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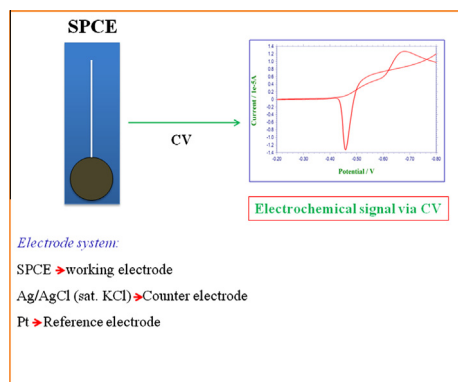
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Development of electrochemical sensor for the determination of palladium ions (Pd^{2+}) using flexible screen printed un-modified carbon electrodeMurugan Velmurugan^a, Balamurugan Thirumalraj^a, Shen-Ming Chen^{a,b,*}, Fahad M.A. Al-Hemaid^b, M. Ajmal Ali^b, Mohamed S. Elshikh^b^a Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan, ROC^b Department of Botany and Microbiology, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

GRAPHICAL ABSTRACT

Electrochemical pathway for the determination of Pd^{2+} ions via CV.

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ABSTRACT

To date, the development of different modified electrodes have received much attention in electrochemistry. The modified electrodes have some drawbacks such as high cost, difficult to handle and not eco friendly. Hence, we report an electrochemical sensor for the determination of palladium ions (Pd^{2+}) using an un-modified screen printed carbon electrode has been developed for the first time, which are characterized and studied via scanning electron microscope and cyclic voltammetry. Prior to determination of Pd^{2+} ions, the operational conditions of un-modified SPCE was optimized using cyclic voltammetry and showed excellent electro-analytical behavior towards the determination of Pd^{2+} ions. Electrochemical determination of Pd^{2+} ions reveal that the un-modified electrode showed lower detection limit of $1.32 \mu\text{M}$ with a linear ranging from 3 to $133.35 \mu\text{M}$ towards the Pd^{2+} ions concentration via differential pulse voltammetry. The developed sensor also applied to the successfully determination of trace level Pd^{2+} ions in spiked water samples. In addition, the advantage of this type of electrode is simple, disposable and cost effective in electrochemical sensors.

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1. Introduction

Palladium (Pd^{2+}) is a soft silver-white important common metal and widely used in modern industrial applications, including chemical industry, metallurgy, fuel cell and dentistry due to its physical and chemical properties such as high melting point, corrosion resistance and catalytic properties [1–3]. Especially in the field of automotive catalytic converters and chemical catalysis, Pd^{2+} is widely used become significant and prevalent, which leads to the accumulation of Pd^{2+} in the environmental [4–6]. The Pd^{2+} compounds easily contaminate to biological and soil water samples from the industrial waste, which leads to potentially toxic and impact to carcinogenicity for human health such as skin problems, eye irritation, damage of DNA and cell mitochondria, and inhibition of enzyme activity [7,8]. Hence, the accurate and trace level determination of Pd^{2+} is much important for human health, while the direct detection and removal of Pd^{2+} is still difficult in research community. Therefore, various analytical methods such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), high performance liquid chromatography (HPLC), fluorescence spectrometry, and electrochemical methods have been developed for the low level determination of Pd^{2+} in environmental samples [9–16]. Obviously compared with electrochemical method, all aforementioned methods are sensitive and highly expensive. However, the electrochemical method is easy to handle, cheaper and sensitivity for the determination of Pd^{2+} in environmental samples [17]. In past decades, several modified electrodes have been received much attention for the analysis of Pd^{2+} ions determination [14,15,18–20].

