Electrochemical determination of cadmium(II) at platinum electrode modified with kaolin by square wave voltammetry

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ABSTRACT

In this work, determination of cadmium(II) using square wave voltammetry (SWV) was described. The method is based on accumulation of these metal ions on kaolin platinum electrode (K/Pt). The K/Pt performance was optimized with respect to the surface modification and operating conditions. The optimized conditions were obtained in pH of 5.0 and accumulation time of 25 min. Under the optimal conditions, the relationship between the peak current versus concentration was linear over the range of 9×10^{-8} to 8.3×10^{-6} mol L^{-1}. The detection limit (DL, 3σ) was 5.4×10^{-9} mol L^{-1}. The analytical methodology was successfully applied to monitor the Cd(II) content in natural water. Interferences were also evaluated.

1. Introduction

Cadmium provides no known biological benefit to humans. Instead, cadmium can produce adverse effects on virtually every system in body; it can damage the kidneys, the nervous system, the productive system, and cause high blood pressure. The quantification of trace levels of cadmium has a challenging analytical problem of long-standing interest. Several analytical approaches have been applied for cadmium quantification. Currently, quantification of heavy metals at surface and subsurface hazardous waste sites relies upon the collection of liquid discrete samples for subsequent laboratory analysis using techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy (AAS) [1]. Sensors for obtaining real-time ppb level heavy metal concentrations would reduce time and costs associated with the characterization and treatments of hazardous waste sites. Desirable characteristics of the metal ion sensors include specificity for targeted metal ions, enhanced measurement frequency and precision, robustness, inexpensiveness, and infrequent regeneration of sensor material. Electrochemical sensors appear to be a promising technique that meets these requirements [2].

Mercury-based electrodes, especially mercury-film electrodes (MFEs), have been widely used for cadmium determination [3]. The formation of an amalgam enables the analyte to be accumulated in the mercury-film, thus providing the stripping with high sensitivity and reproducibility. However, because of the toxicity of mercury, it is important to develop the mercury-free electrodes for voltammetric determination of cadmium. Various materials have been used as free-mercury working electrodes for detection of heavy metals, the most popular being bismuth-film based electrodes (BFEs) [4].

The most significant advantage of BFEs is that they are environmentally friendly, since the toxicity of bismuth and its salts is negligible. However, the advantageous analytical properties of BFEs in voltammetric analysis, roughly comparable to those of MFEs, are attributed to the property of bismuth to form "fused alloys" with heavy metals, which is analogous to the amalgams that mercury forms [5]. However, the determination of copper using bismuth-film electrodes has been relatively ignored due to the similar stripping potentials of copper and bismuth with only a few reports in the open literature [4,6].

Carbon paste electrodes modified with functional ligands have also been employed to detect heavy metal ions [7,8]. However, the ligands in these sensors are in loose association with the conductive carbon matrix, thus the sensors may easily degrade over time from depletion of ligand-bearing material.

Clay modified electrodes are one type of chemically modified electrodes. They are most often prepared by coating thin film of clay

onto conductive substrates. The main objective is to use the properties of the clay films to control the electron transfer reactions at the electrode/solution interface [9]. Clay modified electrodes have potential uses in selective analysis [10,11] for electroanalysis [12,13] and as support matrices for catalysis [14,15].

Kaolin, efficient natural adsorbents [16,17], are the main components of soils and possess a negative charge that is compensated for by exchange cations [18]. Consequently, it is important to study the determination of cationic cadmium with kaolin minerals modified platinum electrode based on the accumulation process.

2. Experimental

2.1. Reagents

Commercial kaolin was supplied by ECESA (Lugo, Spain). Carbon paste was purchased from (Carbone, Lorraine, ref 9900, France). Deionized water from a water purification system was used to prepare all solutions. All reagents were of analytical grade. Metal working solutions were prepared daily by diluting a corresponding 10^{-3} mol L^{-1} solution (Merck). The glassware was kept overnight in 5% (v/v) HNO$_3$ solution. Afterwards, it was rinsed thoroughly with deionized water and dried.

2.2. Apparatus

Electrochemical measurements were performed with a potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). A kaolin-coated platinum plate (0.5×0.5 cm^2) served as working electrode, with the Ag/AgCl (3 mol L^{-1} KCl) and platinum wire acting as reference electrode and counter electrode, respectively. All potentials were given versus the Ag/AgCl (3 mol L^{-1} KCl) electrode.

