

Full Paper

Evaluation of the Recognition Characteristic of Nano-structured Eu³⁺-imprinted Polymer via Competitive Extraction of Different Metal ions in the Imprinted Polymer-Modified-Carbon Paste Electrode

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Abstract- In this work, a new method was proposed for the evaluation of recognition capability of the ion imprinted polymers based on competitive displacement coupled with indirect electrochemical detection technique. Nano-sized Eu³⁺-imprinted polymer was synthesized using ultrasonic assisted suspension polymerization in silicon oil. Differential pulse voltammetry technique and carbon paste electrode, modified with the synthesized ion imprinted polymer (IIP), were applied for the evaluation of the rebinding characteristics of the IIP. A competitive substitution method was applied for the evaluation of recognition property of the IIP towards lanthanides and some other ions which were non-electroactive in traditional conditions. For this aim, Pb²⁺ ions, included in the selective cavity of the Eu³⁺-IIP, were replaced with Eu³⁺ ions, reducing the differential pulse voltammetry signal of Pb²⁺. Different factors such as extraction pH, IIP amount in the carbon paste electrode and competitive extraction time were evaluated and optimized. By the proposed method the recognition ratios and selectivity coefficients of the synthesized IIP for different lanthanides and some other ions were obtained.

Keywords- Eu³⁺ ion, Nano-sized imprinted polymer, Pb²⁺ ion, Carbon paste, Competitive rebinding

1. INTRODUCTION

Europium is classified as an element in the lanthanide series as one of the rare earth elements. The rare earth elements are divided into the lanthanide and actinide series. Lanthanides are widely used as advanced functional materials [1] and catalysts in the production of petroleum and synthetic products [2]. Europium is usually applied in dope lasers and to absorb neutrons in research. The most common uses of Europium are in Color televisions.

Classification and separation of lanthanides is an extremely difficult task because of their similarity to each other (equal charge and almost similar ionic radii) and presence of them at trace concentration levels in most geological materials [3-8]. Thus, introducing of materials capable to selectively recognize different elements of lanthanides is of most importance.

Molecularly imprinted polymer (MIP), prepared with molecular imprinting technique is capable of binding a molecule among closely related structural analogues with high selectivity [9-12]. Similar to MIPs, ion imprinted polymers (IIPs) can recognize metal ions effectively. So far, numerous IIP materials have been reported for different kinds of metal ions such as Cu^{2+} [13,14], Pb^{2+} [15,16], Hg^{2+} [17-19], Ni^{2+} [20,21], Cd^{2+} [22-25], Cr^{3+} [26], Zn^{2+} [27], Fe^{3+} [28,29], Sr^{2+} [30], Tl^{3+} [31], UO_2^{2+} [32-35] and Th^{4+} [36].

However, the introducing of imprinted materials for lanthanides ions have been attracted special attention because of the well-known separation problem with the lanthanides ions. Up to now, a number of ion imprinted polymers have been synthesized for some lanthanide ions including Gd^{3+} [37], Ce^{3+} [38], Nd^{3+} [39], Sm^{3+} [40], Dy^{3+} [41-43] and Er^{3+} [44]. The synthesized IIP have been used for the aim of sensing or solid phase extraction.

The obtained polymers in all of the aforementioned cases have been bulky IIP particles. Bulky shaped imprinted polymers suffer from some drawbacks such as slow rebinding kinetics and high heterogeneity in the binding sites. This is mainly because of situation of recognition sites of the polymer in the interior sections of the IIP. On the other hand, nano-structured, imprinted materials have a small dimension with extremely high surface-to-volume ratio. Thus, the majority of imprinted sites are situated at the surface or in the proximity of surface. Therefore, the forms of imprinted materials are expected to greatly improve the binding capacity, affinity, rebinding kinetics and site accessibility of imprinted materials [45-48]. Binding capacity refers to the population of the active sites, capable of selectively adsorbing the target agent from the solution. Rebinding kinetic means the rate of penetration of the target ions into the selective sites of the imprinted polymer, when the polymer is used to up take the target agents from the solution.

