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Synthesis of nano-sized Eu^{3+}-imprinted polymer and its application for indirect voltammetric determination of europium

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ABSTRACT

Europium(III)-imprinted polymer nanoparticles were synthesized using suspension polymerization in silicon oil. Vinyl pyridine and methacrylic acid were used either as the complexing ligand or functional monomer. Divinyl benzene was applied as cross-linker agent. Carbon paste electrodes, impregnated with the ion imprinted polymer (IIP), were incubated in the solutions containing Cu^{2+} and different kinds of lanthanide ions. The oxidative stripping differential pulse voltammetry method was then utilized to measure the signal of adsorbed Cu^{2+}, after removal of the electrodes from the first solutions and immersion of them in the electrochemical cell. The response of the IIP-modified electrode to Cu^{2+} decreased in the solution containing both Cu^{2+} and Eu^{3+}; but, it was not influenced in the solutions of Cu^{2+} and other lanthanides. This suggested that Eu^{3+} could compete against Cu^{2+} to capture the selective sites of the IIP; whereas, other lanthanide ions were not capable of replacement with Cu^{2+} in the IIP sites. However, In the case of non-imprinted polymer (NIP)-modified electrode, no considerable signal difference was found between the pure Cu^{2+} solution and the solution containing both Cu^{2+} and Eu^{3+}. This indicated that the selective sites of the IIP were responsible for the observed phenomenon. The decrease in the response of IIP-based electrode to Cu^{2+} was found to be reasonably proportional to Eu^{3+} concentration. This finding was utilized for the indirect voltammetric determination of Eu^{3+}. The effect of different factors on the method was then investigated and the optimum conditions were chosen. The electrode showed high selectivity for Eu^{3+}, even in the presence of other lanthanide ions. The developed method exhibited concentration linear range of 5×10^{-7}–3×10^{-5} mol L^{-1} and detection limit of 1.5×10^{-7} mol L^{-1} (signal/noise, *S*/*N*). Relative standard error percent of 5 separate determinations was found to be 2.91%. The developed method was successfully applied for the determination of Eu^{3+} in the synthetic and spiked real samples.

1. Introduction

Europium is really important in industrial applications, material science, electronics and life science [1]. Nowadays, europium is getting into the environment as a result of its increasing use in various fields. Europium is a toxic element and can cause various diseases in human body. The threshold value of 6 mg L^{-1} has been reported for europium in the literature [2]. However, successive exposure to the low concentrations (<6 mg L^{-1}) of europium can cause serious adverse health effects because of its bioaccumulation along the food chains [3]. Therefore, the development of monitoring techniques for europium is crucial. Low-level determination of Eu^{3+} in solution is usually performed by fluorescence spectrometry [4,5], indirect bioluminescence [6], spectrophotometry [7], inductively coupled plasma atomic emission spectrometry [8], chemiluminescence [9] and atomic absorption spectrometry [10]. These methods are efficient tools for Eu^{3+} detection; because, they are sensitive and accurate. However, in these methods the required sample pretreatment procedures are time-consuming and require costly and specialized equipments for analysis.

Electrochemical sensors have been increasingly received attention due to their favorable portability, ease of operation procedure and low-cost [11]. The advanced voltammetry techniques have been utilized for determination of Eu^{3+}. Mercury has been utilized as the best electrode material for the electrochemical determination of Eu^{3+} because of good electroactivity of europium at the mercury electrode [12]. However, because of toxic characteristic of mercury, some other electrodes like glassy carbon and diamond electrodes have been proposed for Eu^{3+} determination by the electrochemical techniques [13–16]. The sensitivities of these electrodes are not satisfactory enough for low level Eu^{3+} determination. Thus, these electrodes have been modified with nafion or nafion–carbon nanotube materials in order to achieve a proper sensitivity and detection limit for the determination method.

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Recently, lanthanum hexaboride (LaB_6) has been reported as a novel electrode material for Eu^{3+} determination in place of toxic mercury electrodes [17]. Although, chemists have achieved excellent successes in the improvement of sensitivity, detection limit, selectivity and safety of the electrochemical determination of Eu^{3+}, a main drawback still exists with the electrochemical technique, used for Eu^{3+} determination. This problem is the interference effect of other lanthanide ions which influences usually the Eu^{3+} signal at equal or even lower concentrations, because of high similarity existing among lanthanides. Therefore, any progress in the solving of the interfering problem is highly important in this field.

Molecularly imprinted polymer (MIP), prepared with molecular imprinting technique, is capable of selectivity binding to a molecule among closely related structural analogs [18–21]. Similar to MIPs, ion imprinted polymers (IIPs) can effectively recognize metal ions [22–26]. Development of imprinted materials for lanthanide ions has 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 such as: gadolinium (Gd^{3+}) [27], cerium (Ce^{3+}) [28], neodymium (Nd^{3+}) [29], samarium (Sm^{3+}) [30], dysprosium (Dy^{3+}) [31–33] and erbium (Er^{3+}) [34]. The synthesized IIP have been used for the aim of sensing or solid phase extraction.

Our research group has already shown that the imprinted polymers could be incorporated in the carbon paste electrodes (CP) to develop high selective sensors for determination of different kinds of molecules as well as ions [35–39]. In this work, nano-sized imprinted polymer containing Eu^{3+}-selective sites was synthesized by a new formulation and then mixed with carbon powder in the presence of n-eicosane as the binder. Since, Eu^{3+} was not capable of creation a considerable voltammetric signal on the CP electrode; an indirect technique was applied for its determination. For the determination purpose, Eu^{3+} ions were let compete with Cu^{2+}, as an electroactive ion, for capturing the Eu^{3+}-selective sites of the IIP in the electrode surface. This led the Cu^{2+} signal of the IIP-modified electrode to decrease in accordance with Eu^{3+} concentration.

As far as we know, this is the first report on the IIP-based E^{3+} selective voltammetric sensor. Moreover, a new formulation for the synthesis of nano-sized Eu^{3+} imprinted polymer has been described at the present work which can also be used for the preparation of other lanthanide ions-imprinted polymers.

