



Electrochemical synthesis of Alizarin Red S doped polypyrrole and its applications in designing a novel silver (I) potentiometric and voltammetric sensor



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ARTICLE INFO

Article history:

Received 23 January 2015

Received in revised form 22 June 2015

Accepted 26 June 2015

Available online xxxx

Keywords:

Silver (I) modified selective electrode

Alizarin Red S polypyrrole film

Voltammetry potentiometry

ABSTRACT

Conducting polymer modified electrodes based on the incorporation of the Alizarin Red S (ARS) into polypyrrole (PPy) film during electropolymerization were used for potentiometric and voltammetric detection of silver (I) ion in solutions. In the potentiometric mode, the electrode showed a good Nernstian slope of 59.6 ± 0.4 mV decade⁻¹ with a wide linear activity range of 5.0×10^{-8} to 6.3×10^{-3} M for Ag⁺ cation and a detection limit of 2.5×10^{-8} M. The PPy/ARS modified electrode was also used for preconcentration and differential pulse anodic stripping voltammetric measurements of silver (I) ion in solution. A linear relationship was observed between the voltammetric responses of the PPy/ARS modified electrode and the concentration of Ag⁺ ion ranging from 9.2×10^{-10} to 2.8×10^{-6} M with a detection limit of 4.6×10^{-10} M. The effect of some transition metal ions on the response of the electrode was studied and the corresponding results showed that there is not any significant interference in potentiometric and voltammetric determination of silver (I) ion except for the mercury (II) ion. Finally, because of a lower detection limit of anodic stripping voltammetric measurement compared to the potentiometric method, the former technique was applied for determination of silver (I) ion in real samples.

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1. Introduction

Silver is an indispensable element in our daily life. This element and its compounds and alloys are extensively used in the production of photographic film or paper, jewelry, mirrors and other electrical and electronic applications [1,2]. Because of its marked antibacterial properties, its compounds and alloys have been widely used to disinfect the water used for drinking and recreational purposes, in dental and pharmaceutical preparation, and in implanted prosthesis [3,4]. Considering the wide use of silver, it can be discharged into the environment from its industrial applications, and this may cause the aquatic and terrestrial organisms to be exposed to silver. Bowen [5] suggested that silver may pose a potential risk as a water pollutant, because of the lack of recycling of mined silver. Also, recent information about the interaction of silver with essential nutrients, especially selenium, copper and vitamins E and B₁₂, has focused attention on its potential toxicity [6]. Therefore, the silver (I) determination in industrial and environmental samples is very important.

Various techniques such as electrothermal atomic absorption spectrometry (ETAAS) [7,8], fluorescence spectrometry [9–11], inductively coupled plasma atomic emission spectrometry (ICP-AES) [12], inductively coupled plasma mass spectrometry (ICP-MS) [13–15] and ion chromatography method [16] have been developed for measurement of Ag⁺ ion in solutions. Although these instrumental techniques are commonly used for trace measurement of silver (I) ion in laboratories, these methods are not suitable for in situ testing and monitoring. Electrochemical methods are far less expensive and are more portable than the aforementioned techniques. Specifically, stripping voltammetry has proven to be a useful technique for trace metal ion measurement, as it combines excellent sensitivity, good selectivity and high accuracy and precision [17].

Polymer coating is possibly one of the most versatile approaches for preparing chemically modified electrodes with high electrical conductivity [18]. Among the various conducting polymers, polypyrrole (PPy) is one of the most frequently investigated. PPy film modified electrodes can be easily prepared by electrochemical oxidation of the pyrrole monomers in aqueous or non-aqueous media [19,20] and PPy can be used as a conducting substrate to incorporate different functional groups for different purposes [21,22]. The potentiometric responses of PPy film electrodes to anions and cations have been studied extensively