The common method for rebinding and selectivity characterization of the IIPs in the aforementioned works is the batch solid phase extraction of the template ion and other tested cross-reactants by using the IIP particles. The polymeric particles are then usually separated from the solution by a paper filter or centrifugation technique. In some of the works a column

or cartridge solid phase extraction method has been used for rebinding experiments. However, in spite of the mentioned advantages of the nano-sized IIP, compared to the bulky IIP particles, the evaluation and investigation of recognition characteristics of the nano-sized IIP particles by abovementioned techniques is partly difficult. Since the particle sizes of these IIPs are very small, the design of SPE column is difficult. In such a case, also, the filtering with filter paper is not possible. Besides, the centrifugation of the particles after every rebinding experiment seems to need high speed centrifuge instruments.

Electrochemical method such as cyclic voltammetry and potentiometry [49-57], has been used as a simple, easy and effective technique for the determination of various electroactive species. The evaluation of the recognition characteristic and selectivity of the synthesized IIP by voltammetric techniques can also be interesting field of research [58]. However, direct application of the electrochemical methods for the evaluation of the recognition characteristic of the IIP for non-electroactive ions, faces with a real challenge.

In this study, ultrasonic assisted suspension polymerization in silicon oil was applied for the synthesizing of the Eu^{3+} -IIP at nano-sized scale. In order to evaluate the rebinding characteristics of the IIP toward Eu^{3+} ions, it was incorporated with carbon paste electrode, leading to the IIP-modified carbon paste electrode. Since no electrochemical signal was detected for Eu^{3+} on carbon paste electrode, a competitive extraction was proposed by introducing Pb^{2+} as electroactive probe ion, capable of competition with target ions for occupying the selective cavities of the IIP. Differential pulse voltammetry method was then utilized for the tracing of any change in voltammetric signal of Pb^{2+} as the result of its replacing with Eu^{3+} , during competitive extraction process. The obtained data were then used for the evaluation of recognition capability of the IIP for Eu^{3+} and other metal ions including both electroactive and electrochemically inactive cations.

2. EXPERIMENTAL

2.1. Instrument and reagents

Electrochemical data was obtained with a three-electrode system using a potentiostat/galvanostat model PGSTAT302, Metrohm. The carbon paste electrodes modified with IIP or non-imprinted polymer (NIP) was used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Methacrylic acid (MAA) (Merck, Germany), Vinyl pyridine (VP) and divinyl benzene (DVB) (Sigma-Aldrich, USA) were purified by distillation under reduced pressure. 2, 2'-azobisisobutyronitrile (AIBN) was obtained from (Acros Organic, Geel, Belgium) and used as an initiator. $\text{Eu}(\text{NO}_3)_3$ were from (Merck, Germany). Other chemicals were of analytical grade and were purchased from (Merck, Germany).

2.2. Preparation of MIP nanoparticles by suspension polymerization in silicon oil

The method utilized for the preparation of imprinted polymer has been reported previously [59]. Briefly, In order to prepare nano-sized IIP by suspension polymerization in silicon oil, 0.3 mmol of $\text{Eu}(\text{NO}_3)_3$ (template), 1.8 mmol of vinyl pyridine (functional monomer and complexing ligand), 0.6 mmol of MAA (functional monomer and complexing ligand), 12 mmol of DVB (cross-linker) were dissolved in 5 mL of acetonitrile (porogen). After 1 h, 0.05 g of AIBN (initiator) was added to the mixture.

