

Electrochemical Determination of Cu(II) Ions Based on Ag/Pd Alloy for Water Quality Early Warning

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Received: 6 March 2017 / Accepted: 29 March 2017 / Published: 12 May 2017

With a chemical and eco-friendly in situ reduction technique, an excellent Ag-Pd bimetallic nanoparticle (Ag-Pd)-based hybrid was successfully synthesized in this study. To determine copper(II) ions in water, this work employed differential pulse adsorptive stripping voltammetry (DPAdSV) and preconcentration methods. Furthermore, the sensor feasibility was studied with river and tap water as real specimens. The results revealed the potential of the proposed electrochemical sensor to be applied for the early testing of water quality based on its desirable behavior in Cu(II) determination in real specimens.

Keywords: Silver; Palladium; Alloy; Water quality; Electrochemical determination; Copper ions

1. INTRODUCTION

Heavy metals such as iron, zinc and copper are of vital importance to fish metabolism. However, other heavy metals, such as lead, cadmium and mercury, exhibit no recognizable function in biological systems. The absorption of necessary metals from sediment, food or water is imperative for the ordinary metabolism of fish, but the same procedure would also occur for the unnecessary metals, leading to their accumulation in the tissues of the fish. In spite of the importance of temperature, hardness, pH, salinity and other environmental elements to metal accumulation in tissue, the major determinative elements for the accumulation include the length of exposure and the water concentrations of the metals, according to laboratory and field studies. Metal accumulation in marine animal tissues has also been observed to be influenced by other factors, including their molt, size, sex and ecological needs [1-9]. The tissue metal contents have been reported to be significantly affected by

the sizes of marine animals, with marine animals of diverse species exhibiting similar trends in terms of mercury. For instance, the sizes of animals have been positively related to the levels of mercury in mussel, decapod crustacean [10-12], fish [13, 14], marine mammals [15] and seabirds [16] that exist in the marine food chain. With mercury accumulating up through the levels to human diets, this phenomenon is also an important issue in the food chain. Nonetheless, other metals (apart from mercury) show no trend of being significantly and consistently related to animal sizes, exhibiting much less consistent behaviors [15, 17-20].

Thus, it is of crucial importance to have a facile and inexpensive method to selectively and sensitively determine toxic heavy metals. Electrochemical [21], mass spectrometric [22] and optical methods [23] in addition to other strategies have been used to detect heavy metal ions. For instance, the industrial detection of metal ions has witnessed the widespread application of atomic absorption spectrophotometry (AAS), which features superbly accurate, selective, sensitive and simultaneous detection of diverse ions. Nevertheless, the process must be performed by professionals and with comparatively costly devices. In the field of heavy metal ion detection, focuses have been fixed on electrochemical detection approaches that are inexpensive, highly sensitive and easily adaptable for in situ assessment [24] with short analytical periods. Ordinarily, a counter electrode (CE), a reference electrode (RE) and a working electrode (WE) constitute a triple-electrode system to perform electrochemical detection. In order to achieve specific recognition or/and concentration of metal ions, diverse materials can be adopted for the modification of a WE [25, 26]. Electrochemiluminescence, capacitance, electrochemical impedance, potential or current are varied by the existence of heavy metal ions, and detection can be accomplished through these factors [27, 28].

The fabrication of an Ag/Pd nanoalloy with superb quality was achieved by the convenient, eco-friendly and chemical in situ reduction technique proposed herein. The synergistic effect of the bimetallic nanoparticles was revealed to grant excellent performance in determining Cu(II) in comparison with the monometals, with the electrocatalytic trait improved through the Ag-Pd alloying, as suggested by the electrochemical characterizations. Quantitative Cu(II) detection was accomplished by the Ag-Pd alloy with superb catalytic capacity over a wide range of 1.5-31 μM and a detection limit as low as 0.3 μM . Finally, the successful application test of river and tap water Cu(II) detection was achieved through the proposed approach.

2. EXPERIMENTS

Aladdin Chemical Reagent Co. (China) was the material source for vanillin, silver nitrate and palladium chloride. An appropriate quantity of CuCl_2 was dissolved into deionized water and stored at 4 °C to prepare a stock Cu(II) solution. NaOH and H_3PO_4 solutions (0.1 M) were used to adjust the pH of a phosphate-buffered solution (PBS) (0.1 M) that was usually used as the supporting electrolyte. Being of analytical-reagent grade, all other chemicals were utilized with no further purification. Ultrapure water with a resistivity of no more than 18 $\text{M}\Omega$ cm from a Millipore system was adopted for the preparation of all solutions.

