions is pH, because pH can affect the solubility of the metal ions and the ionization state of functional groups on the polymer. The effect of pH on the La(III) binding at varying pH values in the range of 2.0–9.0 is shown in Figure 5. As can be seen from the figure, the maximum binding was obtained at the pH range of 6.0–7.0. Thus, in all subsequent experiments, the pH was adjusted to 6.5.

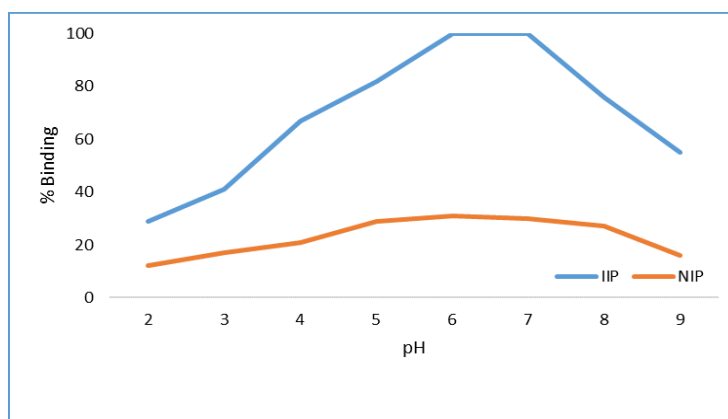


Figure 5. Effect of pH on La(III) binding. (Conditions: $C_{La(III)} = 10$ ppm, $m_{polymer} = 25$ mg, $t = 1$ h, and $T = 25^{\circ}\text{C}$)

La(III) binding to the polymer is low in the lower pH (2–4), since more protons are available and functional groups are protonated on the polymers. The protonated functional groups exert a repulsive force toward La(III) that prevent positively charged

La(III) ions from approaching the polymer surface. Increasing the pH (to 6–7), the negative charge density of functional groups increases, because of their deprotonation, and the La(III) binding to the polymer increases. At higher pH values ($\text{pH} > 7$), precipitation of the La(III) ions occurs. This leads to a decrease in La(III) binding to the polymers.

The effect of time on binding capacity of the polymers toward La(III) is given in Figure 6. This figure shows that La(III) binding increased with the contact time until maximum binding was obtained at 20 min. This was attributed to utilization of the most readily available binding sites on the polymer surface. IIP was bound to La(III) very rapidly and the removal of La(III) from aqueous solutions was $> 50\%$ within 10 min and 80% within 15 min. The rapid binding of La(III) could be explained by the high complexation affinity toward folic acid in the polymeric structure.

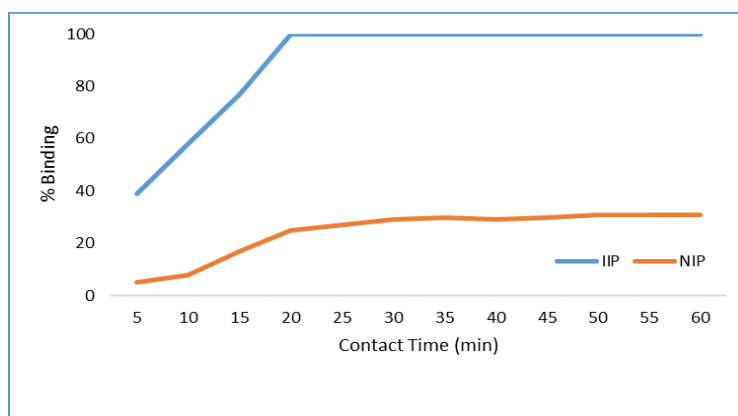


Figure 6. Effect of time on La(III) binding: (Conditions: $C_{\text{La(III)}} = 10 \text{ ppm}$, $m_{\text{polymer}} = 25 \text{ mg}$, $\text{pH} 6.5$, $T = 25^\circ\text{C}$)

Initial La(III) concentration dependence of the bound amount of the La(III) onto the IIP and NIP is shown in Figure 7. The amount of bound La(III) increased with increasing La(III) concentration, and a saturation value was obtained at a La(III) concentration of 0.5 mg mL^{-1} , which showed saturation of the accessible binding sites of the polymers. The maximum binding capacity of IIP for La(III) is 21.5 mg g^{-1} of polymer.