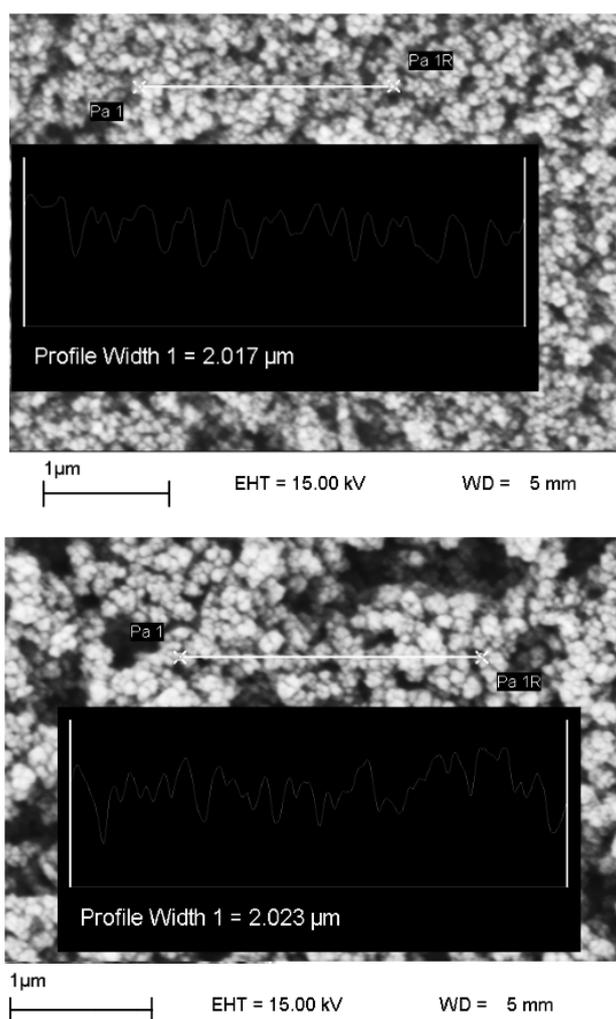


Fig. 1. Scanning electron microscopy images of the synthesized Eu^{3+} -imprinted polymer (up) and the corresponding NIP (down)

The pre-polymerization mixture was added to the silicon oil (100 mL), purged previously with a stream of nitrogen gas for 15 min. Then, the mixture was mixed vigorously by a mechanical mixer at 8000 rpm for 10 min. Next, the solution was further mixed by ultrasonic mixer in order to prepare smaller polymerizable droplets. The mixture was then purged with nitrogen gas for 15 min. Polymerization was carried out in a water bath, fixed at 70 °C, for 24

h. The synthesized particles were washed with petroleum ether and toluene several times. Centrifugation at high speed was applied for the separation of the particles from the solvents. To extract the remained monomers from the polymer networks, the particles were further washed with MeOH and acetonitrile. Afterwards, the polymer particles were suspended in a solution containing sodium acetate and EDTA for 2 h in order to remove Eu^{3+} ions from the polymer. This stage was repeated 5 times. Finally, the polymer was washed with distilled water multiple times and then the particles were dried in vacuum at 50 °C overnight. The NIP nanoparticles were prepared and treated in the same manner without Eu^{3+} . Fig. 1 shows the scanning electron microscopy image of the synthesized IIP and the corresponding NIP. It can be seen that the synthesis strategy has led to nano-structured polymeric materials in both IIP and NIP.

2.3. Preparation of the modified electrodes

In order to prepare carbon paste electrodes, modified with different IIP and NIP particles (IIP-CP and NIP-CP), 5mg of graphite was homogenized in a mortar with 1.5 mg of nano-sized Eu^{3+} -IIP or the relevant NIPs for 10 min. Subsequently, n-icosane (3.0 mg) was melted in a dish in a water bath, heated at 45-50 °C. The graphite/IIP (or graphite/NIP) blend was then added to the melted n-icosane and mixed with a stainless steel spatula. The final paste was used to fill a hole (2.00 mm in diameter, 3 mm in depth) at the end of an electrode body, previously heated at 45° C. After cooling at room temperature, the excess of solidified material was removed with the aid of a paper sheet.

2.4. Rebinding experiments

The prepared IIP-modified electrodes were inserted into the solutions containing the Pb^{2+} and Eu^{3+} or other aimed ions (pH=7), being at stirring state (500 rpm). Then, the electrode was placed in the electrochemical cell containing 10 mL of HCl (0.10 mol L⁻¹). In this stage, at first, a negative pre-potential of -1.0 V was applied to the electrode for 20 s to reduce the adsorbed probe ions (Pb^{2+}) and then the differential pulse stripping voltammetry was performed in the potential range of -0.7 to -0.4 V. The obtained responses were then compared with that of the electrode immersed in the Pb^{2+} solution in the absence of any competitive ion.

3. RESULTS AND DISCUSSION

3.1. The principal of the method used for the evaluation of the recognition capability of the IIP

We found no considerable DPV signal for Eu^{3+} on the carbon paste electrode and also the carbon paste electrode modified with the synthesized IIP, even at mM concentration.