1.1. Instrument and reagents

Electrochemical data was obtained with a three-electrode system using a potentiostat/galvanostat model PGSTAT302, Metrohm. Carbon paste electrodes, modified with IIP or non-imprinted polymer (NIP), were used as the working electrodes. 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, Belgium) and used as an initiator. $Eu(NO_3)_3$ was from (Merck, Germany). Other chemicals were of analytical grade and were purchased from (Merck, Germany).

1.2. Preparation of IIP nanoparticles by suspension polymerization in silicon oil

In order to prepare nano-sized IIP, by suspension polymerization in silicon oil, 0.3 mmol of $Eu(NO_3)_3$ (template), 1.8 mmol of vinyl pyridine (as functional monomer and complexing ligand), 0.6 mmol of MAA (as functional monomer and complexing ligand), 12 mmol of DVP (cross-linker) were dissolved in 5 mL of acetonitrile (porogen). After 1 h, 0.05 g of AIBN (initiator) was added to the mixture. 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. High speed centrifugation method 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. Afterward, the polymer particles were suspended in a solution containing sodium acetate and ethylenediaminetetraacetic acid (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 distillated water several 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+}.

1.3. Preparation of the modified electrodes

In order to prepare carbon paste electrodes, modified with IIP and NIP particles (IIP-CP and NIP-CP), 0.05 g of graphite was homogenized in a mortar with a known mass of nano-sized Eu^{3+}-IIP or the relevant NIPs for 10 min. Subsequently, n-eicosane (a determined amount) 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-eicosane 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.

1.4. Evaluation of the modified electrodes for their recognition capabilities

The prepared IIP-modified electrodes were inserted into the solutions containing Cu^{2+} (5×10^{-6} mol L^{-1}) and Eu^{3+} or other aimed ions (pH=7), being at stirring state. Then, the electrode was placed in the electrochemical cell containing 10 mL of HCl (0.1 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 (Cu^{2+}) and then differential pulse stripping voltammetry (DPSV) was performed in the potential range of −0.8 to −0.3 V. The response obtained was then compared with that of the electrode immersed in the pure Cu^{2+} solution (in the absence of any competitive ion). The current response difference, calculated by the subtracting of two abovementioned signals, was applied for conclusion.

1.5. Determination method by the developed electrode

The optimized electrode was prepared by mixing of 0.05 g of graphite powder with 0.04 g of IIP and 0.01 g of n-eicosane according to the procedure, described in details in Section 2.4. In order to determine Eu^{3+} in an aqueous sample, the prepared IIP-modified electrode was inserted in the solution containing Cu^{2+} (5×10^{-6} mol L^{-1}) and undetermined concentration of Eu^{3+}. The pH of this solution was adjusted to 7 and it was continuously stirred (300 rpm) during extraction step. After 15 min, the electrode

was removed from the solution and placed in the electrochemical cell containing 10 mL of HCl (0.10 mol L^{-1}). Then, a negative pre-potential equal to −1.0 V was applied to the electrode for 20 s and then differential pulse stripping voltammetry was performed in the potential range of −0.8 to −0.3 V. The current response obtained was used for the estimation of Eu^{3+} concentration with respect to the calibration graph, obtained previously.

1.6. Competitive rebinding experiment

In order to evaluate rebinding of Eu^{3+} to the synthesized IIP, in the presence of electroactive competitor (Cu^{2+}), a batch rebinding experiment was carried out. For this aim, 0.05 g of the IIP powder was transferred into the beakers, filled with 50 mL of solution of Cu^{2+} (1×10^{-3} mol L^{-1}) and Eu^{3+} (different concentrations ranging from 5×10^{-4} to 5×10^{-6} mol L^{-1}). The solutions were agitated for 2 h and then centrifuged. The supernatant portions were used for the determination of Eu^{3+} and Cu^{2+} via differential pulse polarography technique [40]. The amounts of Eu^{3+} and Cu^{2+}, adsorbed on the IIP particles, were calculated by subtracting of the obtained concentration data from the initial concentration of the ions.

2. Results and discussion

2.1. Synthesis of Eu(III)-imprinted polymer and its characterization

In this work, a new and simple formulation was proposed for the preparation of Eu^{3+}-imprinted polymer. The synthesis procedure is briefly illustrated in Fig. 1. According to this method, MAA and VP were mixed with Eu^{3+} (mole ratio, 2:6:1). MAA and VP functioned as both functional monomer and complexing agent. No additional complexing ligand was required in this proposed method. This strategy led to a simplified synthesis method and deleted the probability of removal of the ligand molecules during the washing stage; since, all of functional

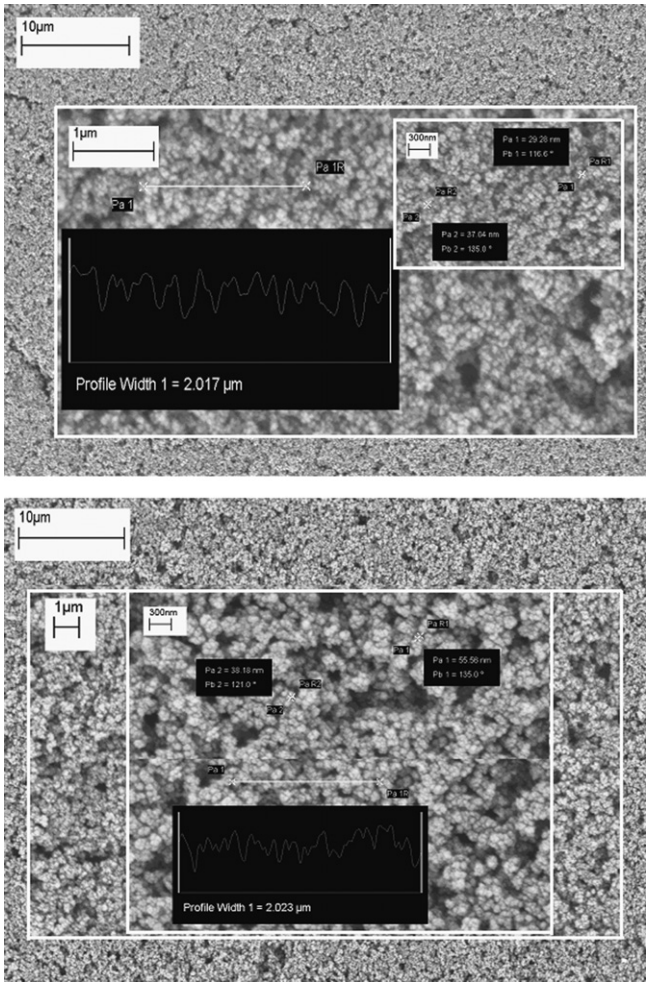

Fig. 2. Scanning electron microscopy images of the prepared IIP (up) and the relevant NIP (down).