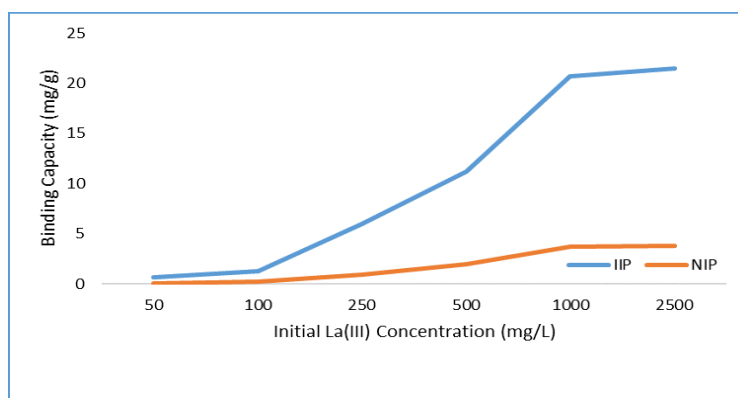


Figure 7. Effect of La(III) concentration on binding. (Conditions: $m_{\text{polymer}} = 25 \text{ mg}$, $\text{pH} 6.5$, $t = 20 \text{ min}$, $T = 25^\circ\text{C}$)

Binding isotherms

During the rebinding experiments in the batch system, binding isotherms were used to evaluate binding properties of the polymers. In the Langmuir binding model (Langmuir, 1918) binding data can be analyzed using the following equation:

$$1 / Q = 1 / Q_{\max}^b (1 / C_{\text{eq}}) + 1/Q_{\max} \quad (\text{Eq.5})$$

where Q is the amount of bound La(III) ions to the polymer (mg La(III) g^{-1} polymer), $Q_{\max}$ represents the maximum binding capacity (mg La(III) g^{-1} polymer), C_{eq} is the equilibrium concentration of La(III) ions in the solution (mg L^{-1}), and b is the Langmuir constant, which represents the affinity between La(III) and the polymer.

Another approach for the characterization of binding sites of the polymers is the Freundlich binding model, which is a generalized model from the Langmuir model. The Freundlich binding isotherm (Freundlich, 1906) is described by the following equation:

$$\log Q = \log k_F + 1 / n \log C_{\text{eq}} \quad (\text{Eq.6})$$

where C_{eq} represents the equilibrium concentration of La(III) ions in the solution (mg L^{-1}), k_F is the Freundlich binding constant and n is the Freundlich exponent, which is a measure of the heterogeneity of the binding site energy.

The parameters obtained from the Langmuir and Freundlich equations for La(III) binding to an ion-imprinted polymer are shown in *Table 2*. As can be seen from the table, the binding of La(III) to the ion-imprinted polymer is well-described by the Langmuir model.

As seen in *Table 1*, the Langmuir constant (b) toward La(III) was found to be $0.17 \text{ mL } \mu\text{g}^{-1}$.

Table 1. Parameters for the Langmuir and Freundlich binding isotherms for La(III) binding to IIP

Experimental	Langmuir			Freundlich		
$Q (\text{mg g}^{-1})$ 21.5	$Q (\text{mg g}^{-1})$ 22.4	$b (\text{mL } \mu\text{g}^{-1})$ 0.17	R^2 0.99	$k_F (\text{mL mg}^{-1})$ 35	n 1.77	R^2 0.91

Binding kinetics

Kinetic modeling is crucial in order to gain insight into the binding mechanisms and rate-controlling steps affecting the binding kinetics. The pseudo-first-order kinetics model and pseudo-second-order kinetics model were used to evaluate the experimental data in order to examine the controlling mechanism of La(III) binding.

The pseudo-first-order kinetic model is described by the following equation:

$$\log (q_e - q_t) = \log q_e - (k_1 / 2,303)t \quad (\text{Eq.7})$$

The polymer at time t (min), q_e (mg g^{-1}) is the amount of La(III) bound to the polymer at equilibrium and k_1 (min^{-1}) is the rate constant of first-order binding.