Furthermore, some of the metal ions which we intended to check the IIP recognition capability towards them were known as the non-electroactive species in nature. Therefore, an indirect method was selected for the investigation of the recognition property of the newly developed Eu^{3+} -IIP. For this aim, a carbon paste electrode was modified with Eu^{3+} -IIP and inserted in a proper electroactive probe ion solution. By this means, the electroactive ion was directed to be adsorbed in the selective cavities of the IIP, situated in the carbon paste electrode surface. The recorded differential pulse voltammetry signal of the mentioned electrode was proportional to the number of probe electroactive ions, located in the electrode surface. However, in the presence of foreign ion (Eu^{3+} or other ions to be evaluated) a competition is started between probe electroactive ion and Eu^{3+} (or other tested ions) in order to capture the selective sites of the IIP. Thus, the number of the electroactive probe ion in the IIP cavities was diminished considerably, decreasing subsequently the voltammetric signal of the electrode. The extent of this decrease was proportional to both foreign ions affinities to the sites of the IIP and the number of them contributed in the competition.

The selection of probe ion in the indirect detection method is of most importance. The probe not only should have appropriate electroactivity but also had to compete strongly with target ion in capturing the selective site of the IIP. Pb^{2+} was found to be the best candidate for the mentioned aim among the tested ions (Ni^{2+} , Cu^{2+} , Cd^{2+} , Bi^{3+} , Co^{2+} , Ag^{+}) since it had considerably better electroactivity in carbon paste electrode as well as higher adsorption capability, compared to other tested ions. This is reasonable, because the ionic radii of Eu^{3+} is close to that of Pb^{2+} . Fig. 2 illustrates schematically the described detection method.

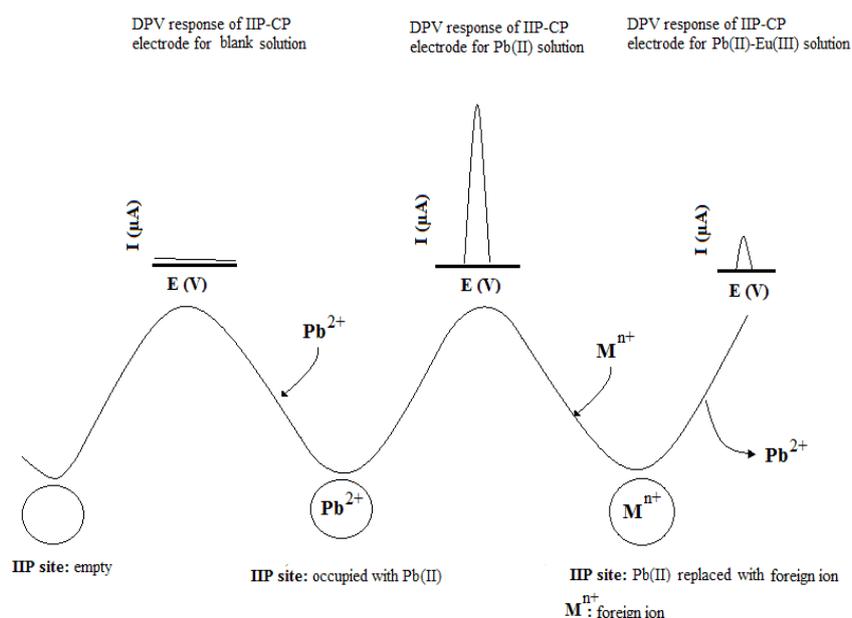


Fig. 2. Schematic representation of competitive extraction-indirect DPV method used for the evaluation of recognition capability of the IIP

3.2. Comparison of the IIP and NIP

Comparison of the IIP with the blank polymer, known as non-imprinted polymer is a usual task, fulfilled generally for the evaluation of the effectiveness of the recognition sites of the IIP, formed during polymerization stage. Fig. 3 represents the comparison of the IIP- and NIP-based carbon paste electrodes. In this figure voltammograms of (a) and (b) represent the DPV signal obtained for the IIP-CP electrode after 10 min incubation in Pb^{2+} and $\text{Pb}^{2+}+\text{Eu}^{3+}$ solutions, respectively. As can be seen, the Pb^{2+} signal is decreased considerably in the presence of Eu^{3+} , as the target ion. On the other hand, the voltammograms of (c) and (d) are related to the NIP-CP electrode for Pb^{2+} and $\text{Pb}^{2+}+\text{Eu}^{3+}$ solutions, respectively. It is clear that, the NIP-CP signal is not affected intensively in the presence of Eu^{3+} . These results indicate that Eu^{3+} compete with Pb^{2+} for capturing the selective sites of the IIP. In other words, there is no noticeable competition between Eu^{3+} and Pb^{2+} in order to achieve to the non-selective sites of the IIP. This experiment suggests that the developed technique can be effectively used to the evaluation of the affinity and selectivity of the selective sites of the synthesized IIP towards different ions.