On the other hand, the commercially available screen printed carbon electrodes have raised much attention in electroanalytical chemistry owing to its simplicity, higher sensitivity and good selectivity [21,22]. Notably, only few reports are available for the determination of Pd^{2+} exists within the literature. Bai et al. demonstrated in-situ polymerization of ion-imprinted membranes at graphene modified electrode for the determination of Pd with higher sensitivity using amperometric technique [14]. Rosolina et al. reported the determination of Pd using unmodified glass

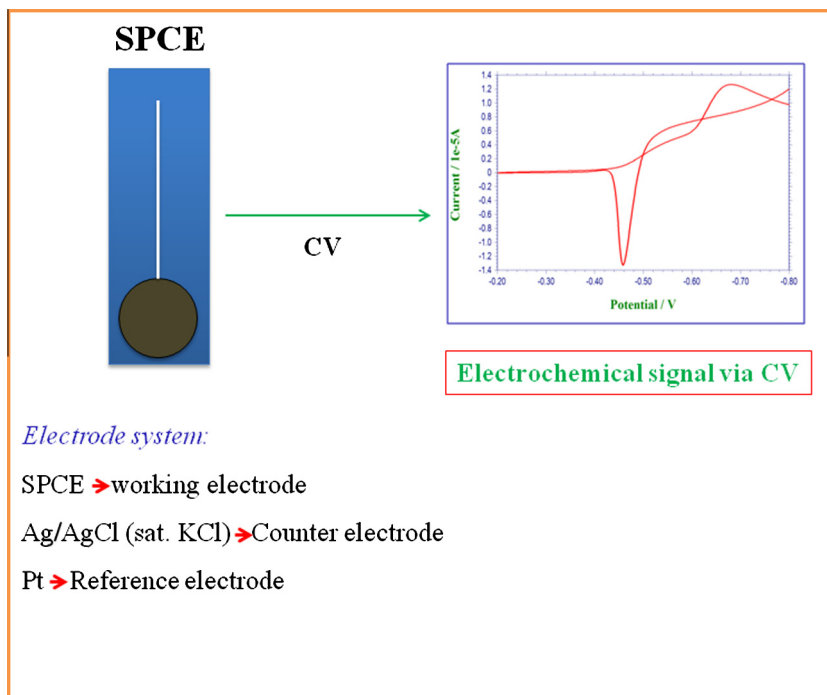
carbon electrode in organic medium for the determination of Pd in active pharmaceutical ingredients [17]. Awual et al., used ligand based efficient conjugate nanomaterials for the detection of Pd in the presence of a high amount of foreign competing cations [23]. Qin et al. developed 9-bromophenanthrene (9-BrP) as a fluorescent probe for the determination of Pd in lake water with excellent analytical performance [24]. Rigdon and Harrar found that Pd by controlled caloric matrix methods with excellent electroanalytical characteristics using Pd(IV)/Pd(II) system in azide media [25]. These aforementioned modified electrodes have several drawbacks such as high cost, difficult to handle and expensive analytical techniques. To overcome this problems, the screen printed carbon electrode has several advantage in electrochemical sensors such as commercially available, user free and disposable [22]. Metters et al. used screen printed graphite microband electrodes with excellent electroanalytical properties towards electrochemical detection of NADH and nitrite [26]. Tan et al. showed excellent electroanalytical results using screen printed microelectrode arrays for the detection of acetaminophen, dopamine and nitrite [27]. Owing to excellent electroanalytical features of screen printed carbon electrode, herein we have utilized un-modified screen printed carbon electrode is an alternate choice for the determination of Pd^{2+} ions.

To the best of our knowledge, in this present study we have been developed new electrochemical sensor for the determination of Pd^{2+} ions using un-modified screen printed carbon electrode for the first time. The advantage of this proposed method is simple and low cost for the determination of Pd^{2+} ions with wide linear range and higher sensitivity. Owing to excellent electroanalytical performance, this sensor also exhibits to detect the Pd^{2+} ions in water samples using spiked method with satisfactory results.

2. Experimental

2.1. Materials

Screen printed carbon electrode was purchased from Zensor R&D Co., Ltd., Taipei, Taiwan. Palladium chloride was supplied from Sigma-Aldrich. The pH solution of 0.5 M acetate buffer was



Scheme 1. Electrochemical pathway for the determination of Pd^{2+} ions via CV.

prepared using glacial acetic acid and sodium acetate were adjusted using either H_2SO_4 or NaOH . All of used chemicals in this work were of analytical grade and all the solutions were prepared using doubly distilled water.

