Electrochemical Sensor Based on Self-doped Polyaniline with Guest-induced Binding Sites for Detection of Lead(II) Ion

Jahangir Shojaei, Ali Reza Zanganeh[*]

Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza, Iran
[*]E-mail: ar.zanganeh@gmail.com, ar.zanganeh@iaush.ac.ir, ar_zanganeh@yahoo.com

An electrochemical approach towards developing a lead(II) ion selective polymer is presented. A poly(aniline-co-3-aminobenzenesulfonic acid), P(Ani-co-3ABSA), membrane would be reconciled with the peculiarities of lead(II) ions by incorporating them. It seems that consecutive embedding/ejecting of lead(II) into-from the mass of P(Ani-co-3ABSA) coating, correspondingly templates the coating towards lead(II) ion. This method results in a highly selective sensor for the measurement of lead(II) ion. The optimal conditions for sensor operation were ascertained. The surface morphology of the freshly synthesized, templated and templated-preconcentrated P(Ani-co-3ABSA) membranes were explored by SEM. The interference effect on the voltammetric response with coexisting ions was also investigated. The developed sensor was applied for lead(II) determination by pre-concentration/differential pulse-anodic stripping voltammetry in concentrations of 1.0 nM to 0.1 mM and by potentiometric method in concentrations of 10.0 nM to 1.0 mM.

1. INTRODUCTION

Electroconducting polymers such as polyacetylene, polythiophene, polypyrrole and polyaniline (PAni) have drawn considerable attention because they are promising materials for constructing sensors [1-5], transistors [6,7], supercapacitors [8,9], electrochromic devices [10-12], and many other applications. Consequently a lot of researches have been conducted on their preparation, properties and applications [13-15]. Among electroconducting polymers, PAni and its derivatives have been widely studied due to their doping-dedoping capability and controllable electric conductance. PAni exists in different oxidation states: the completely oxidized pernigraniline, semi-oxidized emeraldine and completely reduced leucoemeraldine. The doped state of emaraldine, emeraldin salt, is the unique

conductive state of PAni [16]. However, the electroconductivity of PAni will be considerably decreased in neutral and alkaline solutions. In order to enhance the electrochemical characteristics of PAni in higher pH media, a self-doping procedure has been utilized for preparing self-doped polyaniline (SPAni). Self-doping in polyaniline is the existence of acidic functional groups such as sulfonic or carboxylic along the polymer chain which replaces anionic dopants typically existing in polymeric film to retain electroneutrality in the emeraldine salt of polyaniline [15,17].

SPAni has been used for constructing lead electrochemical sensors [18-21]: An electrode modified with poly(4-aminobenzenesulfonic acid) has been used to detect Pb(II) [18]. The construction of a sensor from polyaniline and carbon nitride, to detect lead(II) using voltammetry has been reported [19]. An electrode modified with poly(4-aminobenzenesulfonic acid) has been employed to voltammetric determination of lead [20]. Polyaniline-mercury modified electrode has been applied for measurement of lead(II) [21].

Poor sensitivity and selectivity of the cationic sensors on the basis of PAni in addition to their narrow linear dynamic range are considered the weak properties of PAni in sensor construction since appropriate recognition sites are not obtainable on this polymer [22,23]. This work presents an electrochemical approach for developing a lead(II) ion selective polymer. A poly(aniline-co-3-aminobenzenesulfonic acid), P(Ani-co-3ABSA), coating would adjust to the characteristics of lead(II) ions by incorporating them. As will be detailed in the following parts of this paper, this approach results in a highly selective sensor for lead(II).

2. EXPERIMENTAL

2.1 Equipment and reagents

The electrochemical experiments were conducted using an Autolab PGSTAT100. Studies were conducted in a cell formed from an auxiliary platinum electrode, a silver/silver chloride reference electrode and a glassy carbon (GC) working electrode. Before electropolymerization, the GC electrodes were rubbed with fine-grained Al_2O_3 and cleaned in an ultrasonic bath. Morphological study of the polymeric membrane, SEM, was performed using a MIRA3 TESCAN instrument.

All reagents including 3-aminobenzenesulfonic acid (3ABSA) and nitrate salt of lead(II) (from Merck), were used without further purification. Aniline (Ani) was purified via distillation and was instantly transferred into the electropolymerization cell or hoarded in a cold place. Double-distilled water (DDW) was utilized. The pH of the solutions was adapted by adding sodium hydroxide or nitric acid.

2.2 Electrochemical synthesis and templating of P(Ani-co-3ABSA) coating

The P(Ani-co-3ABSA) coating was formed on the GC surfaces by immersing the polished GC electrode into a solution containing 0.15 M Ani and 0.30 M 3ABSA, under a nitrogen environment. P(Ani-co-3ABSA) film was electrodeposited on GC working electrode at a constant potential of 750 mV for a favorite time. Afterwards the modified electrodes were washed with DDW to remove unreacted

monomers remaining on the surface of P(Ani-co-3ABSA) coating. The modified electrode was moved to the solution of 1.0 mM lead(II) to template the P(Ani-co-3ABSA) coating towards lead(II). The templating step was performed by exposing the polymeric films to successive reduction-oxidation potential steps at -550 and +700 mV correspondingly. The duration of every step was 200 s. This procedure was done in triplicate, and was finally ended by an oxidation stage of 500 s to remove residual lead from the P(Ani-co-3ABSA) film; the overall templating process takes 1500 s. In potentiometry, electrodes were conditioned in 1.0 mM lead, no less than two hours.