If the applicability of the pseudo-first-order kinetic model becomes unattainable, the pseudo-second order model is used and it is based on the binding capacity of the polymer. The pseudo-second-order kinetic model is described by *Equation 8*.

$$t / q_t = 1 / k_2 q_e^2 + (1 / q_e)t \quad (\text{Eq.8})$$

If the pseudo-second-order kinetic model is applicable, the plot of t/q_t vs t gives a straight line and q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-first-order- and pseudo-second-order kinetic parameters for La(III) binding to IIP are shown in Table 2. As can be seen in the table, the pseudo-second order kinetic model with a higher correlation coefficient ($R^2 = 0.98$) seems to best address the kinetics of the overall La(III) binding to IIP

Table 2. Pseudo-first-order and second-order kinetic parameters for La(III) binding to IIP

Experimental	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
Q (mg g ⁻¹) 21.5	q _e (mg g ⁻¹) 16.4	K ₁ (min ⁻¹) 0.07	R ² 0.95	q _e (mg g ⁻¹) 20.0	k ₂ (g mg ⁻¹ min ⁻¹) 0.015	R ² 0.98

Selectivity and reusability studies

Competitive binding of La(III)–Ce(III), La(III)–Th(IV), and Nd(III)–Eu(III) were also studied in a batch system. The outcomes of these experiments are shown in Table 3. As shown in the table, La(III)-imprinted polymer displayed higher selectivity toward La(III) ions over Ce(III), Th(IV), and Eu(III) ions. These results imply that the La(III)-imprinted polymer in the present study exhibited higher selectivity toward La(III) over other potentially interfering ions.

The La(III) binding and elution cycle was repeated 10 times in order to test the reusability of the La(III)-imprinted polymers. As can be seen in Figure 8, the polymers are very stable, even after 10 cycles.

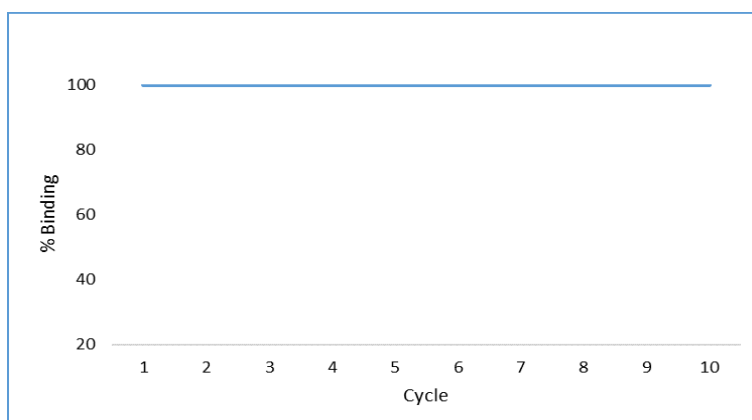


Figure 8. Reusability of the polymers. (Conditions: $C_{La(III)} = 10$ ppm, $m_{polymer} = 25$ mg, pH 6.5, $t = 20$ min, $T = 25^\circ\text{C}$)

Extraction of La(III) from mineral bastnasite

The outcomes of the extraction experiments of La(III) from mineral bastnasite are shown in Figure 9. As can be seen from the figure, the La(III)-imprinted polymer displayed 100% binding toward La(III) with a clear imprinting effect while its corresponding NIP displayed 38% binding.