With no other templates and surfactants used, the in situ reduction of Ag^{2+} and Pd^{2+} was achieved with polyethylene glycol, thus obtaining the Ag-Pd alloy. A homogeneous dispersion system was established through continuous addition of PdCl_2 (5 mL, 0.05 mg/mL) and AgNO_3 (5 mL, 0.12 mg/mL) to water with 0.5 h of ultrasonic oscillation. Then, a mixture of this dispersion with the injected polyethylene glycol (50 μL) was stirred for 2.0 h upon injection. Subsequently, the as-prepared mixture was let sit undisturbed for 5.0 h at atmospheric pressure and ambient temperature. After several rounds of centrifugation and washing the mixture with ultrapure water, the terminal Ag-Pd alloy was consequently synthesized via lyophilization. Additionally, a similar course with the addition of Ag^{2+} or Pd^{2+} into water was employed for the preparation of Ag and Pd.

A UV-2550 spectrophotometer (SHIMADZU, Japan) was employed to obtain UV absorption spectra. A triple-electrode system and a CHI660D electrochemical analyzer (Chenhua Instrument Company, Shanghai, China) were used for the electrochemical measurements. In the triple-electrode system, the counter electrode, reference electrode and working electrode were a Pt wire, a saturated calomel electrode (SCE) and a modified/unmodified glassy carbon electrode (GCE) with a diameter of 3 mm. The de-oxygenation of the electrolyte was performed by nitrogen gas preceding the electrochemical measurements. All experiments was conducted at room temperature. Differential pulse adsorptive stripping voltammograms (DPAdSVs) were recorded in an acetate buffer at pH 5.0 from -0.3 to 0.3 V.

A shiny and smooth surface was achieved on the original GCE through consecutive polishing with alumina powders (1.0, 0.3 and 0.05 μm) prior to its modification. The GCE then went through 5 min sequential ultrasonic cleanings in 1:1 HNO_3 solution, ethanol and water, followed by drying with blowing N_2 . A homogeneous dispersion was fabricated from a mixture of DMF (1.0 mL) and the as-prepared Ag-Pd alloy (1.0 mg) processed by 30 min sonication. The terminal Ag-Pd/GCE electrode was eventually obtained after dropping a certain quantity of the Ag-Pd dispersion on the GCE surface and subsequent infrared lamp drying. An identical process was adopted for the fabrication of Pd/GCE, Ag/GCE and bare GCE components for comparison measurements.

3. RESULTS AND DISCUSSION

Information concerning the fabrication pathway of these materials is revealed in the UV absorption spectra of Pd, Ag and Ag-Pd (Figure 1). The surface plasmon resonance absorption peak of Ag accounts for the 450 nm peak in the Ag spectrum, while a Pd absorption peak is observed as a broad shoulder of 360–450 nm in the Pd spectrum. The fact that the Ag-Pd alloy has been successfully synthesized is suggested by the typical bimetal peaks.

It has been reported that bimetallic NPs can promote the catalytic activity and selectivity of the monometallic species. In recent years, Ag-Pd bimetallic NPs, including Ag-Pd alloy, Ag-Pd core-shell, and monodisperse Ag-Pd alloy NPs supported on carbon-based materials have been developed for the catalytic dehydrogenation of formic acid [29-31]. To confirm the behavior of Ag-Pd in copper ion preconcentration, this work first carried out voltammetric experiments. DPAdSVs obtained using a GCE (without modification) after the preconcentration step and a Ag-Pd/GCE preceding and

succeeding the preconcentration stage are exhibited in Figure 2. The GCE with no modification after the preconcentration stage exhibited no peaks in the acetate buffer solution with the potential ranging from -0.3 V to 0.3 V (versus Ag/AgCl, KCl 3 M). This reveals that the electron-transfer process was remarkably improved on the surface of the electrode.