2.2. Apparatus

The electrochemical experiments were performed using CHI 900 electrochemical workstation with a standard three-electrode cell setup. The un-modified SPCE used as the working electrode, platinum wire (0.5 mm) and an Ag/AgCl electrode (Sat. KCl) used as counter and reference electrodes, respectively. All electrochemical experiments were carried out at a room temperature in an inert atmosphere (N_2 atmosphere). The overall electrochemical procedure for the determination of Pd^{2+} ions is shown in Scheme 1.

3. Results and discussion

3.1. Characterization

The surface morphology of un-modified bare SPCE was characterized by SEM as shown in Fig. 1. The SEM image of bare SPCE reveals that the uniform flake like morphology, the results are shown in Fig. 1 (A) higher and (B) lower magnification. On the other hand, the Fig. 1(C) shows the Pd ions covered flake like morphological structure of SPCE, after the Pd^{2+} ions determination by CV.

In addition, the EDX spectrum also authenticates the presence of Pd on the SPCE surface after determination of Pd^{2+} ions by CV. These results confirm the high current response towards the Pd^{2+} ions determination due to the presence of graphitic carbon on SPCE surface with uniform flake like arrangement.

3.2. Electrochemical behavior of Pd^{2+} ions at un-modified SPCE

The electrochemical behavior of Pd^{2+} ions was studied at un-modified SPCEs by using CV. Fig. 1 shows the CV response of SPCE in the absence (a) and presence (b) of $10\text{ }\mu\text{M}$ Pd^{2+} ions in 0.5 M acetate buffer at a scan rate of 50 mV/s. It can be seen that there is no obvious oxidation or reduction current response in the absence of Pd^{2+} ions on the potential window.

It shows that the bare SPCE was inactive in the electrolyte solution. As can be seen from a cathodic peak and an anodic peak were observed at -0.459 V and -0.68 V in the presence of $10\text{ }\mu\text{M}$ Pd^{2+} in 0.5 M acetate buffer at a scan rate of 50 mV/s, which is correspond to the direct reduction of Pd(II) to metallic Pd on the electrode surface [18,28,29]. This reduction of Pd(II) to metallic Pd can be assigned as a two electron transfer electrochemical process [19]. The possible electrochemical mechanism for Pd as shown in Eq. (1).



In order to improve the sensitivity of un-modified SPCE, solution pH of the electrolyte was optimized first because it's a crucial task in this work. Hence, the effect of different preconcentration medium including 0.5 M acetate buffer, 0.5 M phosphate buffer solution (PBS), 0.5 M sulfuric acid (H_2SO_4), 0.1 M sodium hydroxide (NaOH), and 0.1 M potassium nitrate (KNO_3) was chosen and carefully examined by CV towards the $10\text{ }\mu\text{M}$ of Pd^{2+} at a scan rate of 50 mV/s. The obtained results were shown in Fig. 2B. It can be seen that 0.5 M acetate buffer gave better results in terms of peak current and peak shape compared with other pH medium. Hence, 0.5 M acetate buffer is an optimum for further experiment with similar procedure for the determination of Pd^{2+} ions.