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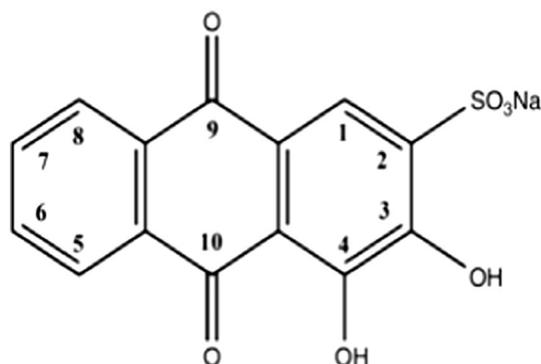
[23–25]. Electrodes modified with polymer containing complexing ligands have been employed for the determination of transition metal ions [26,27]. Recently, Zanganeh and Amini reported the use of an Eriochrome Blue-black B (EBB) doped PPy film (PPy/EBB) electrode as a potentiometric and voltammetric sensor for the determination of silver (I) and copper (II) ions [28,29]. The method is based on the well-known reaction in which, a positively charged polymer backbone is formed during the electropolymerization of pyrrole and the anions present in the medium are incorporated into the polymer to maintain electroneutrality. When the dopant is small, the anionic dopants are mobile and mainly expelled during the dedoping by electroreduction of the polymer. But if the anionic dopants are bulky molecules, the expulsion of these molecules cannot happen. In this case, the electroreduction of the polymer results mainly in the entrance of cationic pseudodopant in order to conserve the electroneutrality of the polymer [30]. This approach can be used for the development of cation selective sensors [31] (for instance, induce cation-selective recognition sites into PPy films).

In this work, the preparation of an Alizarin Red S incorporated (Scheme 1) polypyrrole modified glassy carbon electrode (GC-PPy/ARS) was reported. This modified electrode was used as a novel potentiometric and voltammetric sensor for the determination of silver (I) ion in solutions. The influence of several chemical and instrumental variables such as pH of accumulation medium, polymer thickness, accumulation potential and accumulation time has been evaluated. The method was successfully applied to the determination of silver (I) ion in different water samples, human blood and radiological films. This approach resulted in robust, reliable, maintenance free and good suitability for field trace silver analysis.

2. Experimental

2.1. Reagents

Alizarin Red S (1,2-dihydroxyanthraquinone-3-sulfonic acid) was obtained from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Pyrrole was purchased from Merck (Darmstadt, Germany) and purified by distillation under reduced pressure and refrigerated until use. Nitric acid, sodium hydroxide, silver (I) nitrate, potassium nitrate and the nitrate salts of all other cations were purchased from Merck and used without further purification. Silver (I) nitrate solutions were prepared in triply-distilled water and the concentration of Ag^+ ion in solution was checked by an atomic absorption spectrophotometer (Shimadzu AA-680, Tokyo, Japan). The silver (I) solutions were placed in the dark and protected against the light in amber bottles. High purity nitrogen (99.999%, Sabalan Gas Company, Iran) was used for deaeration of the solutions.



Scheme 1. The chemical structure of Alizarin Red S.

2.2. Apparatus

Electrochemical experiments were performed using a μ -AUTOLAB TYPE III (Eco-Chemie B.V., Utrecht, The Netherlands) potentiostat-galvanostat. The experimental conditions were controlled with NOVA software. A conventional three electrode cell including a glassy carbon electrode (with a diameter of 2 mm, obtained from Azar Electrode Co., Urmia, Iran), with PPy/ARS coating as a working electrode, a platinum wire as an auxiliary electrode and an Ag/AgCl electrode as a reference electrode (using a salt bridge with 0.2 M KNO_3 solution in order to avoid interference from chloride ions) was used in voltammetric experiments. Potentiometric and pH measurements were carried out using a 713 pH-mV meter (Metrohm, Herisau, Switzerland). All electrochemical measurements were conducted at room temperature ($23 \pm 1^\circ\text{C}$).

2.3. Real sample preparation

Three water samples including river water, tap water and waste water samples were selected, and the proposed method was applied to determine their silver content. Tap water was collected from Mashhad (Iran), and river water and waste water were collected from Qareh Su, a village near Mashhad. 250.0 mL of water sample was adjusted to pH 2.0 with nitric acid so as to prevent adsorption of the metallic ions into the flask walls. The samples were filtered to remove any solid particles from the solutions before analysis. For preconcentration, the pH of the appropriate amount of samples was adjusted to 4 before analyzing by the described procedure.

Stored blood samples were obtained from blood banks of three local hospitals in Mashhad, Iran.

Blood samples were treated with anticoagulant and stored at 4°C prior to analysis.

For the X-ray photographic film analyses, the used films were washed with double-distilled water and cut into small pieces after drying. Then the small pieces were placed in an oven at 40°C for 20 min. Twenty milliliters of aqueous nitric acid (5 M) was added to 2.0 g of film. The mixture was filtered, and the solution was diluted to 500 mL and the pH was adjusted to 4 by solution of NaOH (4 M).