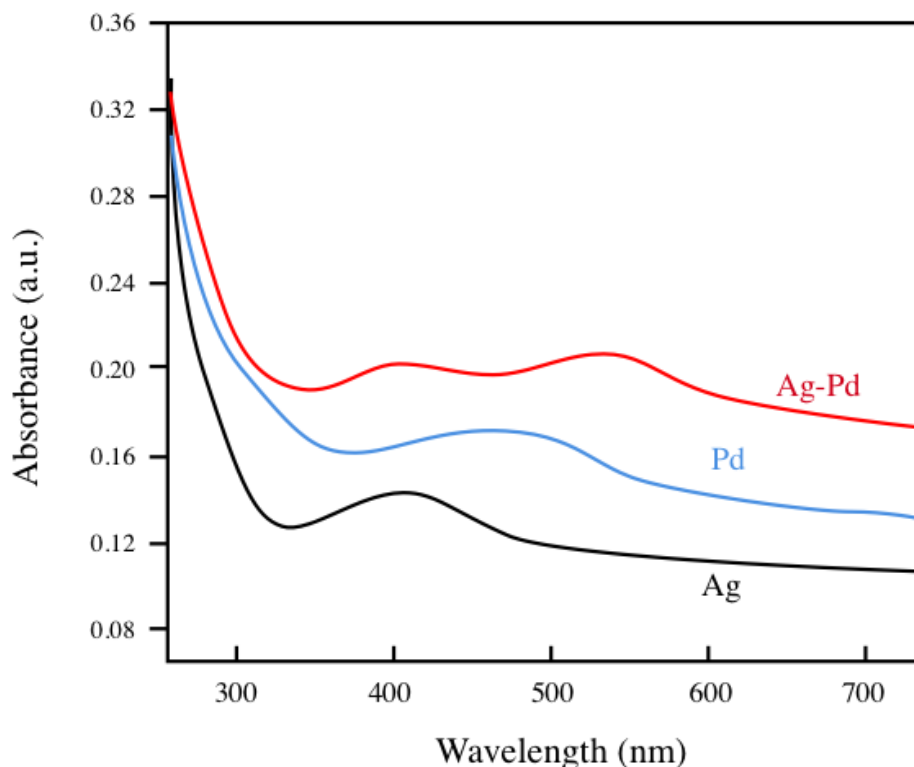


Figure 1. UV spectra of Pd NPs, Ag NPs and the Ag-Pd composite alloy.

The efficacy of the electrode surface and the copper ion interaction could not be enhanced by the GCE, as indicated by this result. An insignificant quantity of electroactive species existed on the surface of the electrode, as indicated by the similar results for the Ag-Pd/GCE prior to the preconcentration stage. Nevertheless, the copper oxidation resulted in an obvious oxidation peak at -0.03 V with the submission of the Ag-Pd/GCE to the preconcentration stage prior to the voltammetric measurement. This was attributed to the Ag-Pd on the surface of the electrode playing a significant part in improving copper ion detection and strengthening the interaction with copper ions. This can be attributed to the well-organized accumulation of metal ions close to the electrode surface by complexation reactions [32]. A desirable voltammetric signal stability appeared through successive measurements.

The Ag-Pd/GCE was cleaned in H_2SO_4 solution to prevent memory effects. The copper oxidation-related anodic peak disappeared after the adsorbed copper ions were replaced with H^+ on the surface of the electrode at this stage. A study with an Ag-Pd/GCE was conducted to determine the influence that the modifier surface area exerts on the voltammetric response. Compared with the voltammetric signals gained through the proposed modifier, those through charcoal-equipped Ag-Pd/GCE were 20 times lower, even though the surface area of Ag-Pd is much more expanded than that

of GCE. To conclude, these results could not confirm that the surface area is not determinative to the efficacious interaction between Ag-Pd and copper ions.