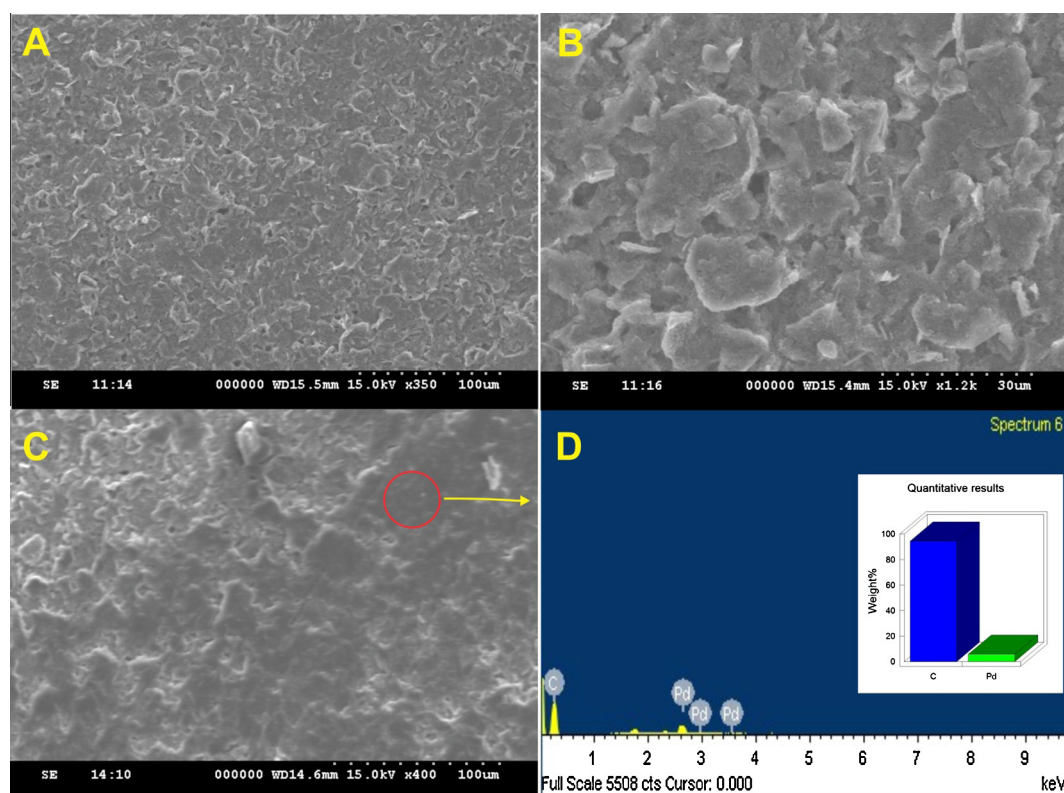


Fig. 1. SEM images of SPCE lower (A) and higher (B) magnification, (C) SEM image of SPCE after Pd^{2+} determination by CV (D) Corresponding EDX spectrum for SPCE after Pd^{2+} determination.

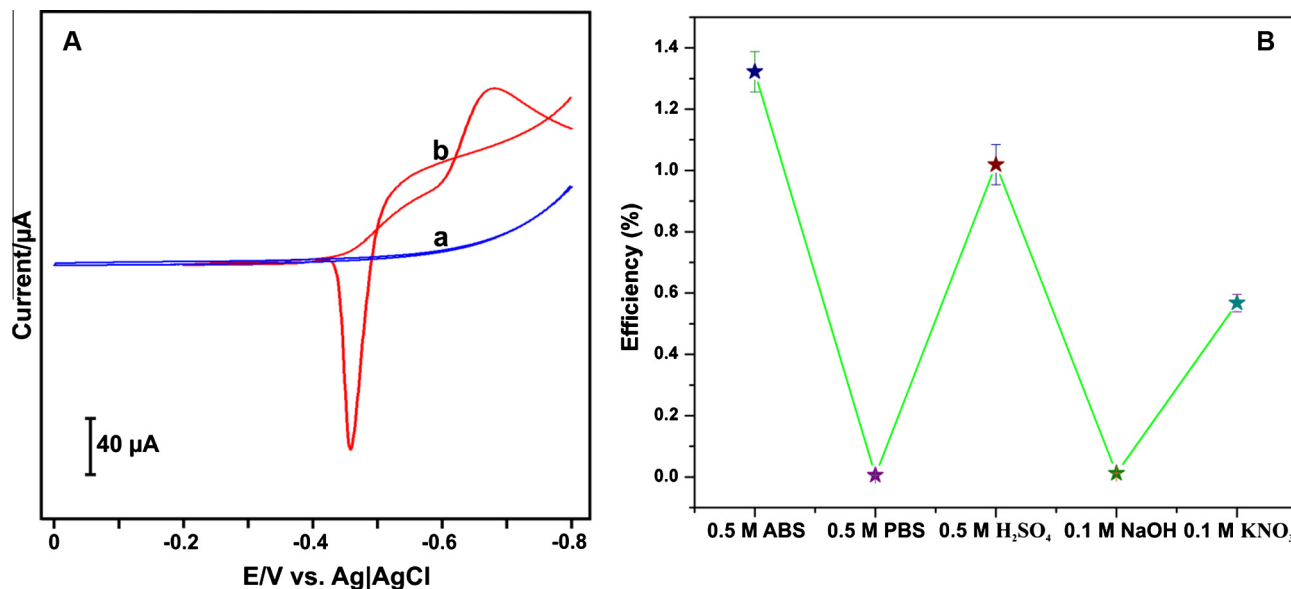


Fig. 2. (A) CV obtained at absence (a) and presence (b) of $10 \mu\text{M}$ Pd^{2+} in 0.5 M acetate buffer using SPCE at a scan rate of 50 mV/s. (D) Efficiency of different pH medium for the determination of Pd^{2+} using CV at SPCE.