2.4. Electrode modification

The GC surface was polished with slurry of $0.5\ \mu\text{m}$ alumina. The polished surface was then rinsed with double-distilled water and sonicated in water-ethanol mixture for 5 min. Electropolymerization of pyrrole was achieved by stepping the potential of the GCE to $+0.75\ \text{V}$ (vs. Ag/AgCl) for a pulse duration of 3 s in a solution containing 0.1 M pyrrole and $10^{-6}\ \text{M}$ ARS (Based on the obtained experimental results, we inferred that when the ARS concentration is fixed at $1 \times 10^{-6}\ \text{M}$, a maximum current is achieved.) as the only added anion, which acts as both supporting electrolyte and dopant anion.

After electropolymerization, the electrode was washed thoroughly with double-distilled water to remove residual monomer from the electrode surface. Then this electrode was subjected to several alternative reduction/oxidation steps in $1 \times 10^{-3}\ \text{M}$ silver (I) nitrate solution as a supporting electrolyte. As pointed out, in the presence of bulky anionic dopant (i.e. ARS), Ag^+ ion acts as a cationic pseudodopant during the reduction step of the polymer. The reduction/oxidation steps were carried out at -0.4 and $+0.5\ \text{V}$, respectively, each step for a period of 300 s. The overall processes were repeated three times, ending with an oxidation step of 600 s in order to assure complete removal of all the silver species from the membrane. The constructed modified electrode was directly used for voltammetric measurements. Apart from voltammetric measurements, the chemically modified electrodes were conditioned in $1 \times 10^{-3}\ \text{M}$ AgNO_3 solution (for at least 4 h prior to their use) in order to exploit as indicator electrodes for potentiometric measurements.

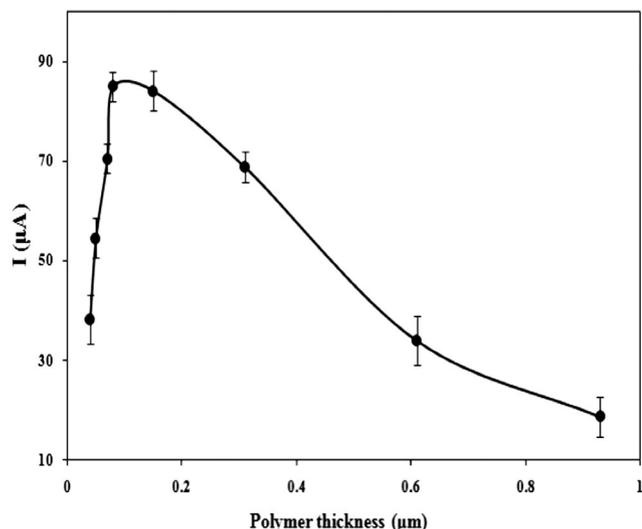


Fig. 1. Effect of polymer thickness on the silver stripping signal at PPy/ARS film. Electropolymerization conditions: 0.1 M pyrrole, 10^{-6} M ARS solution at an applied potential of +0.75 V. Preconcentration conditions: AgNO_3 , 1×10^{-5} M; time, 200 s, applied potential, -0.6 V. DPASV conditions: scan range, -0.2 to $+0.4$ V; scan rate, 20 mV s^{-1} ; electrolyte, 0.2 M KNO_3 solution; pH, 2.

2.5. Potentiometric and voltammetric measurements

All potentiometric measurements with the PPy/ARS modified electrode were carried out with the following cell assemblies:

PPy/ARS modified electrode | test solution | salt bridge (1 M KNO_3) | 3 M KCl | Ag/AgCl.

All standard test solutions were prepared by successive dilution of 0.1 M silver nitrate solution. The solutions were stirred with a magnetic stirrer at equal intervals of time for consistency. The data were plotted as observed potential versus the logarithm of Ag^+ activity. The selectivity coefficient of the electrode for some of the metal ions was evaluated by using the matched potential method (MPM) [32].

Before voltammetric measurement, the PPy/ARS modified electrode was immersed into a preconcentration solution containing 1×10^{-5} M of silver (I) cation at an applied potential of -0.6 V (vs. Ag/AgCl) for 200 s. Then the electrode was rinsed with double-distilled water and immersed into a cell containing 0.2 M KNO_3 solution which its pH was adjusted to 2 for differential pulse anodic stripping voltammetric (DPASV) measurements. The differential pulse voltammetry was

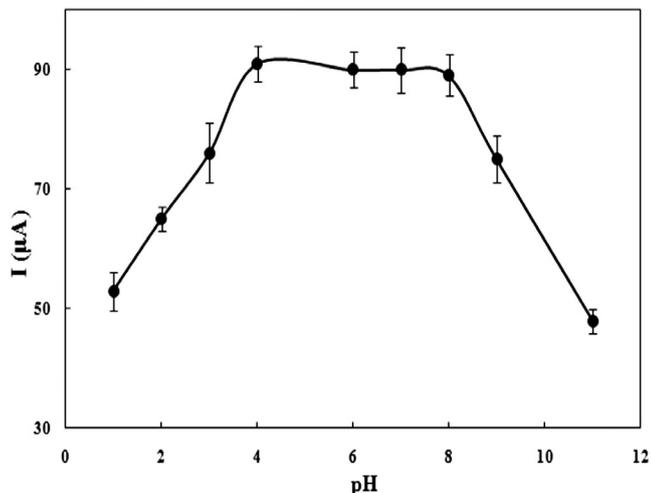


Fig. 2. Effect of accumulation pH on the silver stripping signal.