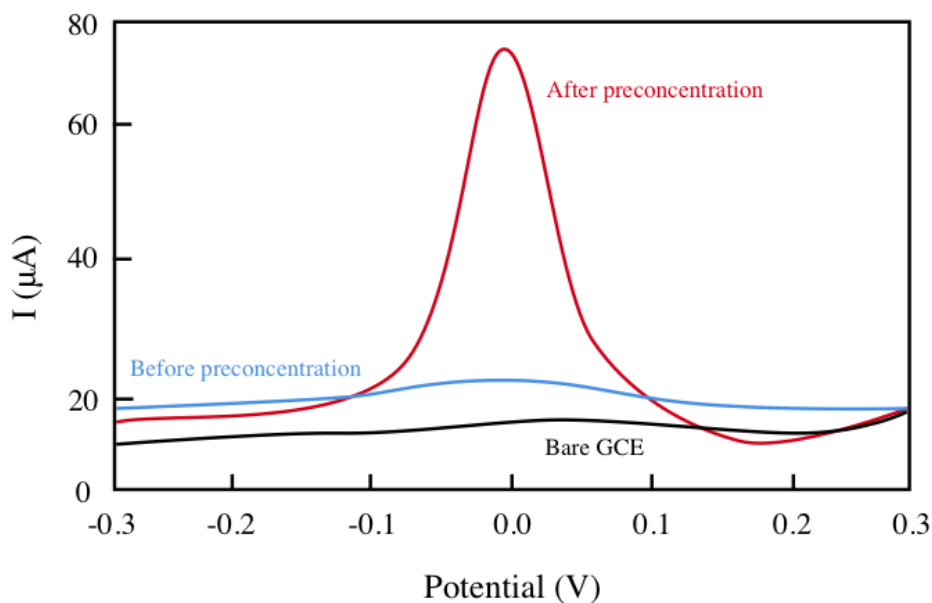


Figure 2. Differential pulse stripping voltammetric responses obtained in acetate buffer at pH 5.0 for the bare GCE after the preconcentration step and for Ag-Pd/GCE before and after the preconcentration step. t_{dep} : 30 s and E_{dep} : 0.3 V.

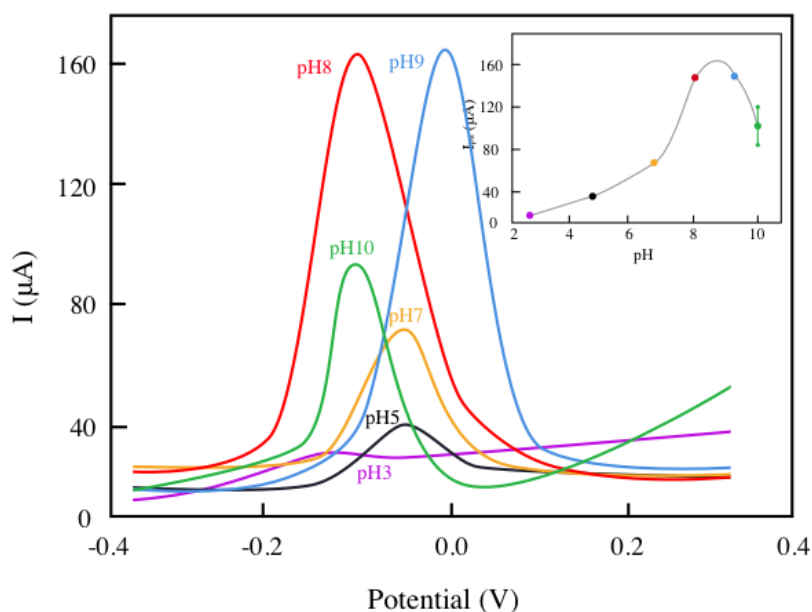


Figure 3. DPAdSV obtained for Ag-Pd/GCE after preconcentration in aqueous solution adjusted to different pH values, pH = 3.0; pH = 5.0; pH = 7.0; pH = 8.0; pH = 9.0 and pH = 10.0, containing $10 \mu\text{M}$ of Cu^{2+} . In detail: effect of pH of the preconcentration solution on the anodic peak current of Cu^{2+} using a CPEM. t_{dep} : 30 s and E_{dep} : 0.3 V.

The effect of the measurement solution pH on the voltammetric response was studied with pH levels from 3.0–8.0. Other studies used the acetate buffer (pH 5.0) with an optimized voltammetric curve. Ammonium (pH > 7.0) and acetate (pH < 7.0) buffer solutions were used to adjust the preconcentration solution to a pH of 3.0 to 10.0, thus investigating the effect of pH on the adsorption step, as indicated in Figure 3. Possibly because Cu^{2+} competed with H^+ ions for surface adsorptive sites, there were no remaining copper ions at the electrode in acidic solutions (pH < 4), as was indicated from the voltammetric behavior of Ag-Pd/GCE. At pH values greater than 4, the decrease in the anodic peak current may be due to the hydrolysis of cations [32]. As the pH values shifted above 6.0 and rose to the peak values of 8.0 and 9.0 in ammonium buffer solution, the anodic peak current exhibited an obvious rise. There was a decline in the signal above this pH value. With a pH above 10.0, only an insignificant wave was revealed, which could be due to the hydrolysis reaction of copper ions. Based on the above results, an ammonium buffer solution with a pH of 9.0 was selected for the preconcentration stage.