The coated specimen was examined using a scanning electron microscope (SEM, Jeol JSM-5500). The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, France) was used for adjusting pH values.

2.3. Synthesis of working electrode

The cathode electrode was a platinum plate, with a dimension of 0.5×0.5 cm^2, was polished on wet SiC paper (grade up to 1200) and washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and dried at room temperature. The current was maintained by a galvanostat with a function generator. The anode electrode was a platinum plate. Then, the electrodes were immersed in electrolyte of kaolin gel contained glass chamber, and subjected to anodic oxidation by applying DC for 10 h at room temperature. The deposit of kaolin on platinum surfaces was processed at 4.0 V.

2.4. Analytical procedure

The kaolin modified platinum electrode (K/Pt) was immersed in magnetically stirred containing 20 ml of cadmium(II) at open circuit. After this step, the electrode was removed, rinsed and dried with adsorbent paper. The electrode was then transferred into 0.2 mol L^{-1} KNO$_3$ solution. A potential of -1.0 V versus Ag/AgCl was applied for 10 s in still solution. Immediately after the reduction time expired, the second order derivative scan voltammogram was recorded by applying a positive-going potential scan from -1.0 to -0.5 V at 50 mV s^{-1} using a step potential of 25 mV; amplitude 5 mV and duration 5 s at scan rate 1 mV s^{-1}. All experiments were performed at room temperature.
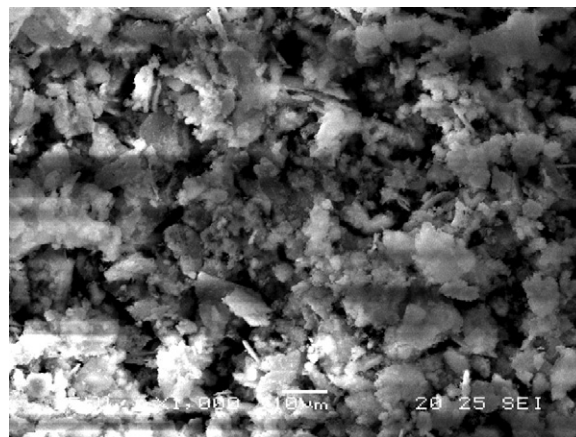

Fig. 1. Scanning electron micrograph of kaolin/platinum.

Electrochemical impedance spectroscopy (EIS) measurements were carried out by the same three electrode-cell setup described above before and after the accumulation step. Impedance spectra were obtained in the frequency range between 100 kHz and 10 mHz with 10 points per decade at the potential of 0 V after 30 min of immersion in non-de-aerated solutions. A sine wave with 10 mV amplitude was used to perturb the system.

In other hand, the deposit powder was analyzed at carbon paste electrode (CPE) by square wave voltammetry. The carbon paste was prepared by mixing high purity graphite powder and a kaolin, in a weight ratio 1:1. The kaolin-(CP) was then compacted carefully in the electrode cavity.

3. Results and discussion

3.1. Electrode synthesis

The surface of platinum electrode modified with kaolin was observed using scanning electron microscopy (Fig. 1). It was observed that the kaolin film exhibited a porous microstructure with micropores, which were relatively well separated and homogeneously distributed over the surface. The micro-porous surface of K/Pt is beneficial to fixing cadmium from preconcentration solution.

3.2. Preliminary voltammetric characterization

The cyclic voltammograms for cadmium(II) obtained at unmodified and modified platinum electrodes are shown in Fig. 2a and b respectively. At the platinum electrode, in the potential range scanned from -1.0 V to -0.5 V, a fairly small peak current due to Cd(II)/Cd(0) redox couple is observed. On the other hand, the Cd(II)/Cd(0) redox reaction occurred at kaolin modified platinum electrode is much more distinguishable. The result indicates that the kaolin can greatly promote the preconcentration of cadmium at the platinum electrode and significantly increase the sensitivity of the determination of cadmium. The performance of the newly developed kaolin modified platinum electrode is based on the accumulation of cadmium from aqueous solution onto the surface of the modified electrode.