2.3 Pre-concentration and stripping analysis of lead species

The modified electrode thus obtained was put into solutions of lead(II) with given molarities. Pre-concentration was done by imposing a potential stage of -0.8 V for 480 s concurrent with stirring. Afterwards, the preconcentrated electrode was introduced to differential pulse-anodic stripping voltammetry (DP-ASV) in blank solution (0.2 M potassium nitrate with pH = 2). The DP-ASV experiments were accomplished in the potential interval of -0.6 to 0.4 V and stripping peak currents of lead were determined. After each DP-ASV test, sensors were cleaned at 0.50 V for three hundred seconds in potassium nitrate with pH = 2 to remove the remaining lead from the P(Ani-co-3ABSA) film and convert the metal ion-chelated-membrane to its original state.

2.4 Evaluation of sensor performances in potentiometry

To evaluate the potentiometric response of the membrane, standard solutions of Pb^{2+} with varying molarities ranging from 1.0×10^{-11} to 1.0×10^{-3} M having 0.1 M potassium nitrate were prepared. All the measurements were conducted at ambient temperature (25 ± 2 °C). The cell potential was registered after reaching a drift rate of ~ 1.0 mV per minute. Calibration graph was established using these recorded potentials. The selectivity of the P(Ani-co-3ABSA) based sensor was assessed via separate solution method (SSM) with 1.0 mM solutions of primary and foreign species [24]. The detection limit (DL) was obtained according to the IUPAC recommendation [25]. Between the potentiometric measurements, the membranes were laid in the conditioning solution.

3. RESULTS AND DISCUSSION

3.1 Electrochemical synthesis and investigating morphology of the P(Ani-co-3ABSA) copolymer

P(Ani-co-3ABSA) coating was potentiostatically synthesized at a potential of 750 mV in an growth solution which solely composed of 0.15 M Ani and 0.30 M 3ABSA. Similar polymerization procedure [26] and concentration ratio of comonomers [27] have been used formerly. It has been recognized that synthesis of a conductive polymer in the absence of any supporting electrolyte produces a polymer coating with more favorable electrochemical properties [28]. Our experimental data indicates

this electropolymerization procedure and constitution of the polymerization mixture causes the electrosynthesis of durable coating in a suitable time.

3ABSA has amino and sulfonate moieties and acts as monomer and doping agent [29]. The sulfonate moieties restrict the generation of bipolarons and copolymer deterioration [30,31]. Moreover, 3ABSA is an easily available and low-priced monomer.

After polymerization, electrodes were immersed in 1.0 mM lead(II) for doing templating stage, as described above. Conducting polymers have a distinctive characteristic, and their physical and chemical behavior can be changed reversibly by doping-dedoping. The polymer coated electrode was subjected to triplicate reduction-oxidation potential stages at -550 and +700 mV, in order. During the application of negative potential, the polymeric chain is changed to its reduced (neutral) state, and the P(Ani-co-3ABSA) membrane becomes negative because of the existence of sulfonate moieties in the copolymer. In this circumstance, lead(II) ions are embedded into the polymeric membrane to preserve electroneutrality [18-20]. However, during the positive potential step of the templating process, the polymer backbone turns to its cationic state and the reverse of the above process occurs, i.e., lead species are ejected from the membrane due to repulsive electrostatic forces [32]. This embedding/ejecting steps result in generation of cavities for lead ions. It seems that repeated embedding/ejecting of lead ion into-from the copolymer coating and subsequent complexation of lead with binding sites of the copolymer cause reorientation of the receptor sites of membrane. Hence, these receptor sites are reconciled with the size and complexing peculiarities (coordination number, geometry) of Pb(II). This technique causes templating of copolymer towards Pb(II). After templating, the P(Ani-co-3ABSA) membrane acquires effective lead(II) ion recognition ability and it is possible to determine lead(II) ion with a high degree of selectivity; this will be discussed in the following parts. These discussions are compatible with the information of prior experiments [32,33]. We found that in order to create sufficient recognition elements in the P(Ani-co-3ABSA) coating, templating procedure must be replicated 3 times. No peak for lead was identified in the voltammogram of polymeric film recorded in 0.2 M potassium nitrate with pH=2, indicating that the last phase of the templating expels the lead from the copolymer layer.

The absorption profiles recorded for the untemplated and templated copolymer P(Ani-co-3ABSA), electrochemically synthesized on ITO-coated glass plates are exhibited in Figures. 1a and 1b, respectively. The observed red-shifting of absorption profiles of the copolymer are considered to arise from (i) ion-induced conjugation enhancement along the polymer chain caused by metal ion coordination to the binding sites of the membrane, (ii) electron density variations on the backbone of the polymer caused by introducing positively charged lead ions into the membrane. These explanations are in consistency with the results of other researches [32,33].
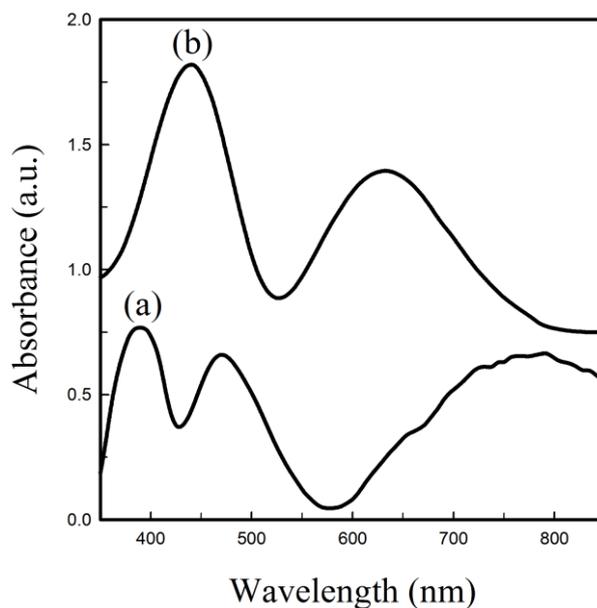
Figure 1. The UV spectrum of the copolymeric film on ITO electrodes earlier than (a) and later than (b) the templating process.