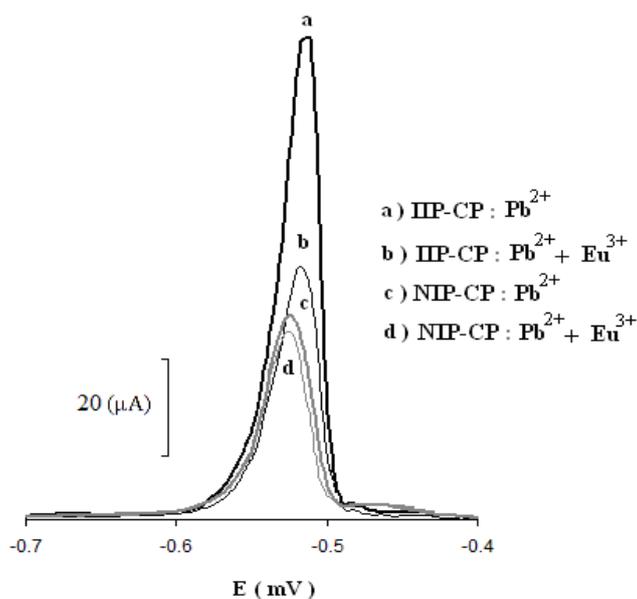


Fig. 3. Differential pulse voltammetry responses of the IIP-CP and NIP-CP electrodes, immersed in the solution of pure Pb^{2+} and that containing both Pb^{2+} and Eu^{3+} (II); $[\text{Pb}^{2+}] = 5 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{Eu}^{3+}] = 1 \times 10^{-6} \text{ mol L}^{-1}$, Extraction condition: extraction time=15 min, agitation speed:400 rpm; electrochemical analysis: 15 ml HCl solution (0.1 mol L^{-1})

3.2. The effect of IIP content of the electrode on the competitive recognition of Eu^{3+}

In order to enhance the competition between target ion and probe ion to capture the selective sites of the IIP, the amount of polymer in the carbon paste electrode is important factor. Fig. 4 represents the change in the IIP-CP electrode response with varying of the IIP

amount in the carbon paste electrode composition. As can be seen, the electrode response for Pb^{2+} solution increases with increasing of the IIP amount till a definite amount and afterwards, it keeps constant. However, the electrode response to the mixture of Pb^{2+} and Eu^{3+} increases as the IIP amount increases. Presence of higher amount of IIP on the electrode surface decreases the competition probability; since, Eu^{3+} ions can inter in the IIP sites, not occupied with the probe ions, and thus no suitable information can be obtained from the rebinding experiment. According to this figure, at a certain IIP amount (1.5 mg) a maximum competition is observed between Eu^{3+} and Pb^{2+} for capturing the positions of the selective sites.