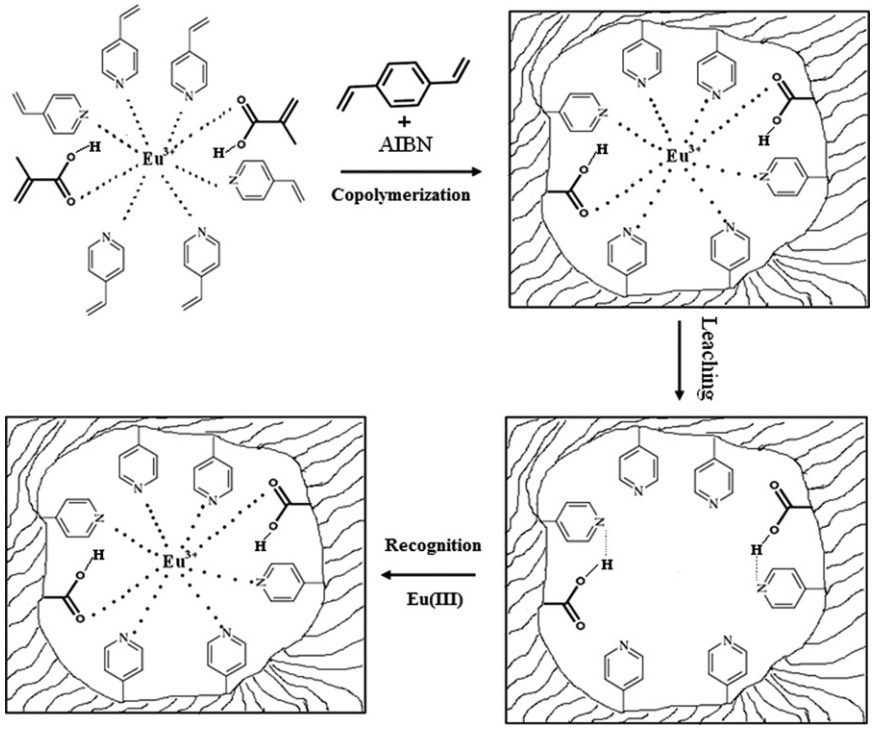

Fig. 1. Schematic representation of the method used for the preparation of Eu^{3+}-imprinted polymer, including steps of functional monomer arrangement around Eu^{3+}, co-polymerization, template removal and target ion recognition.

monomers could undergo polymerization, attaching to the polymer network. Scanning electron microscopy images (SEM) of the obtained polymer particles (including IIP and NIP) are shown in Fig. 2. As can be seen, the sizes of the synthesized polymer particles are at nano-scale range (average size of about 50 nm, calculated from the depicted SEM topographic map). This is because of establishment of separate polymerization reactions in the single and very tiny polymerizable droplets, suspended previously in the silicon oil by using mechanical and then ultrasonic mixing [39]. Fourier transform-infrared spectrometry (FT-IR) spectra of the unleached IIP, leached IIP and NIP are shown in Fig. 3. At first glance, it seems that the FT-IR spectra of the leached IIP and NIP are highly similar. This is reasonable; since, after removal of Eu^{3+} from the IIP, the chemical structures of these polymers are exactly the same. Presence of a stretching vibration band at $\sim$1704 cm^{-1} in the FT-IR spectra of the NIP and leached IIP is related to the $\upsilon_{C=O}$ of carboxylic acid group of methacrylic acid. This peak can not be seen in the unleached IIP. This is due to the coordination bonding of –C=O to Eu^{3+} that forces the initial band to shift toward low frequency region. Presumably, a small band at 1620 cm^{-1} in the FT-IR spectrum of unleached IIP is due to the –C=O group coordinated to Eu^{3+}. Furthermore, in the FT-IR spectrum of the unleached IIP an explicit band is observed at $\sim$1303 cm^{-1} which is absent in both NIP and leached IIP. Likely, this band is related to the C–O bond of carboxylic acid of the IIP sites. Additionally, in the FT-IR spectrum of the unleached IIP a distinct band can be seen at wave number of about $\sim$3303 cm^{-1}. However, it seems that this band in the NIP and leached IIP is broadened and shifted toward higher wave number values. We think that this band is an indicative of presence of O–H band vibration which is present in the unleached IIP where the carboxylic acid functional groups are bonded to Eu^{3+} via oxygen atom of carbonyl. After removal of Eu^{3+}, the hydrogen atom of carboxylic acid group can interact with nitrogen of vinyl pyridine (see Fig. 1). This phenomenon can lead υ_{O-H} of the carboxylic acid groups of selective sites to shift and broaden.