3.3. Electrochemical impedance spectroscopy (EIS)

The behaviour of modified platinum electrode before and after accumulation step is also investigated by the electrochemical impedance spectroscopy (EIS) at room temperature (Fig. 3). The charge-transfer resistance (R_{tc}) values are calculated from the difference in impedance at lower and higher frequencies, as suggested
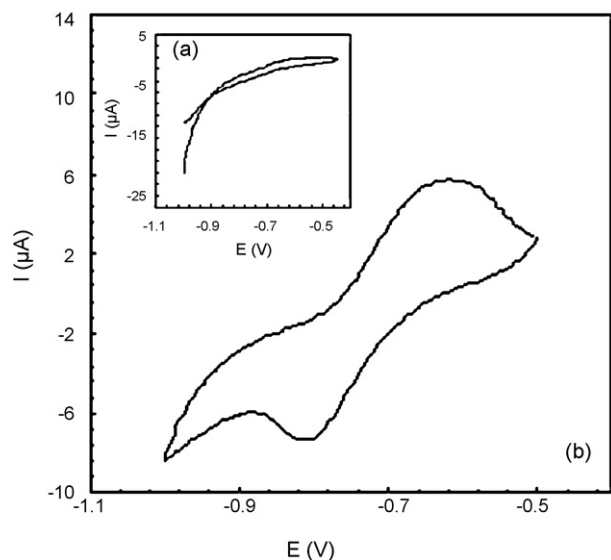
Fig. 2. Cyclic voltammogram of kaolin modified platinum electrode: (a) before any contact with cadmium(II). (b) after incubation with cadmium(II) species during 30 min; supporting electrolyte is 0.2 mol L^{-1} KNO$_3$, pH 5.6; the scan rate was 100 mV s^{-1}. [Cd(II)] = 3 mol L^{-1} × 10^{-5} mol L^{-1}.
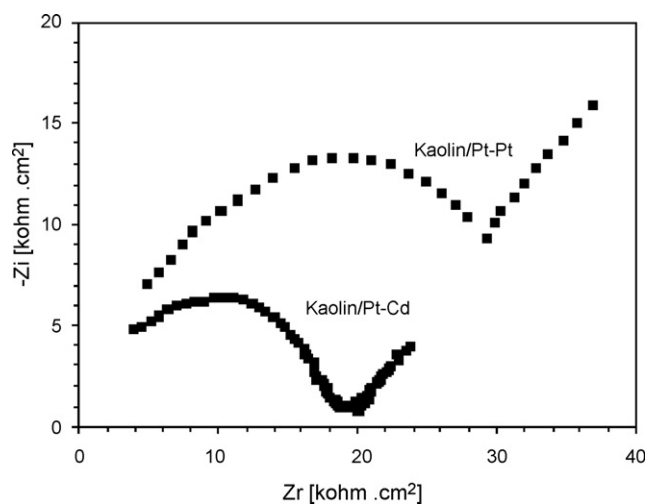

Fig. 3. Impedance spectra at 0 V (a) kaolin modified platinum electrode and (b) kaolin/Pt/Cd(II). Conditions are as described in Fig. 2.

by Tsuru et al. [19]. The double-layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in the equation:

$$(C_{dl}) = \frac{1}{\omega R_t}, \quad \text{where } \omega = 2\pi f_{max} \tag{2}$$

Impedance diagrams are obtained for the frequency range from 100 kHz to 10 mHz at the potential of 0 V. Table 1 gives the values of the charge-transfer resistance, R_t, double-layer capacitance and (C_{dl}) derived from Nyquist plots. From the impedance data, we conclude that the R_t values decrease with the presence of accumulated cadmium(II). The values of double-layer capacitance

Table 1
Electrical parameters calculated from the impedance spectra in 0.2 mol L^{-1} KNO$_3$ for the kaolin/Pt and kaolin/Pt-Cd(II) solution interfaces.