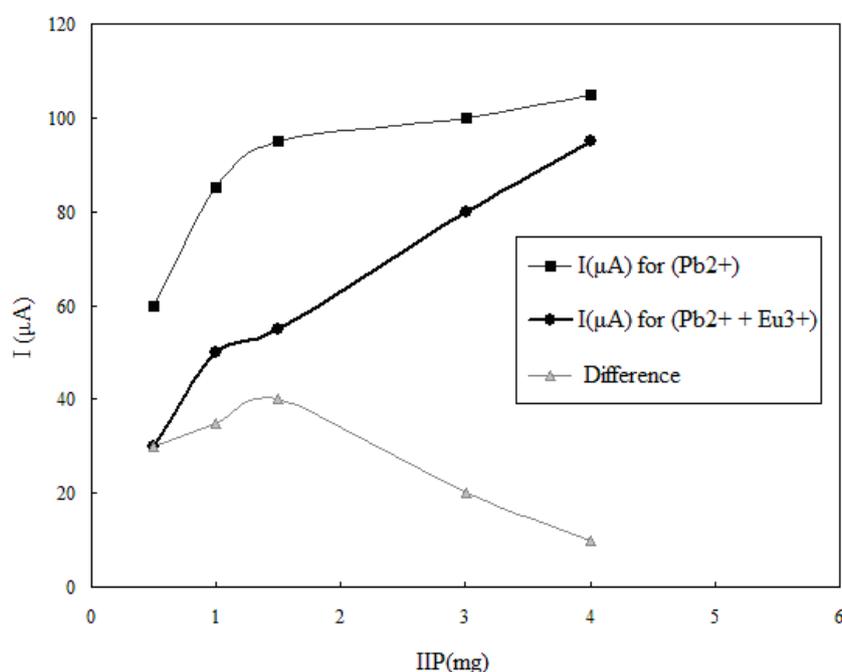


Fig. 4. The effect of the IIP amount on the IIP-CP electrode response; the curves obtained for the pure Pb^{2+} solution (■), $\text{Pb}^{2+}/\text{Eu}^{3+}$ solution (●) and calculated by subtractions of the former curves from each other point by point (▲); $[\text{pb}^{2+}] = 5 \times 10^{-6} \text{ mol. L}^{-1}$, $[\text{Eu}^{3+}] = 8 \times 10^{-6} \text{ mol L}^{-1}$; electrochemical analysis: 15 ml HCl solution (0.1 mol L^{-1})

3.3. The effect of pH on the competitive recognition of Eu^{3+}

Fig. 5 shows the effect of extraction solution pH on the competitive recognition of Eu^{3+} by the IIP, situated at the electrode surface. As can be seen, at neutral pH the best condition is provided for the recognition of Eu^{3+} by the IIP; since, at this pH the signal difference between electrodes immersed in the Pb^{2+} solution and that entered in the $\text{Pb}^{2+}/\text{Eu}^{3+}$ solution is maximum. Lowering of pH decreases the ability of functional groups of IIP sites to establish the coordination bonding of the sites to both Pb^{2+} and Eu^{3+} ; because of interference effect of H^+ ions. On the other hand, at alkaline media the swelling of the IIP particles and also

interference of hydroxide ions on the tested ions can decrease the interaction of both ions with the IIP sites. Therefore, in order to properly evaluate the recognition capability of the IIP, a neutral pH should be applied in the extraction stage.

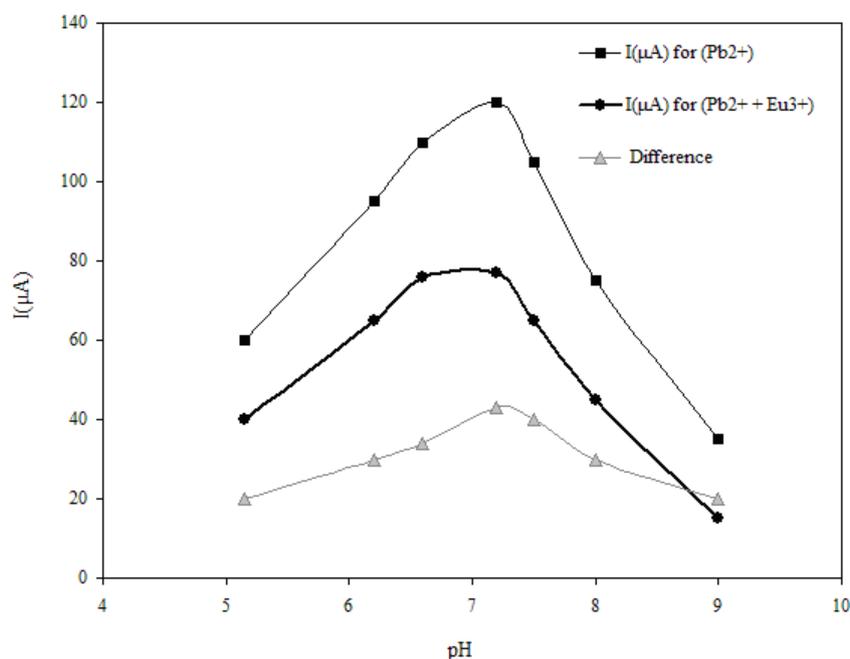


Fig. 5. The effect of extraction pH on the IIP-CP electrode response; the curves obtained for the pure Pb²⁺ solution (■) Pb²⁺/Eu³⁺ solution(●) and calculated by subtractions of the former curves from each other point by point(▲); [Pb²⁺]=5×10⁻⁶ mol L⁻¹, [Eu³⁺]=8×10⁻⁶ mol L⁻¹; electrochemical analysis: 15 ml HCl solution(0.1 mol L⁻¹)