From the SEM micrograph of the freshly prepared P(Ani-co-3ABSA) membrane, shown in Figure 2a, it can be understood that the electropolymerization of Ani in the presence of 3ABSA led to the creation of a homogeneous copolymer. The microstructure of the copolymer after templating is presented in Figure 2b. Two events can be assumed for variation of morphological characteristics of the templated copolymer: in the negative step of the templating technique, the initially-formed-lead seeds act as the active sites to form larger lead aggregates. These aggregates dissolve (oxidize) in the positive step of the templating technique, leading to pore production in the copolymer. Moreover, because oligomers are more easily oxidized than monomers [27,34], during the templating process, oligomers remaining in the polymer film undergo further polymerization, resulting in enhancement of the degree of conjugation and change in the morphological characteristics of the P(Ani-co-3ABSA) film. Figure 2c illustrates the surface topography of the templated copolymer after precipitation of lead at E = -0.8 V from 0.1 mM Pb^{2+}. The film is thinner at the pores created by the templating; consequently, the electric field is higher at the pores, which are the active sites for metal nucleation [35,36]. It may be assumed that precipitation of lead within the copolymer occurs by diffusing lead ions through the pores and creation of nucleation centers within the pores and at the boundary between the electrode and the copolymer [37]. As illustrated in Figure 2c, after pre-concentration, the pores are occupied by lead particles.

The CV of the templated electrode in potassium nitrate is presented in Figure 3a. At the potential of approximately 0.36 V, the membrane exhibits an anodic peak connected with the conversion between leucoemeraldine-emeraldine and emeraldine-pernigraniline forms. The CV contains two reduction peaks at roughly 0.05 and 0.25 V. This electrochemical behavior is close to that already reported for the redox transfers of SPAni films [27]. There was no considerable difference between CVs in sequential sweeps. This stability of the prepared copolymer can be accredited to the sulfonate moieties present in the polymer chain which diminishes the formation of bipolarons [30]. Figure 3b presents CV for lead

deposition and dissolution using P(Ani-co-3ABSA) film. This CV illustrates a peak for lead reduction at about -0.61 V, to which an anodic peak is coupled. Comparable behavior has been informed for electrodes modified with conductive polymers in lead solutions [37].
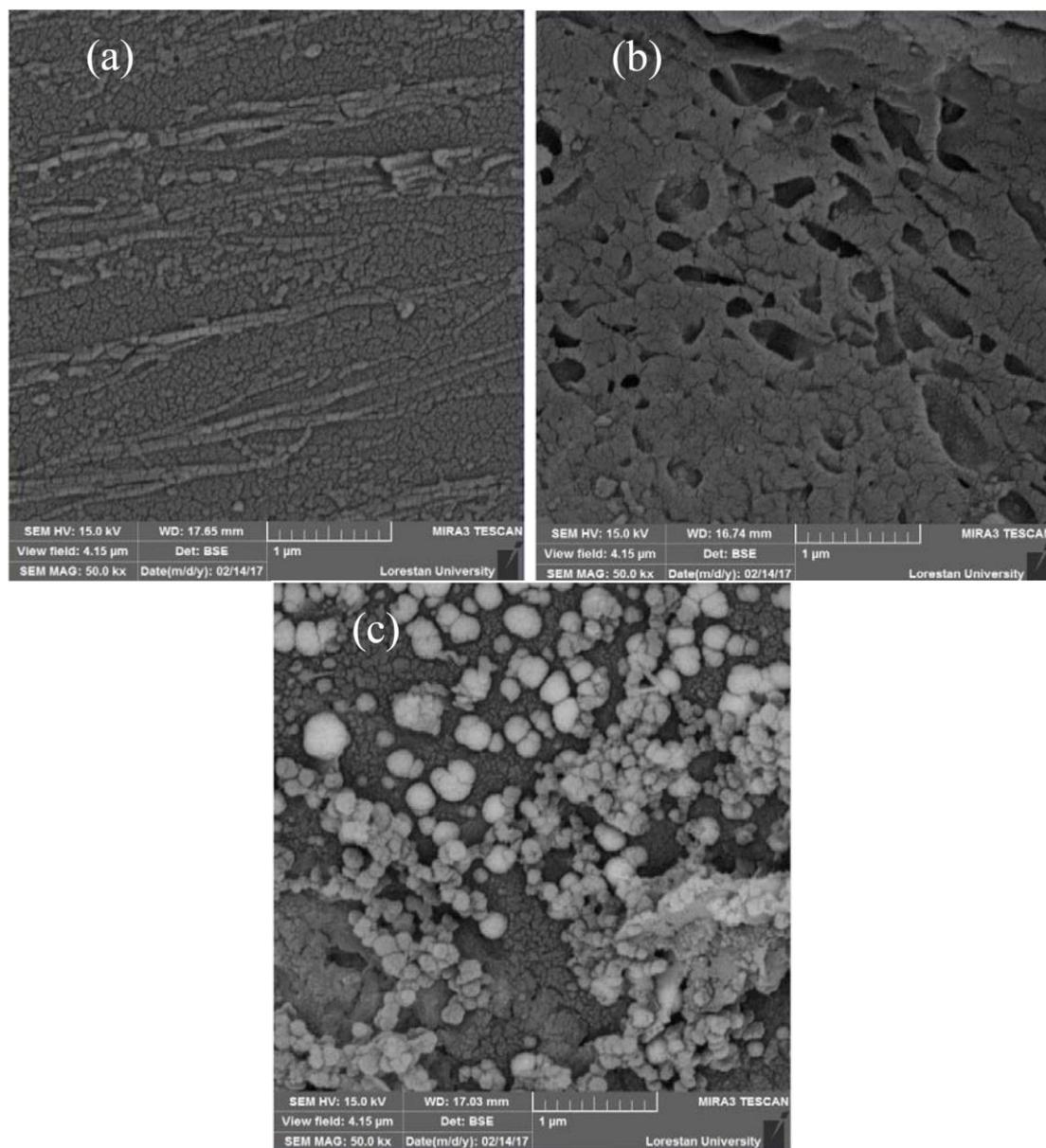
Figure 2. The SEM of the P(Ani-co-3ABSA) coating, (a) as synthesized, (b) after templating, and (c) after templating and preconcentrating at E = -0.8 V from 1.0×10^{-4} M Pb^{2+} solution.
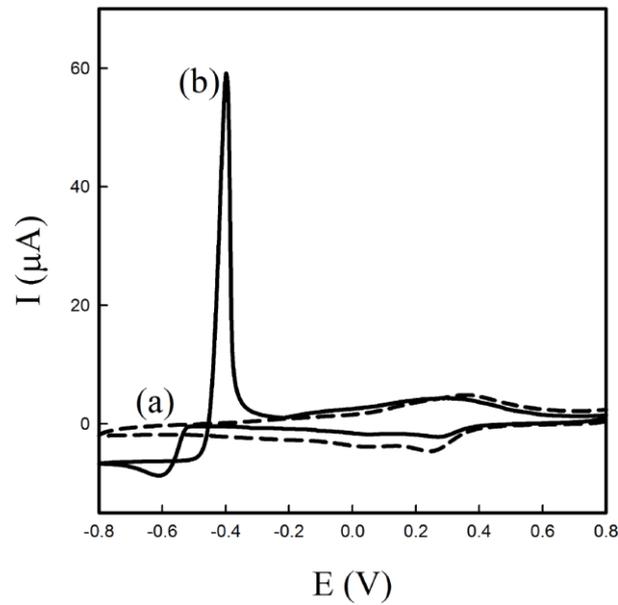
Figure 3. CV of the P(Ani-co-3ABSA) electrode (a) in 0.2 M potassium nitrate and (b) in 1×10^{-7} M Pb^{2+} plus 0.2 M potassium nitrate.