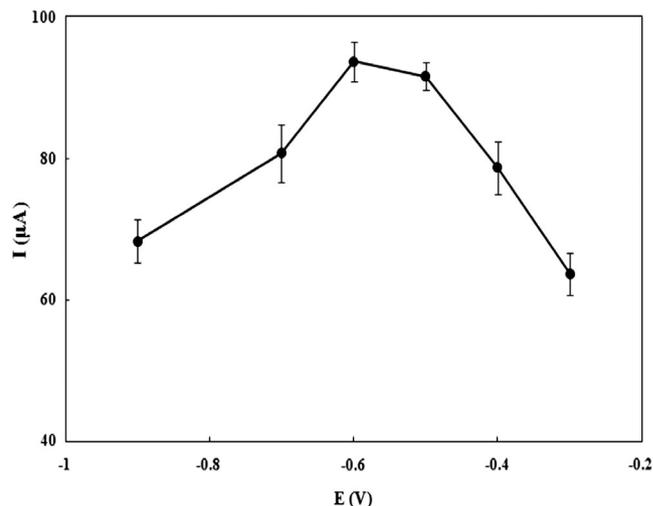


Fig. 3. Effect of preconcentration potential on the silver stripping signal.

applied in the potential range -0.2 to $+0.4$ V using a pulse amplitude of 50 mV and a scan rate of 20 mV s^{-1} .

3. Results and discussion

3.1. Preparation of PPy/ARS film

PPy/ARS films were prepared from 0.1 M pyrrole monomer and 1.0×10^{-6} M ARS solutions employing a potential of +0.75 V (vs. Ag/AgCl) for 3 s. The thickness of deposited film (d_n) at the surface of GCE was calculated from the following equation:

$$d_n = Q_a M / n F \rho \quad (1)$$

where Q_a is the charge consumed during the electrodeposition of PPy film using Faraday's law, assuming; (i) a two electron mechanism based on the monomer molecule implied in the process; (ii) the current efficiency is 100%; and (iii) a PPy density (ρ) of 1.5 g mL^{-1} and a pyrrole molar mass (M) of 67 g mol^{-1} [33–37].

3.2. Some effective parameters on DPASV peak current of silver (I) ion

3.2.1. Effect of polymer thickness

To demonstrate the effect of polymer film thickness on the DPASV peak current of silver (I) ion, a serial of experiments were carried out. As is evident in Fig. 1 the peak current increases sharply for film thickness up to 0.08 μm and then decreases progressively for the higher film thickness. The reason for decreasing the intensity of the stripping peak at both higher and lower film thicknesses is that the thinner films do not provide enough binding sites on the electrode surface for interaction with silver (I) ion and the thicker films lead to difficulties

Table 1
Potentiometric selectivity coefficients of various interfering ions.

Selectivity coefficient ($\log K_{\text{Ag}^+, \text{M}^n}^{\text{pot}}$)		Selectivity coefficient ($\log K_{\text{Ag}^+, \text{M}^n}^{\text{pot}}$)	
M^{n+}		M^{n+}	
K^+	−3.35	Ba^{2+}	−3.40
Na^+	−3.12	Zn^{2+}	−3.11
Hg^{2+}	−1.09	Ni^{2+}	−3.14
NH_4^+	−3.16	Mn^{2+}	−3.05
Cd^{2+}	−2.85	Cu^{2+}	−2.94
Co^{2+}	3.03	Al^{3+}	−3.08
Pb^{2+}	−2.72	Cr^{3+}	−3.19