3.3. Effect of scan rate

The effect of scan rate on un-modified SPCE was also investigated by CV and the results are shown in Fig. 3A.

Fig. 3A shows the CV response of SPCE in $10 \mu\text{M}$ Pd^{2+} containing 0.5 M acetate buffer at a scan rate of 50 mV/s. It can be seen that the redox peak current of Pd^{2+} ions increases with increasing the scan rates from 20 to 160 mV/s, while upon increasing the scan rate there is change in the peak potential. Usually, the negative shifts indicating the electron transfer ability of the medium on the electrode surface. As from Fig. 3B, the cathodic peak current had a linear relationship with the scan rates from 20 to 160 mV/s with a correlation coefficient of 0.9925. This result concludes that the electrochemical behavior of Pd^{2+} ions is adsorption controlled process. Guy Denuault et al explained the overall electrochemical behavior of Pd in alkaline media using Mesoporous palladium as reported early [30].

3.4. Electrochemical determination of Pd^{2+} ions

DPV was performed for the electrochemical determination of Pd^{2+} ions using un-modified SPCE and the results are shown in Fig. 4A. The potential range was applied for DPV at -0.7 to -0.2 V.

As can be seen from Fig. 4A, different concentration (3–150.55 μM) of Pd^{2+} ions was determined in 0.5 M acetate buffer. While a cathodic peak was observed at -0.516 V upon the addition of 3 μM and the cathodic peak current was increased with increasing concentration of Pd^{2+} ions ranging from 3 to 150.55 μM as shown in Fig 4B. It can be seen that the cathodic peak current of Pd^{2+} ions was linear over the concentration from 3 to 133.35 μM with a correlation coefficient of 0.9909. The estimation limit of detection (LOD) is 1.32 μM ($S/N = 3$) with a analytical sensitivity of $1.546 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ [31]. The excellent analytical performance of SPCE is owing to electron donation nature and good electron transfer mobility of the graphitic surface on SPCE towards the