3.2 Voltammetric experiments

Tests were conducted to ascertain the optimum experimental conditions for voltammetric measurement of Pb^{2+}, founded on obtaining the largest stripping peak current.
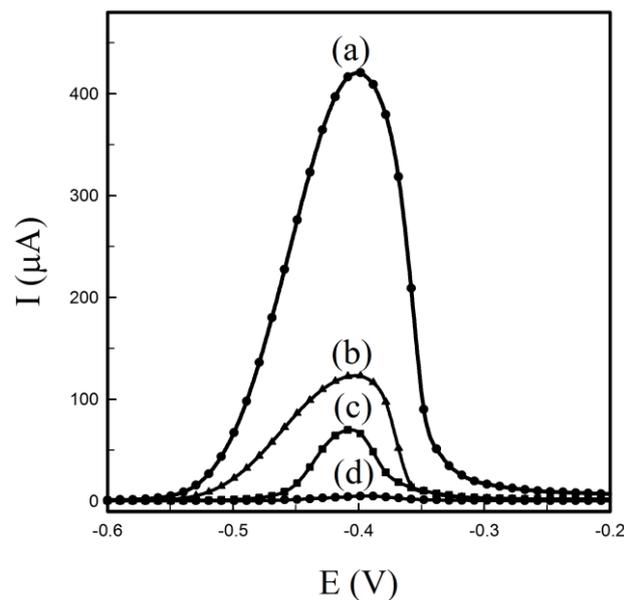
Figure 4. DP-ASV of (a) templated-P(Ani-co-3ABSA) coated electrode, (b) untemplated-P(Ani-co-3ABSA) coated electrode, following the pre-concentration of lead, (c) templated-P(Ani-co-3ABSA) coated electrode following the open circuit pre-concentration of lead (d) bare working electrode. For all instances, the molarity of lead(II) was 1.0×10^{-6} M.

As can be seen in Figure 4, the modified but untemplated electrode yielded a peak current (Figure 4b) which was approximately 30% of that obtained from templated electrode shown in Figure 4a. Comparing the stripping signals of the untemplated and templated polymeric electrodes indicate that conformational and electronic changes that occur during the templating process play a consequential role in creating recognition sites for lead ion. For contrast, the DP-ASV responses of the templated copolymeric electrode after open circuit accumulation in lead(II) and unmodified electrode are illustrated in Figures 4c and 4d, respectively, and they will be described in the following parts.

It was recognized that the polymerization duration and consequently copolymer thickness control the greatness of lead stripping current. The highest stripping peak was reached for polymerization duration of 8 s at conditions used in the present work. The stripping peak currents diminish significantly in other polymerization times because thin films do not provide sufficient binding sites for efficient lead accumulation, and thicker films impose resistance to charge and mass transfer during the accumulation and stripping steps [20,38]. These findings in conjunction with preceding studies [37] prove that lead is entrapped into the bulk of the membrane.

The optimum conditions to achieve the highest efficiency in the pre-concentration step were also ascertained. The relatedness of the stripping peak height and pH of the pre-concentration solution was examined. As illustrated in Figure 5, the peak intensity is flat at the pH limits of 3.0-5.5 and diminishes considerably outside this range. The decay of the peak intensity at lesser pH may be accredited to the electrostatic repulsion among protonated active sites of the polymeric film and positive lead species, and decrease in the accumulation efficiency due to the hydrogen evolution. The decay in the DP-ASV current at high pHs may be accredited to the decrease in the electrochemical activity of P(An-co-3ABSA) film which influences its sensing characteristics along with the formation of insoluble lead species. These explanations are in conformity with previous reports [20,38,39]. It has been described that the conductance of PAni will be considerably decreased while the pH is more than four [19,40], which remarkably limits its application in sensors. As can be seen, the prepared copolymer P(Ani-co-3ABSA) shows electroactivity in solutions with higher pH values. At higher pH, the hydronium ion in sulfonate group can take the role of a buffer; hence, PAni doped by 3ABSA can still show electroactivity in solutions with higher pH values [34].