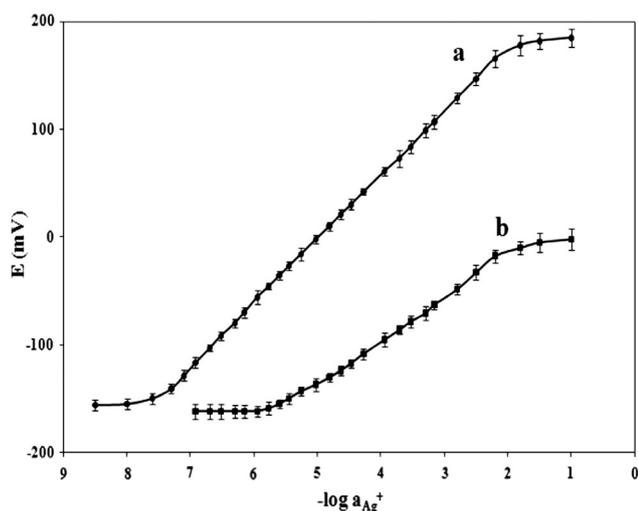


Fig. 4. Potentiometric response of the PPy/ARS modified electrode to different concentrations of Ag^+ (a) after and (b) before carrying out the templating step.

in electron transfer and pose mass transfer limitation to Ag^+ ions during the accumulation and stripping steps.

3.2.2. pH of electropolymerization solution

The influence of pH of the electropolymerization solution on DPASV peak current of silver (I) ion was studied. The pH of the solution was adjusted with HNO_3 and NaOH solutions as appropriate. The results indicated that the DPASV peak current increases with the increase of the pH of the solution up to 2 and then decreases at higher pH values. Therefore, pH 2 was considered as an optimum value and was chosen for electropolymerization of pyrrole in the presence of ARS anionic dopant.

3.2.3. pH of the accumulation medium

The effect of the pH of the accumulation medium on the preconcentration efficiency was investigated and the corresponding results are depicted in Fig. 2. As is clear in this figure, the stripping signal is independent of pH in the range of 4.0–8.0. In addition, the results show that the DPASV signal decreases before pH 4 and after pH 8. It seems that at the highly acidic solutions (pH between 1.0 and 4.0) due to the interference of H_3O^+ ions (i.e. protonation of coordination sites of the ARS) and also the competition between the H_3O^+ and

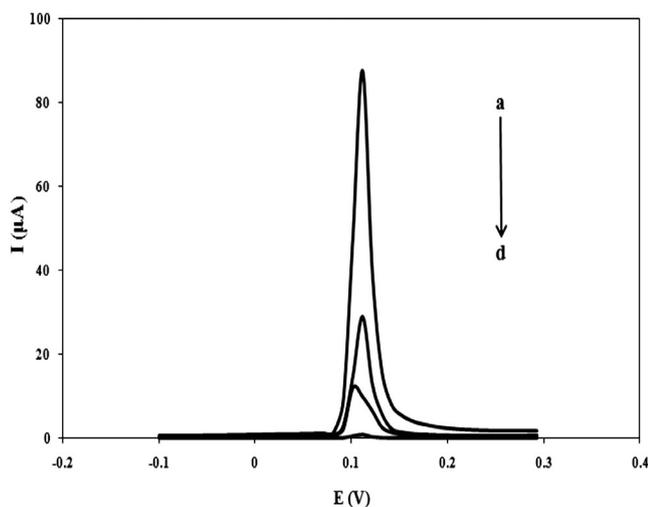


Fig. 5. Effect of templating process, preconcentration and dopant type on the voltammetric response of the modified electrodes: (a) templated PPy/ARS electrode; (b) untemplated PPy/ARS electrode; (c) different types of dopant (ClO_4^-); (d) bare GC electrode.

Table 2

The chemical parameters and instrumental conditions used for polymerization, preconcentration, potentiometry and DPASV.

Process	Type, value or range
<i>Polymerization</i>	
Electrode type	GC disk electrode of 2 mm diameter
Thickness	0.08 μm (3 s at an applied potential of +0.75 V)
Solution	Aqueous 0.1 M pyrrole and 10^{-6} M ARS
pH	2.0
<i>Templating</i>	
Electrode type	PPy/ARS-modified GC electrode
Applied potential	Successive potential steps (-0.4 V and $+0.5$ V, each step for a period of 300 s ending with an oxidation step at $+0.5$ V for 600 s)
Solution	1×10^{-3} M AgNO_3
<i>Potentiometry</i>	
Electrode type	PPy/ARS-modified GC electrode after the templating process
Conditioning solution	1×10^{-3} M AgNO_3
Conditioning time	4 h
pH range	3.0–8.0 (working pH, generally 4.0)
Linear range	5.0×10^{-8} to 6.3×10^{-3} M $\text{Ag}(\text{I})$ ($r = 0.9998$, $n = 5$)
Slope	59.6 ± 0.4 mV/decade of $\text{Ag}(\text{I})$ activity
Detection limit	2.5×10^{-8} M
Response time	10–35 s depending on the $\text{Ag}(\text{I})$ concentration
Selectivity	See Table 1
<i>Preconcentration</i>	
Electrode type	PPy/ARS-modified GC electrode after the templating process
Applied potential	-0.6 V vs. Ag/AgCl
pH	Useful pH range 4.0–8.0, applied pH 4.0
Time	200 s
<i>DPASV</i>	
Electrode type	The modified-templated electrode after the preconcentration step
Solution	0.2 M KNO_3 solution
pH	2.0
DPASV parameters	Applied potential, -0.2 to $+0.4$ V; scan rate, 20 mV s^{-1} ; pulse amplitude, 50 mV
Linear range	0.1 ng/mL to 300 ng/mL $\text{Ag}(\text{I})$ ($r = 0.9996$, $n = 5$)
Detection limit	0.05 ng/mL $\text{Ag}(\text{I})$