2.2. Sensor working mechanism

Europium (III) is an electroactive ion among lanthanides. However, the signal related to the reduction of Eu^{3+} is generally hidden by the hydrogen evolution reaction in the non-mercury electrodes. This is because of highly negative reduction potential of Eu^{3+}/Eu^{2+} redox couple as well as a relatively lower overpotential of hydrogen ion reduction in such electrodes. Proton reduction reaction may cause an increase of the solution pH near the electrode surface, and a consequent hydrolysis of the trivalent, rare earth ions (e.g. Eu^{3+}), which leads to the formation of hydroxide or basic salts, i.e. very complicated and irreproducible electrochemical behavior [16]. In this work, we found no considerable DPSV signal for Eu^{3+} on the carbon paste electrode and carbon paste electrode modified with the synthesized IIP, even at millimolar concentration level. Therefore, an indirect method was utilized for the investigation of the recognition property of the

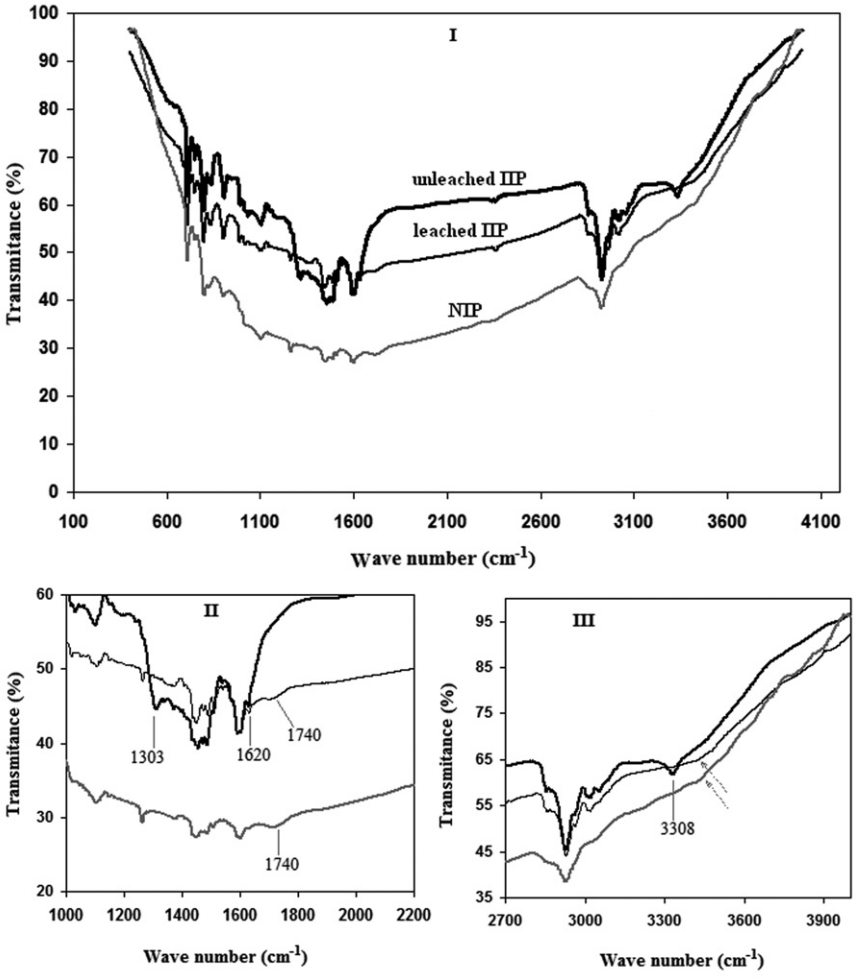

Fig. 3. FT-IR spectra of the leached IIP, unleached IIP and NIP particles (I); the regional magnification of spectrum (I) in different wave number ranges (II) and (III).

newly developed Eu^{3+}–IIP. For this aim, a carbon paste electrode was modified with Eu^{3+}–IIP and inserted in a solution containing Cu^{2+} as a proper electroactive probe ion. 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; although, it was possible for the existing ions to be adsorbed on the non-selective sites of the IIP. The recorded differential pulse voltammetry signal of the mentioned electrode was proportional to the number of probe electroactive ions, interred in the IIP sites. However, in the presence of target ion a competition occurred between the probe electroactive ion and Eu^{3+} in order to capture the selective sites of the IIP. Hence, 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 amount of Eu^{3+} in the solution. Fig. 4(I) represents schematically the described Eu^{3+} determination methodology, used in this work.

In Fig. 4(II) the voltammograms of (a) and (b) represent the DPSV signal of the IIP-CP electrode, after 10 min incubation in Cu^{2+} and Cu^{2+}–Eu^{3+} solutions, respectively. As can be seen, Cu^{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 Cu^{2+} and Cu^{2+}–Eu^{3+} solutions, respectively. It is clear that the NIP-CP signal is not affected noticeably in the presence of Eu^{3+}. These results indicate that Eu^{3+} compete strongly against Cu^{2+} for capturing the selective sites of the IIP, resulting in removal of Cu^{2+} ions from the IIP sites. On the other hand, there is no noticeable competition between Eu^{3+} and Cu^{2+} in order to achieve the non-selective sites of the IIP; because, the effect of Eu^{3+} on the Cu^{2+} signal of the NIP-CP electrode is very smaller than that on the IIP-CP electrode signal. This experiment suggests that the developed technique can be effectively used for the determination of Eu^{3+}. Fig. 4(III) shows the recorded current responses of the IIP-CP electrode, after being immersed in the Cu^{2+} solution and the solutions containing Cu^{2+} and different kinds of metal ions. As can be seen, except the case of Cu^{2+}–Eu^{3+} solution, the electrode responses to all solutions are as the same as that to Cu^{2+} solution. These observations indicate that the electrode response to Eu^{3+} is really selective. The importance of selectivity of the developed