The accumulation potential defines the greatness of the stripping signal; hence its influence was examined. The largest peak current was observed at potential of -800 mV; pre-concentration efficiency and hence stripping peak current decreased significantly at potentials other than -800 mV. The stripping current diminishes while the potential is more positive than -800 mV. This can be assigned to the point that the accumulation potential is not adequate for reducing the lead cations [18]. The decrease in the stripping current at pre-concentration potentials more negative than -800 mV can be accredited to the reducing of
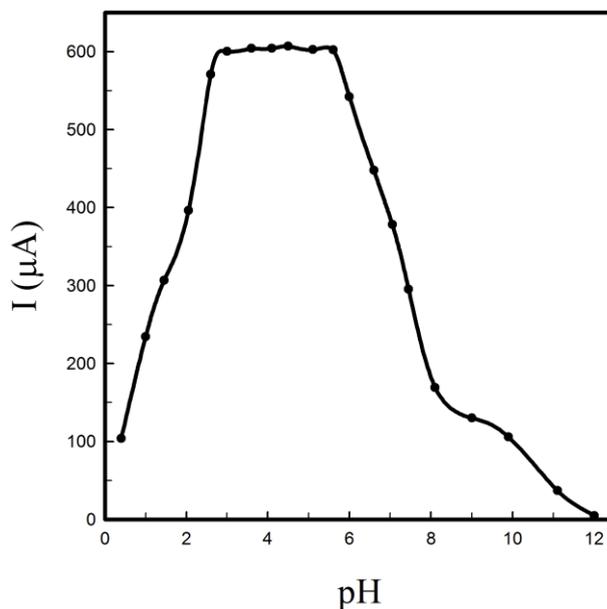
Figure 5. Change of the stripping peak intensity with pH of the pre-concentration solution. Electrosynthesis conditions: 0.30 M of 3ABSA and 0.15 M of Ani with potential of 750 mV. Accumulation circumstances: Pb^{2+}, 1.0×10^{-4} M; accumulation potential of -800 mV. DP-ASV circumstances: scanned potential, -0.6 to 0.4 V; scanning rate, 100 mV s^{-1}; solution, 0.2 M potassium nitrate with pH = 2.

miscellaneous species [20]. In addition, the open circuit pre-concentration of lead was performed by immersing the electrode into the solution of lead(II) with concentration of 1.0 μM, for 24 h. The obtained peak current (Figure 4c) was around seventeen percent of that attained using an accumulation potential of -800 mV (Figure 4a). Formation of the primary nucleation sites during lead electrocrystallization results in the extra-pre-concentration of lead species at these sites, and hence larger peak current. The stripping voltammogram of bare GC electrode, after 480 s accumulation in 1.0 μM Pb(II) at E= -800 mV, revealed a very small peak (Figure 4d) which confirms that the enrichment of lead species results mainly from the polymeric film rather than the underlying substrate.

The pre-concentration time is a significant factor in stripping voltammetry, therefore, its effect on DP-ASV current of 0.1 mM Pb(II) was studied and the outcomes are illustrated in Figure 6. As shown, the peak intensity enhances with pre-concentration time up to 540 s and then remains unchanged, which can be ascribed to the membrane saturation with lead in the reduced state. The literature results support this interpretation [18]. Generally, a pre-concentration time of 480 s was selected in this research to prevent saturation of the membrane and ensure the extensive dynamic range and adequate sensitivity of the method.

The voltammetric figures of merit for modified electrodes were ascertained. The DP-ASV procedure was accomplished by immersing the modified electrodes, later than accumulation, in 0.2 M KNO_3 at pH = 2, and sweeping potential between -600 to 400 mV. At the templated modified electrode, DP-ASV peak intensity depended on the lead(II) ion concentration of accumulation medium between 1.0 nM and 0.1 mM (Figure 7a). DP-ASV current rises linearly with lead ion molarity between 1.0 and 10.0 nM, and Pearson correlation coefficient (r) is 0.9987 (*N*=5). The peak intensity is rectilinear versus Log [Pb^{2+}] in the concentrations of 10.0 nM to 0.1 mM and r value is 0.9996 (*N*=9) (Figure 7b). The