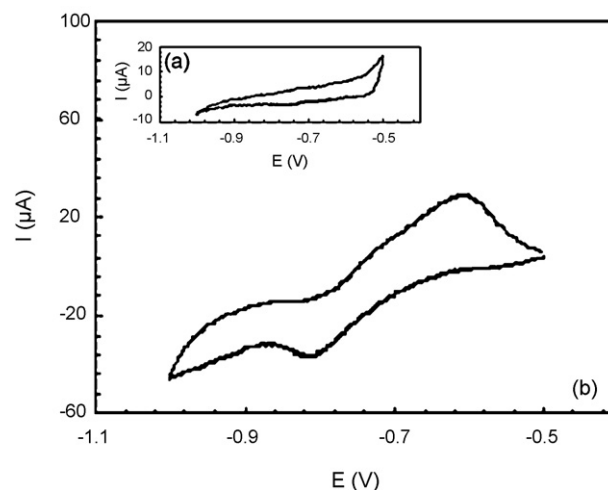|	R_e (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (pF/cm^2)
Kaolin/Pt	1800	30620	207.8
Pb-Kaolin/Pt	722	17900	248.8

Fig. 4. Cyclic voltammogram in HClO$_4$ (0.1 M) for kaolin layer, at carbon paste electrode (CPE) (a): before preconcentration step (b): after preconcentration in 5.0 × 10^{-4} mol L^{-1} Cd(II), pH 5.6. V_b = 100 mV s^{-1}, between −0.4 and −1.0 V.

are also brought down to the minimum extent in the presence of Cd(II) and the increase in the values of (C_{dl}). The increase in (C_{dl}) is due to the accumulation of cadmium(II) on the platinum surface.

3.4. Deposit analysis

The kaolin layer was analyzed at carbon paste electrode (CPE) before and after preconcentration step of K/Pt in cadmium solution (Fig. 4). It may be noted the presence of a cathodic peak P$_1$ observed at −0.79 V, and an anodic peak, P$_2$ recorded at 0.64 V. The peak potentials were attributed to cadmium behaviour in 0.1 M HClO$_4$. This result confirms the presence of cadmium(II) onto kaolin coating platinum electrode after preconcentration in cadmium solution. Our results suggest that the uptake of aqueous cadmium was associated with the kaolin surface immobilization.

3.5. Optimization of the variables

Fig. 5 shows the variation of anodic peak current versus the accumulation time. The peak current increased with the accumulation time, indicating that before adsorptive equilibrium is reached, the longer the accumulation time, the more Cd(II) was adsorbed and thus the peak current became larger. A preconcentration time of 25 min was chosen for further experiments.

The influence of pH on the SWV response of the platinum electrode modified with kaolin was studied over a pH range between 2.0 and 9.0 in a solution containing 1.5 mol L^{-1} × 10^{-6} mol L^{-1} cad-

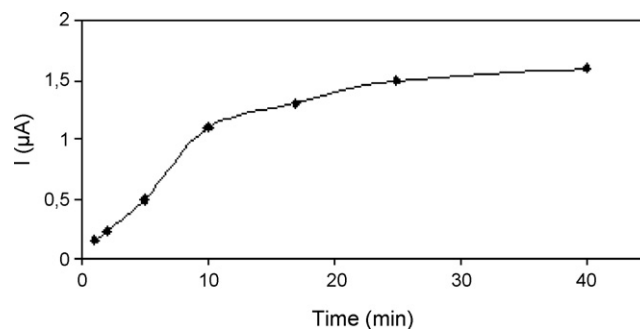**Fig. 5.** Effect of accumulation time on charge transfer of 1.5 mol L^{-1} × 10^{-6} mol L^{-1} cadmium(II) in 0.2 mol L^{-1} KNO$_3$, pH 5.6 at kaolin/Pt.
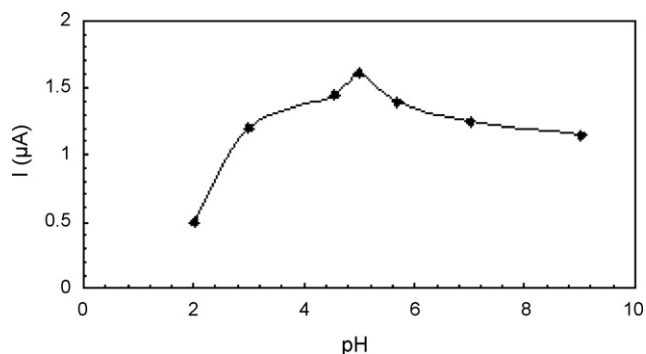
Fig. 6. Influence of pH on SWV oxidation peak for 1.5×10^{-6} mol L^{-1} cadmium(II) in 0.2 mol L^{-1} KNO$_3$ at kaolin/Pt, $t_p = 25$ min.

mium is presented in Fig. 6. The optimum pH range was found between 3.4 and 6.5, showing a maximum response at pH 5.0. The sensitivity decrease in acidic solution accompanied with the decrease of reduction peaks. This is dependant on the fact that kaolin can slowly dissolve in acidic solution and lose its ability of adsorbing. Therefore, pH 5.0 was used in further studies.