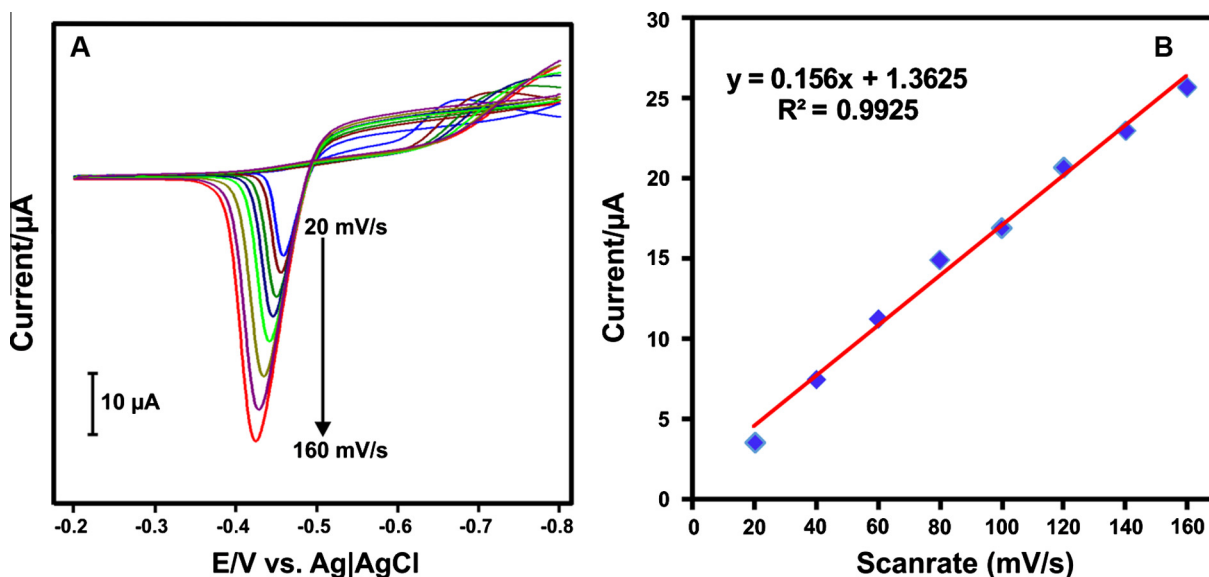


Fig. 3. (A) CV obtained at SPCE for $10 \mu\text{M}$ of Pd^{2+} containing 0.5 M acetate buffer at a scan rate of 20–160 mV/s. (B) Calibration plot for cathodic peak current vs. scan rate.

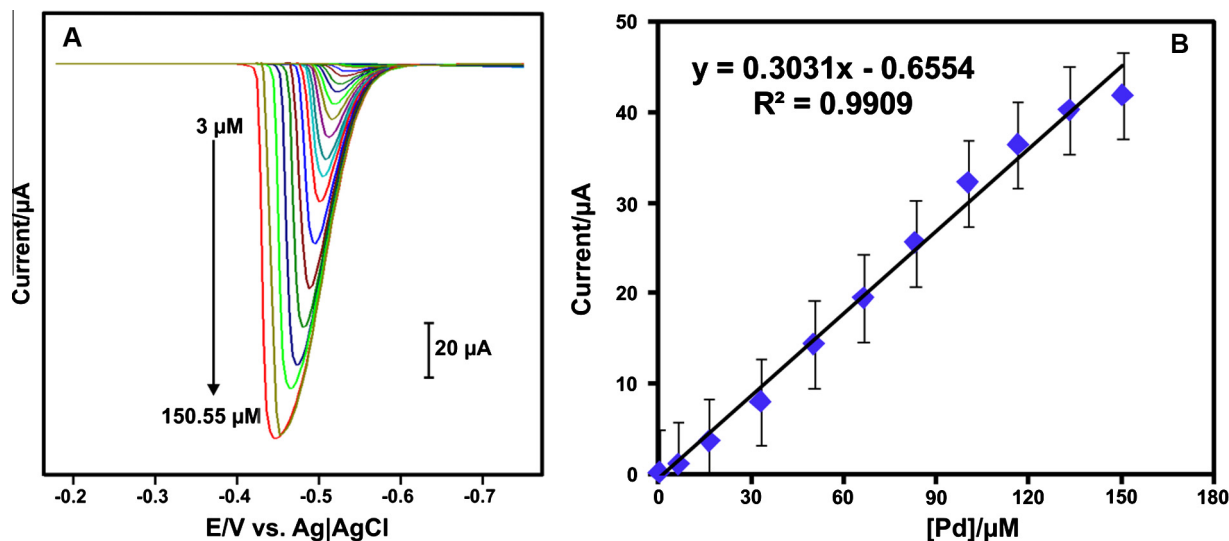


Fig. 4. (A) DPV response for SPCE in the presence of different concentrations of Pd²⁺ ranging from 3 μM to 150.55 μM in 0.5 M acetate buffer. (B) Calibration plot for cathodic peak current vs. [Pd²⁺]. Error bar indicates the relative standard deviations for 3 measurements.

determination Pd²⁺ ions. These results validate that the bare SPCE can be used for low level determination Pd²⁺ ions in environmentally polluted samples for practical applications.

3.5. Anti-interference study

In order to evaluate the selectivity of the fabricated sensor is more important. Hence, the electrochemical determination of Pd²⁺ ions with possibly interfering different metal ions were examined by DPV as shown in Fig. 5. It can be noted that 100 fold excess concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺, Co²⁺, Ni²⁺, Zn²⁺, Mn²⁺, Pb²⁺, Ag⁺, Al³⁺, Hg²⁺ and Cd²⁺ did not affect the concentration of Pd²⁺. It can be noted that the response of Hg²⁺ was observed at 0.44 V in the potential window ranging from −0.1 to 0.1 V. However, the 100 fold excess concentration of other interfering metal ions

slightly affected (>10%) towards the determination of Pd²⁺ ions after careful investigation by DPV. The slight responses of higher concentration for all these ions are neglected towards the response for lower concentration of Pd²⁺ ions. Hence, the SPCE was used for the selective electrochemical determination of Pd²⁺ ions in the presence of possible interfering metal ions.