appearance of plateau at high concentration (Figure 7a) and semilogarithmic character of the calibration curve (Figure 7b) can be assigned to the membrane saturation with lead species [18,20]. Figure 7c shows the declined voltammetric sensing properties of the modified-untemplated sensor. The DL (founded on S/N=3) was reckoned to be 0.1 nM Pb^{2+}.
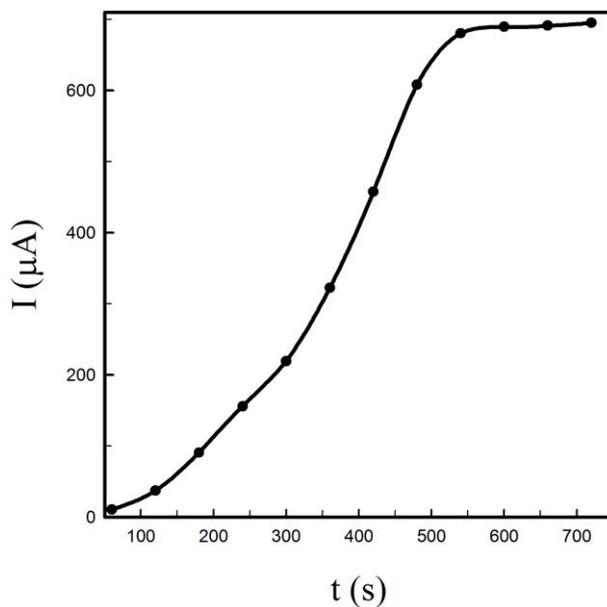
Figure 6. The relationship between DP-ASV peak current and pre-concentration time for 1.0×10^{-4} M lead(II) ion.
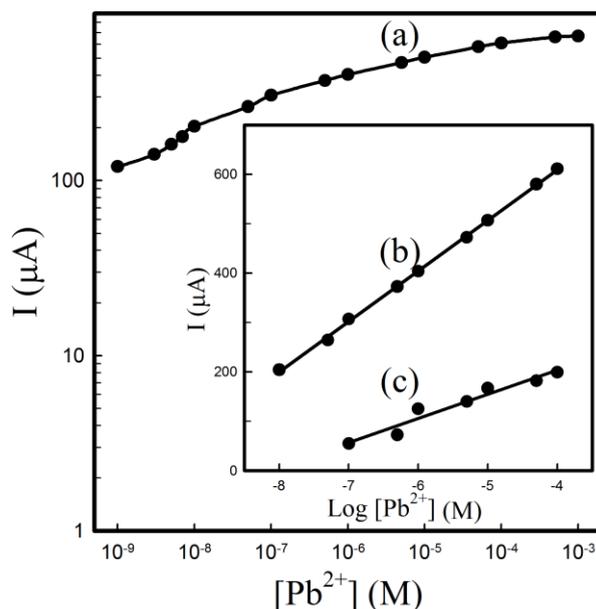
Figure 7. The relationship between DP-ASV peak current and lead(II) ion concentration (a). Calibration curves for templated (b) and untemplated (c) electrodes.

The reproducibility of the templated modified electrodes was explored by consecutive measurements in 0.1 mM Pb^{2+} using five electrodes prepared individually under identical conditions according to the above-mentioned method. The %RSD of the sensor response was nearly 3.7% (*N*=5). The attained %RSD for coated-untemplated sensor was nearly 9.0% (*N*=5). The repeatability of the electrode was checked by consecutive DP-ASV experiment (*N*=5) after electrodeposition from 0.1 mM Pb^{2+}, employing a lone coated-templated sensor, under optimal circumstances. The attained %RSD was nearly 2.8%. The repeatability of the coated-untemplated sensor was found to be approximately 7.4% (*N*=5). The coated-templated sensor had good long-term stability and later than 25 days, the peak height of DP-ASV only decreased 4% contrasted with the primary peak. For the untemplated sensor, following 25 days, DP-ASV peak current declined 55% compared to the original value.

To test the impact of any foreign species on detecting lead(II) ion, interference investigation was carried out via mixture experiments. Accumulation was accomplished in a solution composed of 0.1 mM lead(II) and incremental molarities of foreign species, and then DP-ASV was conducted as stated earlier. The interference was regarded to be effective if the change in the peak current of lead stripping was more than 3σ, where σ is the standard deviation (SD) of repetitive DP-ASV runs for 0.1 mM lead. The majority of ions examined, including Fe^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Mn^{2+}, Zn^{2+} and Cd^{2+}, did not alter the stripping peak intensity of lead(II) ion even at 0.01 M. The existence of Hg(II), Ag(I) and Cu(II) produced interference in detecting Pb(II) because they have an intense tendency for the receptor moieties of the polymeric membrane [37,39,41-44].
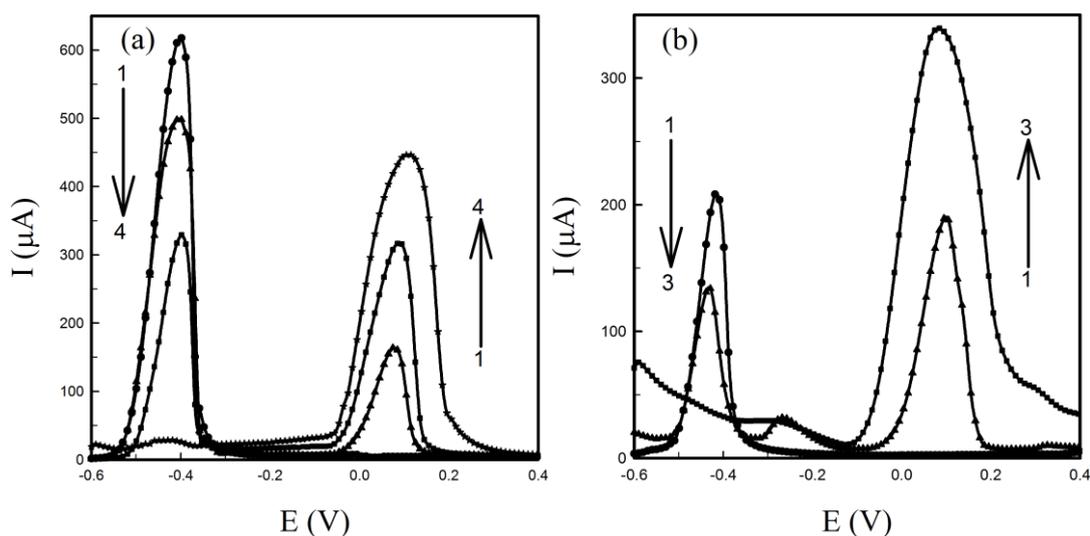
Figure 8. The interference effect of Cu(II) on the voltammetric measurement of lead (a) by template-modified electrode, (1) $[Cu^{2+}]$=0, (2) $[Cu^{2+}]$=$[Pb^{2+}]$, (3) $[Cu^{2+}]$=10$[Pb^{2+}]$, (4) $[Cu^{2+}]$=100$[Pb^{2+}]$, and (b) by untemplated-modified electrode, (1) $[Cu^{2+}]$=0, (2) $[Cu^{2+}]$=$[Pb^{2+}]$, (3) $[Cu^{2+}]$=10$[Pb^{2+}]$. For all instances, 0.1 mM lead(II) was used.