With varied preconcentration times (0–60 min), an Ag-Pd/GCE was loaded into an ammonium buffer solution (pH 9.0) containing copper ions with diverse concentrations to study the effect of the immersion period (preconcentration time). The transfer of the electrode to the electrolyte was performed after the preconcentration stage, with DPAdSVs recorded. The anodic peak current was observed to depend on the preconcentration time (0–60 min). At the concentrations of 1 μM and 10 μM , the anodic peak current rose linearly up to 15 min and 30 min, respectively. That analyte concentration correlated with accumulation time in a well-defined way in the stripping approach was suggested by the dependence of a stationary condition on the surface equilibrium of the copper ions, which could be observed through the plateau of the current signals above these values with extended accumulation time. The same behavior was reported in previous works [33–35], indicating a well-defined correlation between accumulation time and analyte concentration for stripping methods, thus allowing the modulation of analytical performance as a function of preconcentration time. Herein, 30 min accumulation was applied to determine analytes at low levels via the proposed sensor. Some electrodes with an identical accumulation period were used for the preconcentration stage, since the Ag-Pd/GCE was observed to exhibit significantly repeatable and reproducible performance despite a comparatively extended accumulation period. In the case of higher copper ion levels, a short period could be employed, with a preconcentration period of 10 min selected for further studies.

Under optimal test conditions, analytical calibration profiles (in triplicate) were recorded after the investigation with respect to the influence that experimental parameters exerted on the voltammetric signal. A concentration range from 1.5 μM to 31 μM was obtained as the linear dynamic range (LDR) for copper ion concentration and anodic current peak. Concentrations of 0.3 μM and 0.4 μM were determined as the limit of quantification (LOQ) and limit of detection (LOD), respectively. The sensing performance of the proposed sensor was compared with recently reported sensors, as shown in Table 1. Five consecutive measurements of copper ions (10 μM) were performed at the same Ag-Pd/GCE without renewing the electrode surface between consecutive runs to investigate repeatability, with an obtained relative standard deviation of 4.3%. This voltammetric procedure was employed on five diverse electrode surfaces, with a confirmed RSD of 4.7%. With each electrode having a calibration profile, five repeated evaluations were performed on the same day for the

analytical sensor performance. The standard deviation was confirmed to be below 5.8% with the consideration of figures of merits including the LOQ, LDR and LOD offered by the proposed method. The values gained on diverse electrode surfaces are similar to this one. The analytical behaviors in similar experiments performed on diverse days were compared. With other potential differences considered, a desirable consistency between the outcomes was suggested via the confirmed RSD of 7.0%. The outstanding behavior of CPME and paste homogenization could be confirmed by the results reported herein.

Table 1. Performance comparison of the Ag-Pd/GCE and other electrodes for Cu(II) detection.

Electrode	Linear range	Detection limit	Reference
G-Nafion/Bi/GCE	0.05-0.5 μM	0.01 μM	[36]
Nafion/Bi/NMC/GCE	0.1-3 μM	0.02 μM	[37]
MWCNTs-Nafion/Bi/GCE	1.0 -2.0 μM	0.2 μM	[38]
GNFs-Nafion/Bi/GCE	0.1-1.0 μM	0.03 μM	[39]
OMC/Nafion/GCE	1.5 -5 μM	0.5 μM	[40]
Ag-Pd/GCE	1.5-31 μM	0.3 μM	This work

Lead (200 $\mu\text{g/L}$), Ar (100 $\mu\text{g/L}$), Zn (3.0 mg/L) and Fe^{2+} (2.0 mg/L) were applied separately to investigate the influence of a few concomitant species on the voltammetric signal and together in combination into multicomponent specimens, with the outcomes exhibited in Figure 4. River water was selected for the test specimens. When used in specimens of this sort, the assessed groups with desirable selectivity for the as-prepared instrument exhibited no apparent effect.