In addition, the reproducibility and stability of the bare SPCE was investigated towards the current response of Pd²⁺ ions by DPV. For 10 successive electrolytes containing 5 μM Pd²⁺ was studied using a single electrode, the relative standard deviation (RSD) was 4.6%. The reproducibility of the sensor was examined by DPV using 6 different electrode towards the response current of Pd²⁺, the relative standard deviation (RSD) was 5.7%. The excellent performance of the sensor further authenticates the good precision of the sensor.

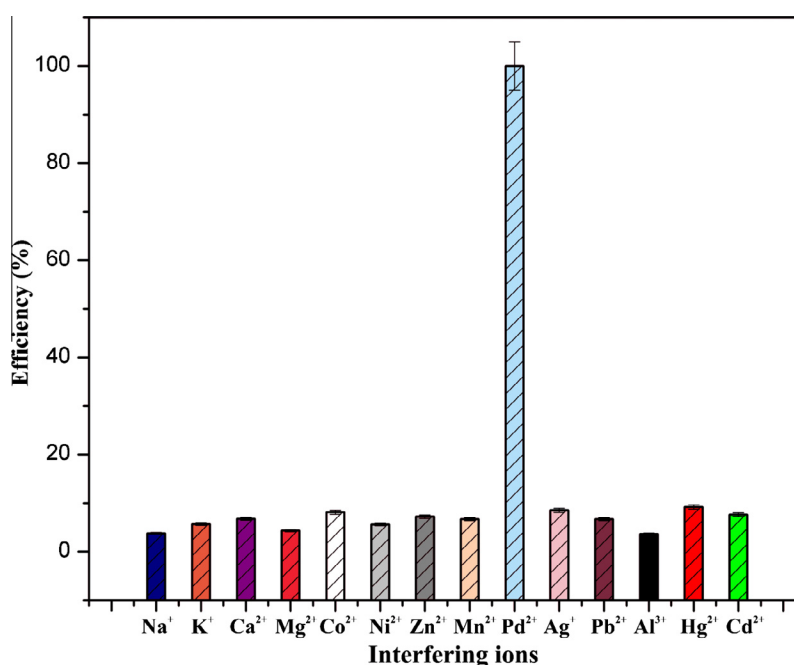


Fig. 5. Selectivity for determination of Pd²⁺ in the presence of various common ions in 0.5 M acetate buffer. Error bar indicates the relative standard deviations for 3 measurements.

Table 1

Determination of Pd²⁺ ions in different water samples using un-modified SPCE by DPV. (The relative standard deviation (RSD) is related for n = 3.)

Samples	Spiked (μM)	Found (μM)	Recovery (%)	RSD
Soil water	1.5	1.47	98	4.2
	1.5	2.93	97.66	4.0
Pond water	1.5	1.46	97.33	4.1
	1.5	2.87	95.66	3.9

3.6. Real sample analysis

To demonstrate the potential application of the sensor in environmental samples were studied using standard addition method by DPV [32]. Three different water samples such as soil water and pond water were studied and showed a satisfactory recovery values for the determination of Pd²⁺ ions as shown in Table 1. The recovery values of Pd²⁺ ions in water samples ranging from 95.66 to 98%. This result authenticates the newly developed sensor was used for the low level determination of Pd²⁺ ions in environmental samples.

4. Conclusions

In conclusion, we developed a simple, eco friendly and cost effective new system for electrochemical determination of Pd²⁺ ions using un-modified SPCE by DPV method. The un-modified SPCE showed a selective electrochemical determination of Pd²⁺ ions even in the 100 folds higher concentrations of possibly interfering metal ions. The excellent electroanalytical parameters (LOD, linear range, sensitivity) were achieved using un-modified SPCE towards the determination of Pd²⁺ ions. The proposed sensor also could be used for the determination of Pd²⁺ ions in environmental samples. The main scope of this work focused on cost effective, simple and handle free electrochemical sensor for the determination of Pd²⁺ ions in environmental applications.

Acknowledgments

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