Figure 8 illustrates interference of Cu(II) during measurement of lead next to the metals pre-concentration from mixtures containing 0.1 mM Pb(II) and several amounts of Cu(II). Comparing untemplated and templated membranes from the view point of interference due to copper (Figures 8a

and 8b), obviously points out the role of templating approach in the sensor selectivity during voltammetric measurements. A further peak was reached in the DP-ASV due to the existence of Cu(II) (Figure 8). At the coated-templated sensor, 100-fold Cu^{2+} omitted the lead signal (Figure 8a); however, at the untemplated electrode, 10-fold Cu^{2+} omitted the lead peak (Figure 8b). These results demonstrate the significant impression of templating on sensor selectivity.

3.3 Potentiometric sensing characteristics

The sensing ability of the prepared sensor in potentiometry was assessed. The modified electrode, after conditioning, was engaged as an indicator electrode in the potentiometry to detect lead ion. The effectiveness of solution pH, during potentiometric experiments with P(Ani-co-3ABSA)-coated electrode, was studied in lead ion solution with concentration of 0.1 mM. The results indicated that the membrane response (potential) is roughly fixed at pH = 3.0-5.6. The more positive potential is assigned to the creation of PAni coating with positive charge at lesser pH, the more negative potential can be accredited to the decrease in PAni conductivity at higher pH. These explanations were supported by previous investigations [38,45]. It has been discussed that PAni is solely electroactive at pH below four [19,40], but the activity of this produced polymer is substantially widened to greater pH.

The potentiometric response of the modified electrodes to the lead(II) ion was explored in concentrations between 1.0×10^{-11} and 1.0×10^{-3} M (Figure 9). The results exhibited a slope of 27.8 mV per decade of lead ion activity, and a linear response between 10.0 nM and 1.0 mM (r= 0.9993, *N*= 6) for templated electrode (Figure 9a). Inspecting calibration plots of the coated-templated and coated-untemplated electrodes in Figures 9a and 9b, respectively, reveals an improvement in the behavior of the membrane after templating. The DL for the prepared sensor was known to be about 1.0 nM. The response time for lead ion selective electrode was established by successive dipping of sensor in various lead solutions with ten-fold variation in their molarities. The steady state values were 17-58 s at the linear segment of analytical curve.

The reproducibility for sensor was found out via subsequent dipping of sensors into the lead solutions with diverse concentrations and conditioning solution [25]. The obtained SD for coated-templated sensors were approximately ±2 mV (*N*=5), and reproducibility of the untemplated membrane was close to ±8 mV (*N*=5). The template-modified electrode exhibited good repeatability with SD of nearly ±1mV (*N*=5), and the untemplated electrode had repeatability of nearly ±5 mV (*N*=5). Exploring the long-term stability specified no considerable failure in the potentiometric peculiarities of the template-modified electrode, even following 25 days of keeping sensors in deionized water. The untemplated electrode showed undesirable analytical characteristics after 25 days.
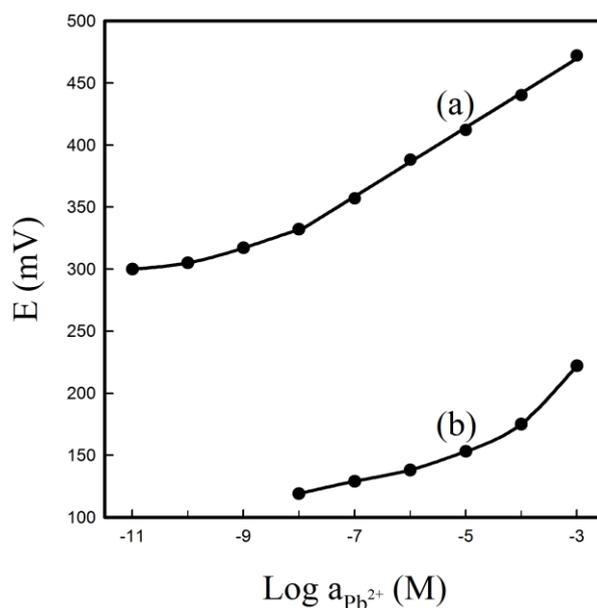
Figur 9. Potentiometric working curves for (a) the templated and (b) untemplated P(Ani-co-3ABSA) sensors.

The selectivity coefficients of the modified electrodes were found by employing SSM [24]. From Table 1, it is evident that the selectivity trend of the copolymeric sensor is considerably affected by the templating technique; hence, the templated electrode has an improved selectivity towards lead ion. The major factors that influence the capability of an ion to compete successfully with other ions in a competition reaction are its size and complexing ability, along with its affinity for receptor sites of the reagent [46]. Based on the improved selectivity of the templated electrode (Table 1), it can be concluded that templating process induces the formation of binding cavities for lead(II) in the P(Ani-co-3ABSA) based sensor.

Table 1. selectivity coefficients of untemplated and templated electrode.