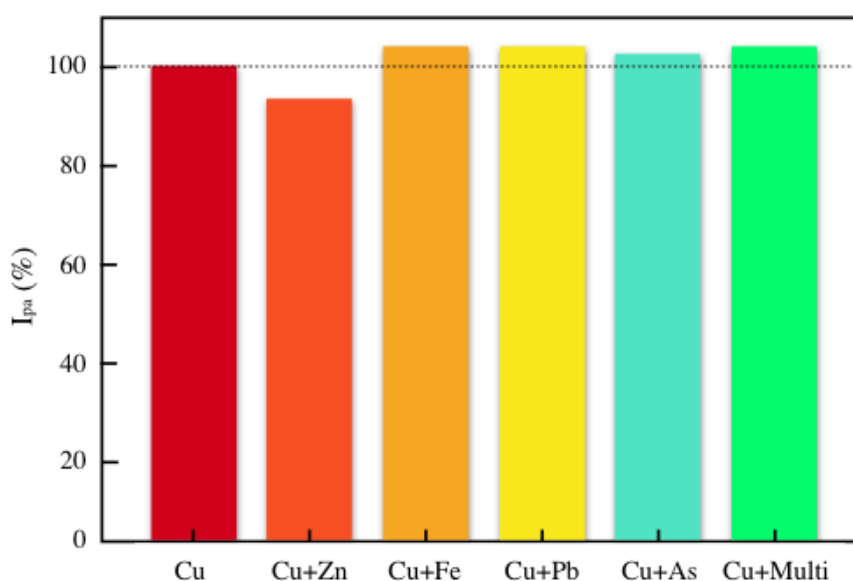


Figure 4. Percent interference of the voltammetric responses verified for Ag-Pd/GCE in the presence of only copper ions.

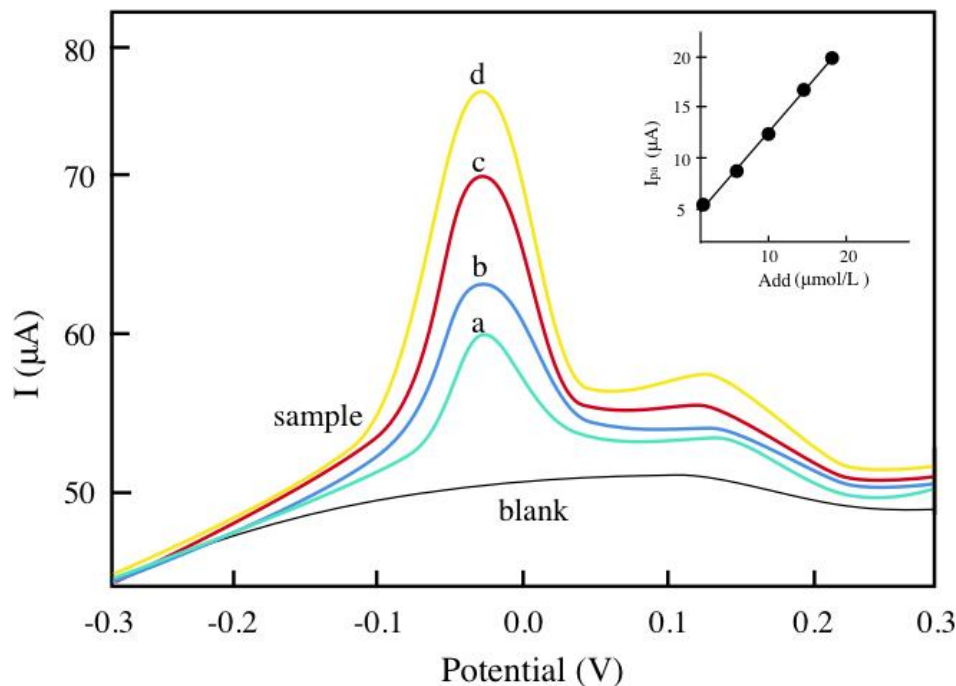


Figure 5. Differential pulse voltammetric response and standard addition curve (inset curve) obtained for the determination of copper ions in the standard sample. t_{dep} : 30 s and E_{dep} : 0.3 V.

The applicability of the sensor to real specimens was shown through assessing the proposed procedure for copper ion determination in diverse water specimens. Figure 5 displays a typical analyte quantification profile via the standard addition approach. The values gained via a comparative approach (ICP-OES) were compared with those of the proposed procedure. A good relationship with a confidence level of 96% was determined from the outcomes in Table 2. It is possible to determine the copper ions in real specimens with no significant matrix influences, as revealed from these values.

Table 2. Mean values obtained for the determination of copper ions in real water samples from the proposed stripping voltammetric (SV) method and the comparative method (ICP-OES).

Sample	Value found μM		RSD (%)
	SV	ICP-OES	
Tap water 1	0.29	0.31	3.56
Tap water 2	0.50	0.48	4.44
River water 1	1.32	1.33	5.62
River water 2	1.81	1.78	1.27

4. CONCLUSIONS

With a convenient and eco-friendly chemical in situ reduction technique, the synthesis of an excellent Ag-Pd alloy was achieved. The promotion of Cu ions and electrode surface charge transfer

was accomplished via an electron transfer medium, namely, the bimetallic Ag-Pd nanoparticles. Using a differential pulse voltammetry approach, this work achieved unprecedented copper ion determination in river and tap water specimens via Ag-Pd/GCE.

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