silver (I) ions for the nitrogen sites of the PPy backbone [24], the stripping signal decreases in this region, but at pH values higher than 8, because of the precipitation of $\text{Ag}(\text{I})$ ion with the hydroxyl ions in solution, the DPASV signal decreases.

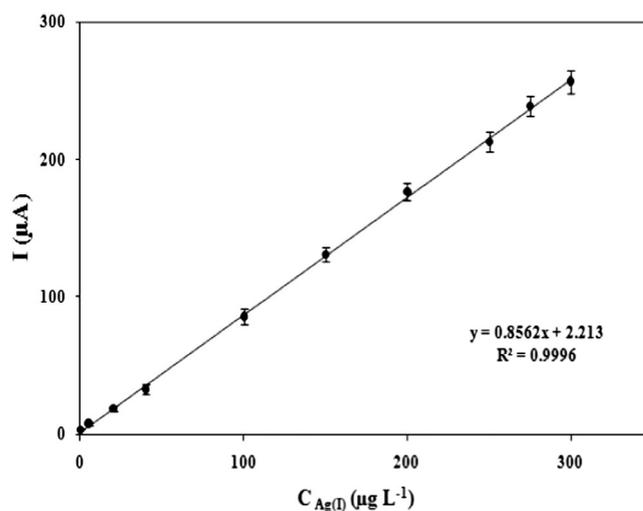


Fig. 6. Stripping voltammetric response to increasing the concentration of silver (I) ion at the modified-templated electrode. Measurement conditions are given in Table 2.

Table 3
The effect of co-existing metal ions.

Co-existing ion	Recovery (%)
K ⁺	100
Na ⁺	99
Hg ²⁺	84
NH ₄ ⁺	100
Cd ²⁺	97
Co ²⁺	98
Pb ²⁺	96
Ba ²⁺	100
Zn ²⁺	98
Ni ²⁺	99
Mn ²⁺	99
Cu ²⁺	97
Al ³⁺	99
Cr ³⁺	98

3.2.4. Accumulation time

The dependence of the stripping signal on the accumulation time was also investigated. Based on the obtained experimental results, we inferred that when the time is fixed at 200 s, a maximum current is achieved; therefore, for all of the subsequent measurements, an accumulation time of 200 s was applied.

3.2.5. Effect of accumulation potential

The influence of the accumulation potential on the peak current of silver (I) ion was studied by varying the accumulation potential from -0.9 to -0.3 V. As can be seen in Fig. 3, maximum preconcentration efficiency for silver (I) ion occurs at an applied potential of -0.6 V. The reason for lower preconcentration efficiency at potentials more positive than -0.6 V is due to incomplete reduction of PPy which results in less preconcentration of silver species into the membrane. It seems that the chelation ability of the carbonyl group is dominant than hydroxyl one [38,39]. Therefore, the lower efficiency at potentials more negative than -0.6 V may be due to the reduction of the carbonyl group to hydroxyl group at position 10 in ARS.

3.3. Potentiometric studies

Prior to the potentiometric measurements, the templated PPy/ARS electrodes were conditioned in 1×10^{-3} M silver (I) nitrate solution. After conditioning for ~ 4 h, a stable Nernstian response was obtained for Ag⁺ ion of various concentrations. In order to test the performance of the electrode characteristics, various operation parameters, such as measuring pH, response time, selectivity, working concentration range and also the sensitivity of the electrode were investigated.