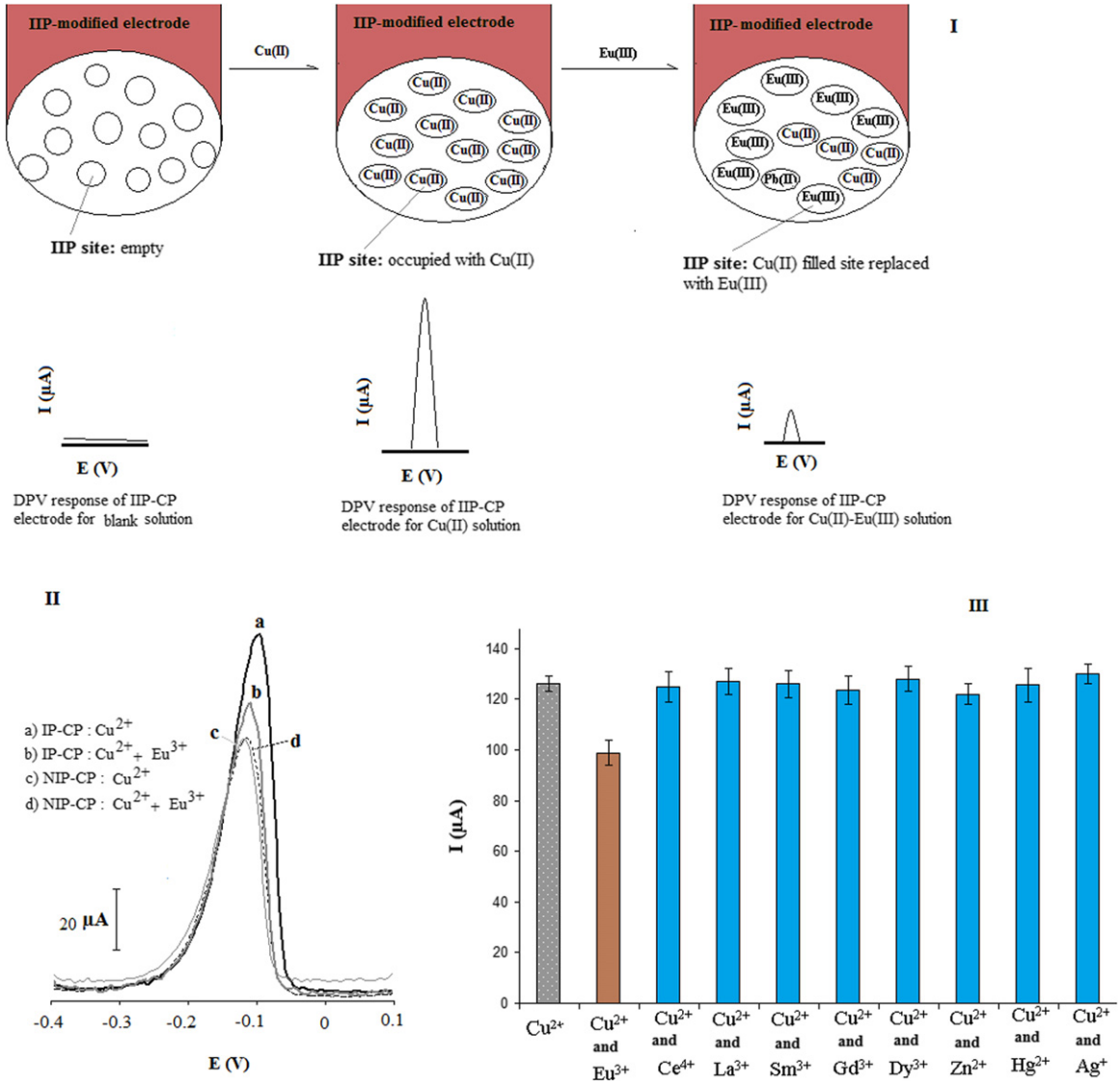

Fig. 4. Schematic representation of the determination mechanism of the developed method (I); differential pulse voltammetry responses of the IIP-CP and NIP-CP electrodes immersed in the solution of pure Cu^{2+} and that containing both Cu^{2+} and Eu^{3+}(II); differential pulse voltammetry response of the IIP-CP electrode recorded to different solutions (III); $[Cu^{2+}]=5\times10^{-6}$ mol L^{-1}, lanthanides ion concentration$=1\times10^{-6}$ mol L^{-1}, extraction condition: extraction time$=15$ min, agitation speed$=400$ rpm; electrochemical analysis: 15 ml HCl solution (0.1 mol L^{-1}).

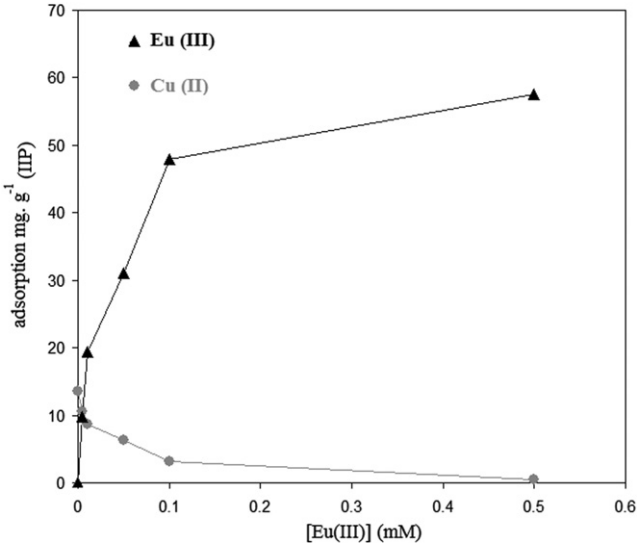

Fig. 5. Variations of the up-taken Eu^{3+} and Cu^{2+} in the IIP as a function of Eu^{3+} concentration (initial concentration).

sensor for Eu^{3+} is further highlighted when considering the responses of other lanthanide ions; because, there is high similarity between lanthanide ions. This experiment indicates that the proposed method can result in effectively recognition of the target ions from the highly similar lanthanide ions, at least, in equal concentrations.

In order to study further the competitive extraction of Eu^{3+} in the IIP particles, a competitive rebinding experiment was carried out in the solution containing suspension of IIP particles. Fig. 5 represents the variations of the up-taken Eu^{3+} and Cu^{2+} in the IIP as a function of Eu^{3+} concentration. It can be seen that as Eu^{3+} increases in the solution, the amount of this ion in the IIP sorbent increases accordingly. However, the adsorption of Cu^{2+} in the IIP decreases with increasing of Eu^{3+} in the solution and thus in the IIP. This experiment confirms that Cu^{2+} ions are replaced with Eu^{3+} ions in the IIP sites, thus liberating the competitor electroactive Cu^{2+} ions in the solution. The amount of the released Cu^{2+} ions can thus be as an indirect indication of Eu^{3+} concentration in the sample.