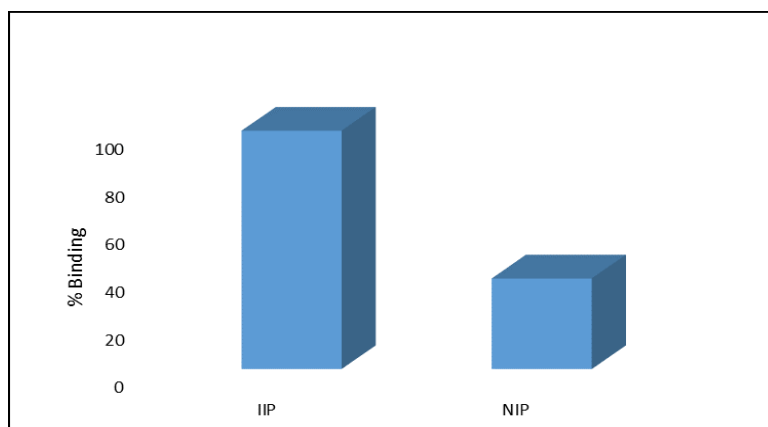


Figure 9. Extraction of La(III) from bastnasite mineral. (Conditions: $C_{La(III)} = 22$ ppm [in the real sample], $m_{polymer} = 25$ mg, pH 6.5, $t = 30$ min, $T = 25^{\circ}C$)

Table 3. Distribution coefficient (K_D), selectivity coefficient (k), and relative selectivity coefficient (k') values of IIP and NIP for different ions

Ion	% Binding		K_D (mL/g)		k		k'
	IIP	NIP	IIP	NIP	IIP	NIP	
La(III)	≥ 99	38.2	8340.0	43.2			
Ce(III)	27	36.3	34.5	30.1	246.6	0.73	330.0
Th(IV)	19	39.2	23.4	46.5	301.5	0.81	542.5
Eu(III)	31	28.6	25.6	32.9	274.0	0.87	390.2

Discussion

It is very important that lanthanum, which has a very common usage area in the industry (Morais and Ciminelli, 2004; Maestro and Huguenin, 1995), is selectively separated from the matrix environment and obtained in pure form. It has been determined that the separator and binding materials used in many studies for the selective removal of rare earth metals from the matrix environment in water samples and various environmental samples are not sufficiently selective (Jain et al., 2001; Dolak et al., 2011; Yener Et al., 2017; Kim et al., 1997).

When ion imprinted polymers are used, it has become possible to separate lanthanum and all other rare earth elements from the matrix environment with high selectivity (Dolak et al., 2015; Dolak, 2019; Xiaogang et al., 2020; Shi et al., 2022).

In our study, using La(III) imprinted polymer synthesized by using a new functional monomer containing folic acid, whose synthesis belongs to us, separation of La(III) ions in solution medium and bastnasite ore with high selectivity was achieved.

The characterization processes of the synthesized monomer, imprinted and non-imprinted polymers were performed and the obtained results showed that all desired syntheses were accomplished successfully.

In the experiments carried out to determine the optimum pH, experiments were carried out in the pH range of 2-9, and it was determined that the pH with the highest binding efficiency was in the range of 6-7. At this pH, it was determined that while La(III) imprinted polymer binds all La(III) in the solution medium, the non-imprinted polymer binds 30% La(III).

In the experiments carried out to determine the optimum time, periods of 5-60 min were studied and it was determined that 20 min was sufficient for the La(III) imprinted polymer to bind all the La(III) in the solution.

In the experiments carried out to determine the maximum La(III) binding capacity of the imprinted and non-printed polymer, it was determined that the La(III) binding capacity of the La(III) imprinted polymer was 21.5 mg, while the La(III) binding capacity of the non-imprinted polymer was 3.87 mg. This result showed that the La(III) imprinted polymer showed approximately 6 times more binding efficiency than the non-imprinted polymer.

In the repeat experiments to determine the reusability of the prepared La(III) imprinted polymer, it was determined that there was no decrease in the bonding efficiency even after 10 reuses.

The selective binding conditions of the prepared La(III) imprinted polymer and other rare earth elements such as Th(IV), Ce(III) and Eu(III) besides the La(III) found in bastnasite ore were examined under the determined optimum conditions and it was determined that the binding efficiency of the imprinted polymer against the other rare earth elements mentioned was at very low levels.

Conclusion

Novel ion imprinted polymers (IIPs) that exhibit selective affinity toward La(III) were designed. The prepared polymers have the potential to selectively extract La(III) ions in the presence of Ce(III), Th(IV), and Eu(III) from water samples due to high affinity binding sites. Rebinding studies showed that high affinity interactions are present between the binding sites of the IIP and the target ions, which leads to selective and high binding efficiency in the extraction of La(III) from bastnasite ore.

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