3.3.1. Effect of pH on potentiometric response

The pH dependence of the potentiometric response of the proposed membrane sensor at 1.0×10^{-4} M of Ag⁺ ion, in the pH range of 1.5–10.5 was tested. The Nernstian response was observed at pH 3.0–8.0. The limit at the lower pH (<3.0) values may be due to the response of the

electrode to H₃O⁺ ion or due to the protonation of coordination sites of the ligand. Moreover, at higher pH values (>8.0), the potential decreases due to the formation of silver hydroxide which results in decreases of the amount of free Ag⁺ cation in solution.

3.3.2. Response time

The dynamic response time is an important factor for evaluation of any sensor. To measure the dynamic response time of the proposed electrode, the concentration of the test solution was successively changed from 1.0×10^{-7} to 1.0×10^{-3} M. The time needed to reach a potential within 1.0 mV of the final equilibrium value after successive immersion of the modified electrode into a series of Ag⁺ ion solutions (each having a tenfold difference in concentration) was found to be between 10 and 35 s.

3.3.3. Potentiometric selectivity

The selectivity of a chemical sensor is clearly one of its most important characteristics as this property often determines whether the sensor can be used reliably for the target analyte or not. The cation selectivity was measured by using the matched potential method (MPM). The selectivity coefficients obtained for the investigated electrode are given in Table 1. The data in this table show that the electrode is selective to silver (I) ion over several alkali, alkaline earth, and some of the transition metal ions. The only interfering cation is Hg²⁺.

3.3.4. Analytical performance of the electrode in potentiometric measurements

Fig. 4 compares the potentiometric response of the templated and untemplated electrodes. As is evident in this figure, the sensitivity, dynamic range and also the detection limit of the templated electrode are improved with respect to the untemplated one. The PPy/ARS modified electrode exhibits a Nernstian slope of 59.6 ± 0.4 mV decade⁻¹ of activity, over a relatively wide dynamic range from 5.0×10^{-8} to 6.3×10^{-3} M (5.4 ng mL⁻¹ to 679 μg mL⁻¹) for Ag⁺ ions and the detection limit was found to be 2.5×10^{-8} M (2.7 ng mL⁻¹) for this metal ion.

3.4. Voltammetric studies

In order to get further insight about the effect of the templating process, dopant type and also PPy film on DPASV signal, several experiments were carried out at room temperature (23 ± 1 °C). Curve b in Fig. 5, shows the DPASV signal for the untemplated PPy/ARS modified electrode with the templated PPy/ARS modified electrode under the same experimental conditions (i.e. similar PPy film thickness and ARS concentration). As can be seen from this figure, the stripping signal obtained for the untemplated PPy/ARS modified electrode, significantly decreases compared to the corresponding templated PPy/ARS modified electrode. These results indicate the necessity of the templating process which causes the generation of the recognition sites for silver (I) ion and therefore, attainment of a higher analytical sensitivity.

Table 4
Determination of Ag⁺ ion in natural water and X-ray photographic film samples.

Sample	Preconcentration/DPASV method				GF-AAS method
	Found ^a	Added Ag ⁺	Total found ^a	Recovery (%)	Mean ^a
Tap water	N.D. ^b	20.0 (ng mL ⁻¹)	20.4 ± 0.4 (ng mL ⁻¹)	102.0	–
River water	N.D.	20.0 (ng mL ⁻¹)	20.6 ± 0.5 (ng mL ⁻¹)	103.0	–
Waste water	2.26 (ng mL ⁻¹)	–	–	–	2.39 (ng mL ⁻¹)
Waste water	2.26 (ng mL ⁻¹)	10.0 (ng mL ⁻¹)	12.48 (ng mL ⁻¹)	102.2	12.66 (ng mL ⁻¹)
X-ray film	5.3 ± 0.7 (mg g ⁻¹)	–	–	–	5.2 ± 0.6 (mg g ⁻¹)
Human blood	1.24 (ng mL ⁻¹)	–	–	–	1.20 (ng mL ⁻¹)

^a Average of five determinations ± S.D. (Standard Deviation).

^b N.D.: Not Detected.

Table 5
Different stripping voltammetric techniques applied for the determination of silver.