3.6. Calibration curve

Fig. 7 shows the anodic peak current of Cd(II) versus its concentration. Under the optimized conditions, the relationship between the peak current of cadmium(II) and its concentration is linear with regression equation of $I(\mu A) = 0.8825[Cd(II)]$ $(\mu mol\,L^{-1}) + 0.217$ ($r^2 = 0.9938$) in the linear dynamic range of 9×10^{-8} to 8.3×10^{-6} mol L^{-1}. The detection limit (DL, 3σ) and quantification limit (QL, 10σ) for the determination of cadmium(II) were 5.4×10^{-9} mol L^{-1} and 8.7×10^{-9} mol L^{-1}, respectively. The relative standard deviation (RSD) for seven replicate analysis of a solution containing 5.4×10^{-6} mol L^{-1} was 2.05%.

It should, however, be pointed out that even though the DL and the QL obtained in the present study are comparable to the values obtained in the literature [20]. However, it was higher than those obtained with bismuth film [21]. The detection limit can be improved by modifying of kaolin surfaces. Particularly, the detection limit can be improved significantly by increasing the surface area of the modifier.

3.7. Interferences

The selectivity of this approach for the determination of cadmium was evaluated by introducing concentrations of other ions into the cadmium sample solution during the preconcentration step. The interferences of some metal ions on the determination of cadmium(II) were investigated. The kaolin modified platinum electrode was immersed in a mixture of Cd(II), Cu(II), Ag(I), Pb(II) and Hg(II) (5.0 mol L^{-1} $\times 10^{-6}$ mol L^{-1} each one). The voltammogram of Fig. 8 shows one oxidation signal attributed to Cd(II) in position -0.6 V, no interfering under our conditions. The clean separation of the potential peaks offers us the possibility of the determination of Cd(II) without any harmful interference from other common heavy metals.

3.8. Analytical application

The proposed methodology was successfully applied for the determination of cadmium in natural water samples (Oum Er Rbia) in Tadla–Azilal region, Morocco without any pretreatment. It should be mentioned at this point that the reason for using the standard addition technique is to compensate the matrix effect from natu-
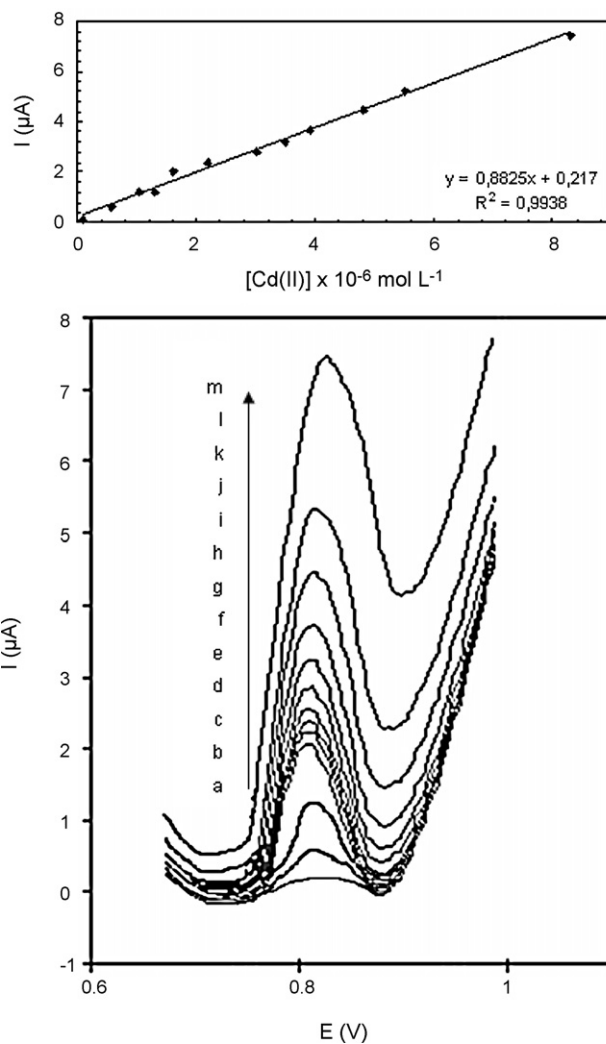