2.3. The effect of the electrode composition on the sensor performance

Fig. 6(I) represents the change in the IIP-CP electrode response as a function of the IIP amount in the carbon paste composition. As can be seen, the electrode response to Cu^{2+} increases with increasing the IIP amount till a definite amount and afterward, it keeps constant. However, the electrode response to the mixture of Cu^{2+} and Eu^{3+} grows as the IIP amount increases. Increasing of the IIP amount in the electrode augments the available recognition sites for Cu^{2+} adsorption, thus increasing the electrode signal. However, further increase in the amount of the IIP in the electrode surface can decrease its signal because of insulating characteristic of the electrode surface. On the other hand, presence of higher amount of IIP in the electrode surface decreases the competition probability between probe and target ions; since, Eu^{3+} ions can inter in the sites, not occupied with the probe ions, because of presence of high population of available sites in the electrode surface. For this reason, the DPSV signal of the IIP-CP electrode, in the presence of both Cu^{2+} and Eu^{3+}, increases as the IIP content of the electrode grows. According to this figure, at a certain IIP amount (4 mg) the highest competition is observed between Eu^{3+} and Cu^{2+} for capturing the positions of the

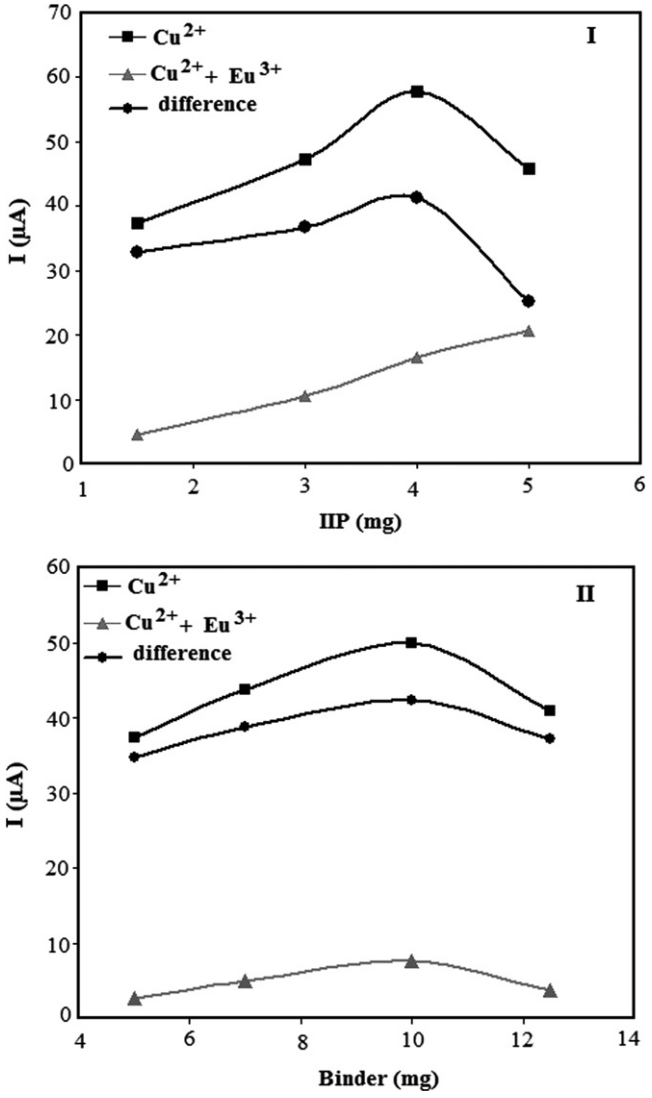

Fig. 6. The effect of the amounts of the IIP (I) and n-eicosane (II) on the IIP-CP electrode; the curves obtained for the pure Cu^{2+} solution (■), Cu^{2+}/Eu^{3+} solution (▲)and calculated by subtractions of the former curves from each other point by point (●); $[Cu^{2+}]=5\times10^{-6}$ mol L^{-1}, $[Eu^{3+}]=8\times10^{-6}$ mol L^{-1}; electrochemical analysis: 15 ml HCl solution (0.1 mol L^{-1}).

selective sites. Therefore, in order to establish a rational relationship between Eu^{3+} concentration and DPSV signal of the IIP-CP, originated from electrolysis of probe ion, it is necessary to use optimum amount of the IIP in the modified electrode composition.

The effect of n-eicosane amount, used as the binder, on the electrode efficiency was also investigated. The results of this experiment are shown in Fig. 6(II). As can be seen, the IIP-CP electrode in both solutions of Cu^{2+} and Cu^{2+}–Eu^{3+} results in optima point at binder amount of 10 mg. In both cases, the electrode signal decreases when the binder amount becomes higher than optimum value due to the insulating effect of the binder. However, it seems that higher amount of the binder is beneficial for Cu^{2+} to keep its occupied sites of the IIP against Eu^{3+} ions; since, the electrode signal in the solution containing both Cu^{2+} and Eu^{3+} increases when increasing the binder amount. This is reasonable; because, the affinity of an ion with more charge to the non-polar area (corroborated by higher amounts of the binder material) is lower than that of the ion with less charge. However, according to the curve, representing the difference of two other curves, 10 mg of binder is an