Modifier	Linear range (nmol L ⁻¹)	Detection limit (ng mL ⁻¹)	Procedure	Ref.
3-Amino-2-mercapto quinazolin-4(3H)-one	8.3–2780	0.34	Differential pulse Anodic stripping voltammetry at a modified CPE	[17]
Phenylthiourea-nanoporous silica gel	0.008–0.08	0.005	Differential pulse Anodic stripping voltammetry at a modified CPE	[40]
2-Mercaptobenzoxazole	5–1000	0.54	Flow injection stripping voltammetric method at a bulk-modified graphite tube electrode	[41]
Ion exchanger Dowex	15–7400	0.27	Square-wave anodic stripping at a modified CPE	[42]
p-Isopropylcalix[6]arene	50–2000	5.18	Differential pulse anodic stripping method at a modified CPE	[43]
4-(2-Pyridylazo)-resorcinol	4.64–2781	0.12	Differential pulse anodic stripping method at a modified CCE	[44]
N,N'-bis(2-hydroxybenzylidene)-2,2'-(aminophenylthio) ethane	4.6–1854.2	0.092	Differential pulse anodic stripping method at a modified CPE	[45]
Alizarin Red S	0.92–2800	0.05	Differential pulse anodic stripping voltammetric method at PPy/ARS-modified GC electrode	This work

3.4.1. Analytical performance of the electrode in voltammetric measurements

The optimum values for the effective parameters on the electrochemical response of the electrode are presented in Table 2. DPASV calibration plot (i.e. peak current vs. silver (I) ion concentration), was constructed at the optimized conditions. The DPASV measurements were carried out by placing the electrode after preconcentration into a cell containing 0.2 M potassium nitrate at pH 2.0, and scanning the potential from -0.2 to $+0.4$ V using a pulse amplitude of 50 mV and a scan rate of 20 mV s⁻¹. The calibration plot which is shown in Fig. 6, indicates that the plot is linear in the concentration range of 9.2×10^{-10} to 2.8×10^{-6} M (0.1 to 300 ng mL⁻¹) for Ag⁺ ion with a correlation coefficient of 0.9996 ($n = 5$) and the practical limit of detection is 4.6×10^{-10} M (0.05 ng mL⁻¹) for this metal ion.

3.4.2. Voltammetric selectivity

The effect of possible interferences with the differential pulse anodic stripping voltammetry signal of silver (I) ion by some of the other metal cations was studied by the addition of the interfering ions into a preconcentration solution containing 1×10^{-5} M of silver (I) cation, under the optimized conditions, with a 200 s accumulation time. The results of this study are summarized in Table 3. From this table it can be seen that when the developed procedure was used for the determination of 1×10^{-5} M of Ag (I) ion in optimum conditions, additions of 1×10^{-2} M of the interfering ions did not cause an effect more than 5% on the silver ion peak currents. However, the presence of 1×10^{-5} M of Hg (II) caused 16% depression of the Ag (I) ion peak current. This depression could be due to the competition between this metal ion and Ag (I) ion in complexation with ARS and also interaction of Hg (II) with the amine group of PPy film at the surface of the electrode.

3.5. Analytical application

A main advantage of the electrochemical approaches is that there is no separation step for matrix-removal. Hence, these methods are relatively easy, require low sample volumes, and have a low contamination threat. Due to the better detection limit of the DPASV technique compared to the potentiometric method, this method was applied for the determination of silver (I) ion in real samples. In this work, the proposed electrode was successfully applied for the determination of Ag (I) ion in river water, tap water and waste water samples. The proposed electrode was also used for the determination of silver in human blood and X-ray photographic film. As is evident in Table 4, the measured values by the DPASV method are in agreement with those obtained by graphite furnace atomic absorption spectrometry (GF-AAS).

3.6. Comparison of PPy/ARS modified electrode with the previously reported modified electrodes for Ag⁺ ion measurement

A number of analytical characteristics of the PPy/ARS modified electrodes were compared with those previously reported for Ag (I) voltammetric sensors. The results are summarized in Table 5. As can be seen from this table, the proposed electrode shows better analytical characteristics, such as a lower detection limit and a wider linear range except, than that reported by Javanbakht et al. [40].

4. Conclusions

Polypyrrole modified electrodes prepared by electropolymerization of pyrrole in the presence of an anionic complexing ligand (ARS) were templated with respect to silver (I) ion and used for potentiometric and voltammetric detection of this metal ion. The ability of the ARS to extract the silver (I) ion into the polypyrrole membrane, leads to fabrication of an electrode which has a precise and accurate electrochemical response. The proposed sensor has been successfully applied for measurement of Ag⁺ ion in solutions using potentiometry down to 5.4 ng mL⁻¹ and also by voltammetry, after preconcentration, down to 0.1 ng mL⁻¹ with a high selectivity. It seems that by judicious selection of the chelating ligand, and by changing the polymerization and templating factors such as film thickness, type of solvent, pH and reaction time, it is possible to induce a better selectivity for silver (I) ion and to extend this approach to several other cationic species in solutions.

Acknowledgment

The authors wish to acknowledge the financial support (No. 15723) of this work by Ferdowsi University of Mashhad, Mashhad, Iran.

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