Fig. 7. Square-wave voltammograms in 0.2 mol L^{-1} KNO$_3$, pH 5.6, $t_p = 25$ min, at kaolin/Pt of cadmium(II); (a) 9×10^{-8}, (b) 5.6×10^{-7}, (c) 1.04×10^{-6}, (d) 1.6×10^{-6}, (e) 1.3×10^{-6}, (f) 2.2×10^{-6}, (g) 3×10^{-6}, (h) 3.5×10^{-6}, (i) 3.9×10^{-6}, (j) 4.8×10^{-6}, (k) 5.5×10^{-6}, (l) 8.3×10^{-6} mol L^{-1}.
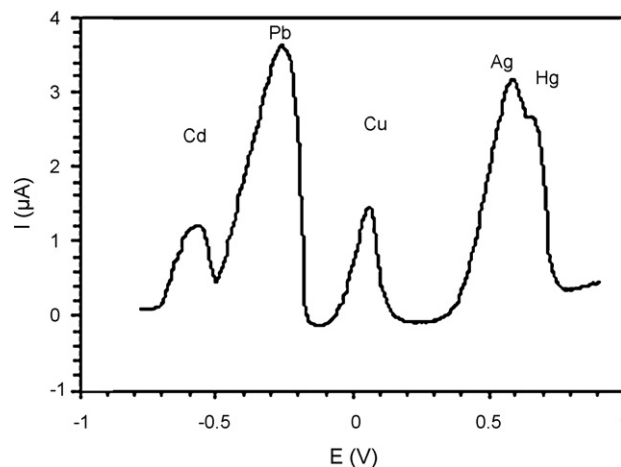

Fig. 8. Cyclic voltammogram after exposure to a solution containing Cd(II), Ag(I), Cu(II), Hg(II), and Pb(II) of concentration 6.3 mol L^{-1} $\times 10^{-6}$ mol L^{-1}.

Table 2
Physico–chemical characterization of water samples.

pH	MES (mg L^{-1})	O$_2$ (dissous) (mg L^{-1})	NH$_4^+$ (mg L^{-1})	Mn^{2+} (mg L^{-1})	NO$_2^-$ (mg L^{-1})	NO$_3^-$ (mg L^{-1})	Nitrogen total (mg L^{-1})
8.85	9.5	11	0.26	0.03	0.18	5.6	0.7

Table 3
Results obtained from the linear regression curves for the determination of Cd(II) at kaolin/Pt in natural waters.

Parameters	Peak
Equation	$Y = 0.857X + 0.165$
r^2	0.991
Slope A (mol L^{-1})	0.857
Standard deviation (σ) ($\times 10^{-10}$ A)	21.42
Relative standard deviation (%)	2.16
Recovery (%) (SWV)	97.86
Recovery (%) (ICP-MS)	96.56

ral water samples that contain high concentrations of nitrate ions and other foreign ions (Table 2). The results obtained, in quadruplicates, were related to interference effects of the constituents of each sample. Recoveries of spike additions to water samples were quantitative (Table 3). The statistical calculations for the assay results showed suitable precision of the proposed voltammetric method. There were no significant differences between the calculated and added concentrations at the 97.86% confidence level and within an acceptable range of error. The mean percentage recoveries of added Cd(II) and the detection limit were found to be 96.56% and 2.3 mol L^{-1} × 10^{-8} mol L^{-1} using inductively coupled plasma-atomic emission spectrometric method (ICP-MS). These results demonstrate the applicability of the procedure for cadmium determination in water samples.

4. Conclusion

Square wave voltammetry was performed for determination of cadmium(II) at kaolin modified platinum electrode. The sensitivity of this electrode for determination of heavy metals open the possibility to consider the kaolin modified platinum electrode as a good alternative electrode. This electrode is characterized by a good sensitivity associated with a satisfying reproducibility. Moreover, kaolin presents the advantage of being more 'environmentally-friendly' ban mercury, the toxicity of which will probably lead to progressively than this electrode material for on-site monitoring of trace pollutants. The proposed methodology has a wider linear range and lower detection limit and is not interfered significantly by other metal ions. The modified electrode was successfully applied in water samples. The electrode construction was extremely simple and with low cost.

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