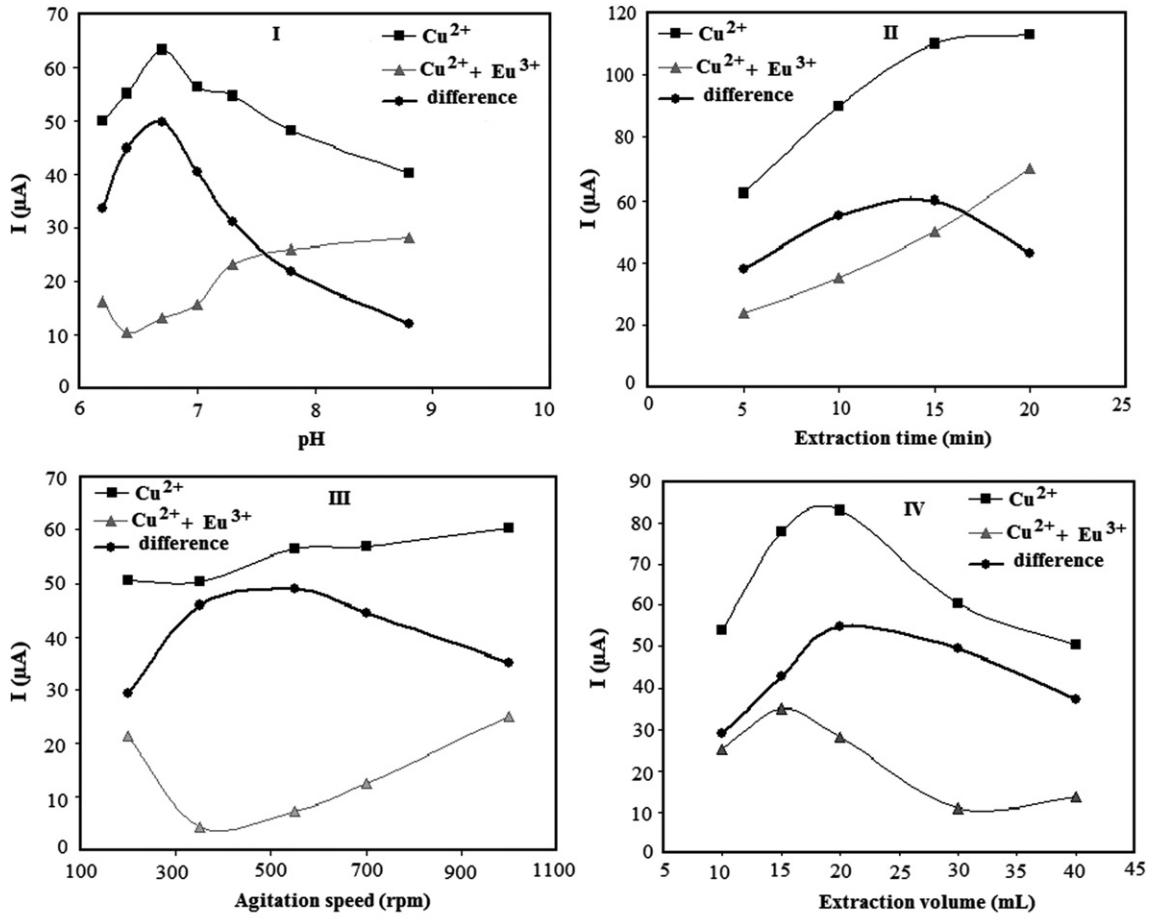

Fig. 7. The effect of extraction parameters including pH (I), time (II), agitation speed (III) and extraction volume (IV) on the IIP-CP electrode response; the curves obtained for the pure Cu^{2+} solution (■) Cu^{2+}/Eu^{3+} solution (▲) and calculated by subtractions of the former curves from each other point by point (●); $[Cu^{2+}]=5\times10^{-6}$ mol L^{-1}, $[Eu^{3+}]=8\times10^{-6}$ mol L^{-1}; electrochemical analysis: 15 ml HCl solution (0.1 mol L^{-1}).

appropriate amount for this parameter to be considered when preparing of the IIP-CP electrode.

2.4. The effect of extraction condition on the electrode performance

Fig. 7(I) shows the effect of extraction solution pH on the competitive recognition of Eu^{3+} by the IIP, situated on the electrode surface. As can be seen, neutral pH provides the best condition for the recognition of Eu^{3+} by the IIP; since, at this pH the signal difference between the electrode immersed in the Cu^{2+} solution and that incubated in the Cu^{2+}–Eu^{3+} solution becomes maximum. Lowering of pH, decreases the ability of functional groups of the IIP sites to establish the coordination bonding with the metal ions (Cu^{2+} and Eu^{3+}) because of interference effect of H^+ ions which can protonate the nitrogen groups of vinyl pyridine in the selective sites of the IIP. On the other hand, at alkaline media swelling of the IIP particles and also the interference effect of hydroxide ions on the tested ions can decrease the interaction of both ions with the IIP sites. In order to properly recognize the target ion by the IIP, neutral pH was applied in the extraction stage.

As it is evident in Fig. 7(II), the amount of Cu^{2+} adsorption in the electrode increases sharply as the extraction time increases; but, after a definite time, the adsorption increment rate is decreased strongly. The first adsorption regime is assigned to the adsorption of Cu^{2+} ion in the high selective sites 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, compared to previously described behavior. This indicates that there is a really strong competition between Eu^{3+} and Cu^{2+} for accessing the binding sites of the IIP. However, according to the difference curve in Fig. 7(II), there is a maximum signal at the extraction time of 15 min. Therefore, this extraction time was chosen as the best option for the determination of Eu(III).

According to Fig. 7(III), the response of the IIP-CP electrode, immersed in the Cu^{2+} solution, is not highly influenced by the stirring rate of the extraction media. The electrode response increases slightly with increasing agitation speed. However, it can be seen that the signal of the electrode depends strongly on the agitation speed, when immersing it in the solution containing both Cu^{2+} and Eu^{3+}. This behavior can be attributed to different adsorption kinetics of two kinds of ions. Increasing of agitation speed, increases the adsorption amounts of both ions; however, it seems that the effect of mixing rate on the extraction of Cu^{2+} is bigger than that on the Eu^{3+} adsorption. Initially, the agitation speed increment, decreases the response of the electrode, immersed in the solution containing Cu^{2+} and Eu^{3+}. Then, it starts to grow noticeably as the mixing rate is enhanced further. According to the curve representing the difference of two above mentioned curves, the stirring rate equal to 300 rpm is an appropriate condition for Eu^{3+} determination by the developed sensor.