M^{n+}	$\log K^{pot}_{Pb^{2+},M^{n+}}$	
	Before templating	After templating
Mn^{2+}	-1.62	-3.21
Al^{3+}	-2.10	-3.07
Cu^{2+}	0.45	-1.91
Ba^{2+}	-1.36	-3.90
Co^{2+}	-1.29	-2.44
Ni^{2+}	-1.79	-2.82
Hg^{2+}	2.41	2.27
Cd^{2+}	-1.22	-2.23
Ag^+	1.95	1.70
Cr^{3+}	-2.35	-3.17
Zn^{2+}	-1.50	-2.83
K^+	-1.12	-2.43

Through templating, suitable recognition element for lead (II) is produced in the P(Ani-co-3ABSA) as a result of the guest-persuaded realignment of the receptor positions of the copolymer. The enhanced tendency of the templated electrode towards lead ion can be accredited to the formation of binding sites which are conformable to the complexing peculiarities, size and softness character of the lead(II) [33]. These complexing cavities, with dimensions equal to the lead ion, can efficiently accommodate this ion. The sensor shows high selectivity for Hg(II) and Ag(I) because their ionic radii are similar (1.19 Å and 1.15 Å, respectively) to the lead (II) ion (1.19 Å), and both of them have a high tendency for interaction with receptors of the P(Ani-co-3ABSA) membrane [43,44]. The higher tendency of the sensor for copper(II) can be accredited to the high tendency of this ion for receptor positions of the copolymeric film [39,42].

Previously, we have reported the generation of recognition elements for Ag(I) in polyaniline doped with 5-sulfosalicylic acid (SSA) as chelating ligand [47], but it must be taken into account that PAni films intrinsically show considerable sensitivity towards silver ion because as a soft acid Ag(I) have extreme tendency for π electrons of PAni and SSA [48,49]. In addition, the nitrogen atoms in PAni have interaction with Ag(I) for generation of recognition sites for this ion [43]. Moreover we have studied the creation of recognition elements inside SPAni modified electrodes for electrochemical measurement of Cu(II) [50]. According to the Irving-Williams series [51] and Pearson HSAB principle [52], copper(II) forms highly stable complexes with ligands that contain nitrogen as the donor atom because copper(II) and nitrogen-based ligands are borderline acid and bases respectively. Hence, nitrogen atoms of the PAni chain have a strong interaction with copper(II) ions [42]. Therefore, PAni film shows significant sensitivity for Cu(II). In the current work, we have evaluated the effect of templating procedure on the performance of P(Ani-co-3ABSA) based electrochemical sensors in the measurement of lead(II) ion. In comparison to our previous works about silver and copper determination [47,50], the generation of recognition elements for lead(II) in P(Ani-co-3ABSA) copolymer is more difficult because: (i) there is no doped chelating ligand in the P(Ani-co-3ABSA) membrane for lead complexation, whereas SSA coordinates silver in SSA-doped PAni membrane [47]; (ii) based on Edwards equation [53,54], lead(II) has a substantially soft character; hence, it has poor affinity to interact with relatively hard nitrogenic receptor sites of the P(Ani-co-3ABSA) copolymer [55], whereas copper [42,56] and silver [43] have extreme tendency for the receptor sites of the PAni-based membranes. Although the P(Ani-co-3ABSA) film inherently shows low tendency for lead (II), the outcomes of the present study reveal that the analytical performance of the prepared sensor may be amended by templating the P(Ani-co-3ABSA) copolymer with respect to lead(II) ion. As a result, we inferred that the templating procedure is appropriate for the generation of recognition elements, even for cations that have low interaction with the receptor sites of the conducting polymer membranes without doped chelating ligands.

3.4 Application of the method

The proposed electrode was applied in the potentiometric and voltammetric detection of lead content in rice, corn and pepper under optimum circumstances (Table 2). Rice samples (10.0 g) were

dispersed in 15.0 mL of concentrated nitric acid and 5.0 mL of dihydrogen dioxide, and then they were warmed for 6 hours and filtered. Finally, solution volume was adjusted to 25 ml to follow the analysis. For the corn and pepper, 10.0 mL of high molarity nitric acid and 5.0 ml of high molarity HCl were added to 10.0 g of dried samples, and the mixtures were heated for 2 hours at 80 ˚C prior to being filtered and diluted to 25.0 mL for eventual analysis. To confirm the reliability of the method, lead content of the samples was determined by Atomic absorption spectrophotometry (AAS). Table 2 shows the conformity between the results of the electrochemical techniques and reference AAS method.

Table 2. Lead amount in rice, corn and pepper (µg/kg).[a]

sample	AAS (N=5)	Electrochemical (N=5)		t_{crit}	t_{exp} (P=0.05)	
		voltammetry	potentiometry		voltammetry	potentiometry
rice	78.65±3.88	80.04±3.79	72.35±5.12	2.31	0.57	2.19
corn	57.14±3.66	61.37±3.14	52.24±6.32	2.31	1.96	1.50
pepper	42.43±4.53	46.69±3.78	39.56±5.32	2.31	1.61	0.92

[a]The ± values are standard deviations.

4. CONCLUSIONS

This work is an extension of our preceding studies [47,50] aimed at improving the analytical characteristics of PAni based electrochemical sensors. The results of this work indicated that the proposed templating process is suitable for producing recognition sites in SPAni membrane even for lead(II) ions that have a low tendency for receptors of the membrane. Cationic recognition elements were introduced in a P(Ani-co-3ABSA) film, and the prepared sensor was applied for potentiometric and voltammetric detection of lead(II). The recognition elements were produced by templating the polymeric coating towards Pb(II). The suggested sensors were applied for lead(II) detection in an extensive concentration interval. The peculiarities of the established sensor are obtainable from table 3. The templating technique has the capability of providing suitable sensors for the detection of lead in environmental, industrial and food samples.

Table 3. Statistical data for lead(II) determination by the established sensor

Method	Linearity	Repeatability (*N*=5)	Reproducibility (*N*=5)	DL
Voltammetry	1.0 nM - 0.1 mM	2.8%(%RSD)	3.7%(%RSD)	0.1 nM
Potentiometry	10.0 nM - 1.0 mM	±1mV(SD)	±2 mV(SD)	1.0 nM

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