3.4. The effect time on the competitive recognition of Eu³⁺

As can be seen in Fig. 6, the Pb²⁺ adsorption amount variation versus time, in the absence of Eu³⁺ represents a well-known behavior. Herein, initially, the amount of adsorption increases sharply and after a definite time, the adsorption increment rate decreases strongly. The first adsorption regime is assigned to the adsorption of Pb²⁺ ion in the selective sites of the IIP with high adsorption affinity and the second is attributed to the adsorption of probe ions to the non-specific binding sites of the IIP. The adsorption behavior of the IIP in the presence of both target and probe ions is different from that of previously described behavior. This indicates that there is a competition between Eu³⁺ and Pb²⁺ for accessing the binding sites of the IIP. The curve 3 in Fig. 6 shows the difference of two described curves, point by point. As can be seen, the difference is maximum at 15 min. Therefore this extraction time is the best option for the evaluation of the recognition characteristic of the Eu³⁺-IIP.

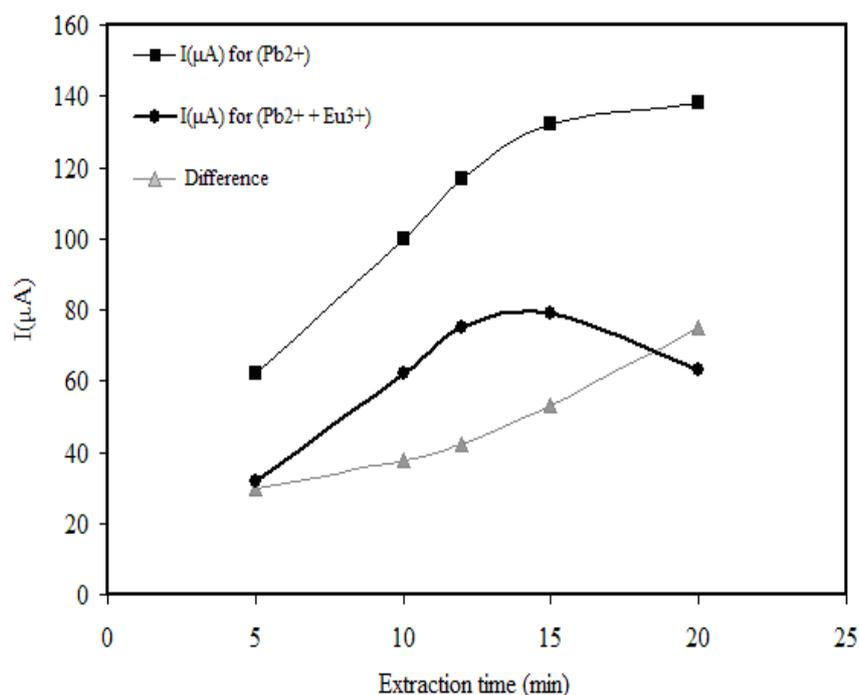


Fig. 6. The effect of extraction time on the IIP-CP electrode response; the curves obtained for the pure Pb^{2+} solution (■) $\text{Pb}^{2+}/\text{Eu}^{3+}$ solution (●) and calculated by subtractions of the former curves from each other point by point (▲); $[\text{Pb}^{2+}] = 5 \times 10^{-6} \text{ mol L}^{-1}$, $[\text{Eu}^{3+}] = 8 \times 10^{-6} \text{ mol L}^{-1}$; electrochemical analysis: 15 ml HCl solution (0.1 mol L^{-1})

3.5. Evaluation of the recognition capability and selectivity of the prepared IIP for different ions

The developed electrode was utilized for the evaluation of the recognition capability of the IIP towards different ions other than Eu^{3+} . This was carried out at the optimized conditions, found for the recognition of Eu^{3+} ions by the IIP. A recognition ratio is defined as an index of imprinted polymer selectivity toward the templated ion, compared to that of the non-imprinted polymer. The recognition ratio is given by equation (1):

$$R = K_{\text{IIP}}/K_{\text{NIP}} \quad (1)$$

Where K_{IIP} and K_{NIP} are the distribution coefficients of the ions in the imprinted and non-imprinted polymers, respectively. In the same electrochemical cell, keeping constant the concentrations of the foreign ions, the recognition ratio R is calculated by the peak current in the DPV voltammograms.