Extraction volume is important parameter in the determination purposes involving a pre-extraction step. According to the curves depicted in Fig. 7(IV), using more than 30 mL of extraction

solution, leads to the highest exchange power for Eu^{3+} to remove Cu^{2+} ions from the IIP sites. However, this volume range is not favorable; since, higher than 20 mL, the extraction efficiency of Cu^{2+} is diminished. Obviously, the difference curve indicates that the extraction volume of 20 mL can be the best option in this case.

2.5. Analytical characterization

After establishment of the determination method, the interference effects of various species were examined. The tolerance limit was established as the maximum concentrations of foreign species that caused a relative error of 5% in the analytical signal. The obtained results, showing the mole ratios of the interfering agent to Eu^{3+} that produces 5% error in the Eu^{3+} determination, are given in Table 1. According to these results, the developed determination method is not influenced in the presence of considerable amounts of Ca^{2+}, Mg^{2+}, Zn^{2+}, Hg^{2+}, Pt^{2+} and Ag^{+}. However, 10-fold excess of Cd^{2+} and Cu^{2+} influences the electrode signal significantly. In the case of lanthanide ions Gd^{3+} and Sm^{3+} have the most influence on the electrode signal. However, compared to the other previously reported Eu^{3+} sensors, these results indicate that the efficiency of the sensor for the determination of Eu^{3+} is interestingly high.

Table 1
Evaluation of interfering effect of different ions on the determination of Eu^{3+} with the developed IIP-based electrode.

Interfering ion	Interference level (mole ratio)[a]
Ca^{2+}	100
Mg^{2+}	100
Zn^{2+}	70
Hg^{2+}	50
Ag^{+}	50
Cd^{2+}	10
Er^{3+}	20
Dy^{3+}	10
La^{3+}	10
Pt^{2+}	30
Ce^{3+}	5
Gd^{3+}	5
Sm^{3+}	5

[a] The mole ratios of the interfering agent to Eu^{3+} that produces 5% error in the Eu^{3+} determination.

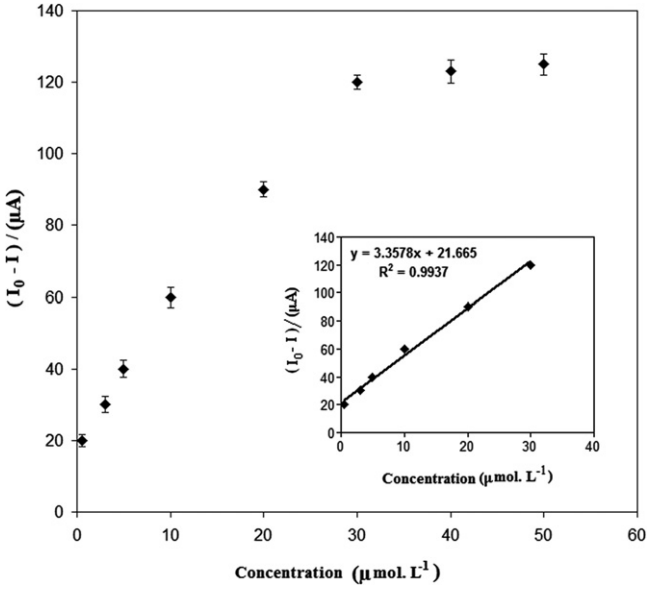

Fig. 8. Calibration graph obtained for the developed IIP-CP electrode and used for the determination of Eu^{3+}; inset: the linear range of the calibration curve; I_0: the electrode signal in the pure Cu^{2+} solution (5×10^{-6} mol L^{-1}) I: the electrode signal in the solution containing Cu^{2+} (5×10^{-6} mol L^{-1}) and different concentration of Eu^{3+}.

Table 2
Determination of Eu^{3+} in different synthetic and real spiked samples (n=4).

Sample	Added (μ mol L^{-1})	Found (μ mol L^{-1})	Recovery (%)	ICP-OES
Synthetic water	2.00	2.07	103.5(±3.7)	1.88
(Na^{+}, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^{-})	5.00	4.70	94.0(±3.5)	5.21
Tap water[a]	1.00	0.90	90.0(±4.2)	1.10
River water[b]	0.70	0.82	108.7(±4.6)	0.78

[a] The samples contain different amounts of the following ions: high level: > 20 mg L^{-1}: Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}, SO_4^{2-}, Cl^{-}, NO_3^{-}.
[b] The samples contain different amounts of the following ions: low level: < 2 mg L^{-1}: F^{-}, Zn^{2+}, Fe^{2+}, Cu^{2+}, Mn^{2+}.

The optimized electrode was utilized to plot a calibration graph for the determination of Eu^{3+}. For this aim, voltammetric response of the sensor, obtained for constant concentration of Cu^{2+} (5×10^{-6} mol L^{-1}) in the absence of Eu^{3+}, was subtracted from that recorded in the presence of different concentrations of Eu^{3+} and the same fixed concentration of Cu^{2+}. The values obtained were plotted as a function of Eu^{3+} concentration in order to obtain a calibration graph for the developed electrode. This plot is represented in Fig. 8. As can be seen, this electrode exhibits concentration linear range of 5×10^{-7}–3×10^{-5} mol L^{-1}. The detection limit was calculated equal to 1.5×10^{-7} mol L^{-1} (S/N). Relative standard error percent of 5 separate determinations by the proposed sensor was found to be 2.91%.

The proposed method was used to determine Eu^{3+} in several synthetic and real samples, spiked with Eu^{3+}. A comparison with an inductively coupled plasma emission spectrometry (ICP-OES) suggested that the developed voltammetric determination method gave reliable results in a wide range of samples (Table 2).

3. Conclusion

A new voltammetric sensor based on the nano-sized Eu^{3+}-imprinted polymers was introduced. The competition of Eu^{3+} ions against Cu^{2+} ions in order to capture the Eu^{3+}-selective sites of the IIP-modified carbon paste electrode, caused to effectively reduce the DPSV signal of Cu^{2+} in the electrode. This was a principle for Eu^{3+} detection procedure, developed in this study. This sensor showed high selectivity for Eu^{3+} determination, even in the presence of other lanthanide ions. The sensor was capable to determine Eu^{3+} in spiked water samples.

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