$$R = C_{\text{IIP}}/C_{\text{NIP}} = I_{\text{IIP}}(\text{Pb}) - I_{\text{IIP}}(\text{Pb} + \text{foreign ion}) / I_{\text{NIP}}(\text{Pb}) - I_{\text{NIP}}(\text{Pb} + \text{foreign ion}) \quad (2)$$

where C_{IIP} is the adsorption concentration of the foreign ions in an imprinted polymer; C_{NIP} is the adsorption concentration of the foreign ions in a non-imprinted polymer; $I_{IIP(Pb)}$ is the peak current of DPV voltammograms of Pb^{2+} , using the imprinted polymer; $I_{IIP(Pb+ \text{foreign ion})}$ is the peak current of DPV voltammograms of Pb^{2+} in the presence of foreign ions; $I_{NIP(Pb)}$ is the peak current of DPV voltammograms of Pb^{2+} , using the non-imprinted polymer and $I_{NIP(Pb+ \text{foreign ion})}$ is the peak current of DPV voltammograms of Pb^{2+} in the presence of foreign ions, using the non-imprinted polymer. Moreover, the selectivity coefficients of the synthesized IIP for different ions can be calculated according to the equation 3:

$$\alpha = R_{Eu} / R_{\text{foreign ion}} \quad (3)$$

Where R_{Eu} and $R_{\text{foreign ion}}$ are the recognition ratios of Eu^{3+} and the aimed ions, respectively.

Table 1. the recognition ratios and selectivity coefficients of the synthesized IIP for different ions

Ion	R ($\alpha = R_{Eu} / R_{\text{foreign ion}}$)	selectivity coefficient
Eu^{3+}	25.5	-
La^{3+}	2.2	21.7
Er^{3+}	2.3	11.1
Ce^{3+}	3.6	7.1
Dy^{3+}	2.7	9.4
Ho^{3+}	2.1	12.1
Gd^{3+}	1.8	17.0
Sm^{3+}	1.6	15.9
Hg^{2+}	2.0	12.7
Ag^+	1.5	17.0
Cd^{2+}	1.2	23.2
Ni^{2+}	1.3	19.6
Cu^{2+}	1.8	14.1
Ca^{2+}	1.1	52.7
Mg^{2+}	1.1	107.0
Ba^{2+}	1.0	83.2
Al^{3+}	1.1	112.1

Table 1 represents the defined R values as well as the selectivity coefficients of the synthesized IIP for different ions. As can be seen, the synthesized IIP possess a satisfactory

selectivity for the Eu^{3+} , compared to the other tested metal ions including lanthanides, transition and alkaline earth metal ions. The selectivity of the IIP for Eu(III) ions with respect to the other lanthanides is particularly important because of existence of real challenge in the field of lanthanide separations. It seems that both factors of metal ion size and its tendency to be coordinated by the functional groups of the IP, situated in the IIP sites, influence the tendency of the ions to be adsorbed in the IIP. The closer the metal ion size to that of the printed ion, the more is the tendency of the IIP for its up taking to the polymer. It can be seen that lanthanides and heavy metal ions with the sizes closer to Eu^{3+} are somewhat attracted by the polymer and thus the selectivity coefficients of the polymer for these ions are low. However, we think that the presence of nitrogen atom in the polymer structure, originating from vinyl pyridine, is a key factor in increasing the polymer tendency to some heavy metal ions like Hg^{2+} and Ni^{2+} . The tendency of the polymer to some ions like Mg^{2+} and Al^{3+} is very low because of their higher selectivity coefficients, represented in the table 1. This can be mainly attributed to the smaller ionic radius of these metal ions (particularly Al^{3+}) compared to Eu^{3+} . However, the intrinsically weaker complexing powers of these ions (compared to Cu^{2+}) may also hinder their adsorption in the polymer sites.

4. CONCLUSION

A new method for the evaluation of the recognition capabilities of the nano-sized Eu(III)-imprinted polymer was proposed. The IIP-modified carbon paste electrode coupled with the competitive extraction of Eu^{3+} in the presence of probe Pb^{2+} ions, was shown to be efficient strategy for evaluation of recognition characteristic of the synthesized IIP particularly towards non-electroactive ions. Different factors, effective on the recognition capability of the IIP by the introduced method, were evaluated and discussed in detail. The recognition ratios and selectivity coefficients of the synthesized IIP for different ions were obtained by the method of competitive displacement coupled with differential pulse voltammetry technique.

Acknowledgements

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