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Development of Differential Pulse Anodic Stripping Voltammetry Technique for Cadmium(II) Detection and Its Application in Water Spinach

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Abstract

Cadmium is a toxic pollutant that is harmful to the environments and humans. The purpose of this research was to develop a method for cadmium(II) detection using differential pulse anodic stripping voltammetry (DPASV) using a glassy carbon electrode. The developed method was then applied for cadmium detection in the vegetable samples which is water spinach. The developed method was optimized in several parameters such as potential window, deposition potential, deposition time, and scan rate. The developed method for cadmium(II) detection was also investigated in its analytical performance includes linearity, precision, detection limit, and quantitation limits. The optimum conditions for cadmium(II) detection in 0.1 M KCl using the DPASV technique obtained such as potential window from -1200 to -100 mV, deposition potential of -1100 mV (vs Ag/AgCl), and deposition time of 360 s. It was obtained good linearity for cadmium(II) detection using DPASV technique with an R^2 of 0.996. The precision was expressed as %SBR with 0.66%. The detection and quantitation limit for cadmium(II) detection were 0.4206 µM~0.0771 ppm and 0.5525 µM~0.1013 ppm, respectively. The developed method was then applied for cadmium(II) measurement in the water spinach sample and the obtained cadmium(II) concentration in water spinach was 0.2399 mg/Kg.

Keywords: Cadmium(II), DPASV, glassy carbon electrode, analytical performance, water spinach

INTRODUCTION

Nowadays, food safety is becoming a serious public health problem across the world. Due to the increasing risk of food contamination by heavy metals, pesticides, or toxins, the concerns about food safety have lately drawn the attention of researchers (D'Mello, 2003). The contamination and accumulation of heavy metals in agricultural products is a serious issue to the human health and have been attributed to enzyme dysfunction, neurological disorders, hormone imbalances, nutritional deficiencies, damage brain chemistry, and even lead to cancer (Rahman, Adil, Yusof, Kamaruzzaman, & Ansary, 2014; Chowdhury, Mazumder, Al-Attas, & Husain, 2016). Several factors are affecting the heavy metals concentration in plants such as climate, environmental pollution, the composition of the soil on which the plant is grown, and the degree of plant maturity at the harvesting time (Scott, Keoghan, & Allan, 1996; Voutsa, Grimanis, & Samara, 1996). It is well known that fertilizers also contain heavy metals and making them as an additional source of metal contamination in vegetables(Mortvedt, 1995; Yusuf, Arowolo, & Bamgbose, 2003). Plants and leafy vegetables have a high potential to accumulate a higher concentration of heavy metals especially in their leaves part (Farooq, Anwar, & Rasyid, 2008). Among the heavy metals, cadmium is the most abundant metals and their excessive intake has been linked to cardiovascular, kidney, neurological, and bone disorders(Steenland & Boffetta, 2000; (Järup, 2003). The daily intake of cadmium(II) or Cd(II) allowed by the World Health Organization is 3 µg L^{-1} (World Health Organization, 2008). Therefore it is important to follow and monitor the amount of cadmium(II) ions in vegetable samples to ensure a healthy human life.

Various analytical methods have been developed for cadmium(II) detection such as colorimetry

(Laosuwan, Poonsawat, Burakham, Srijaranai, & Mukdasai, 2021), atomic absorption spectroscopy (AAS) (Teheni, Nafie, & Dali, 2016; Male et al., 2017; Bijang, Tanasale, Kelrey, Mansur, & Azis, 2021; Perelonia et al., 2021), inductively coupled plasma-mass spectroscopy (ICP-MS) (Li, Huang, Zeng, Lin, & Huang, 2021), X-ray fluorescence spectrometry (XRF) (Chebakova et al., 2021), inductively coupled plasma-optical emission spectrometry tandem with mass spectrometry (ICP-OES-MS) (Lundovskaya, Medvedev, Tsygankova, Volzhenin, & Saprykin, 2021), and Raman spectroscopy (Guo et al., 2021).

These techniques have been employed for cadmium(II) in complex matrices and offer versatility in terms of simultaneous determination of metal ion concentrations for a wide range of elements at the same time. In addition, these techniques have a very low detection limits up to femtomolar range (Pujol et al., 2014). However, the downside of these spectroscopic techniques are very expensive, requires trained individual to operate the sophisticated equipment, and involves the complex and analytical procedures for sample preparation (Bansod, Kumar, Thakur, Rana, & Singh, 2017). Therefore, there is a need to develop a simple, rapid, low cost, and reliable method that suitable for the real-time and in-situ measurements of cadmium(II) potentially could be used in field analysis. Anodic stripping voltammetry method as one of the electrochemical techniques provide simple operations, faster, and simpler analysis for in-situ monitoring such as cadmium analysis (Silva et al., 2021; Hou, Fan, Ma, Dong, & Yao, 2021; Lai et al., 2020).

In this method, metal ions in solution are accumulated into the surface of working electrode by applying the deposition potential and allow preconcentration step. After the metal deposited on the electrode surface then followed by stripping step to release and oxidize the deposited metal on the electrode surface back to solution as ions. This process can be monitored in a graph called a voltammogram as a function of the current from redox process (y-axis) versus potential applied into the electrode surface (x-axis).

In this study, the detection of cadmium(II) was performed via differential pulse anodic stripping voltammetry using a glassy carbon electrode as well as its parameters optimization. The optimized parameters obtained from the developed method was then used to detect cadmium(II) in vegetable samples in particular water spinach.

METHODOLOGY

Materials and Instrumentals

The materials used include KCl, HNO_3 65%, HCl 37%, $CdCl_2$ were purchased from Merck and used as received without further purification. Aquabidest and water spinach sample were obtained from the local store. The instrumental used are Voltammetric measurements were carried out using EDAQ potensiostat. A single compartment cell with a three-electrode configuration was used for electrochemical measurements. A silver/silver chloride electrode (SCE) (from IJ Cambria Scientific Ltd) and a Pt wire electrode were used as the reference and counter electrodes, respectively. The working electrode was a 3.0 mm-diameter glassy carbon disk electrode obtained from IJ Cambria Scientific Ltd. All measurements were performed at a temperature of 25 ± 2 ^oC. Cadmium(II) analysis was also performed using Atomic Absorption Spectrophotometer (AAS) Shimadzu AA-7000. All voltammetric data were processed using EChem v 2.1.0, and Origin Pro 7.0.

Experimental

In general, the methodology was divided into 3 major steps, determination of optimum condition for Cd(II) measurements, evaluation of analytical performance for Cd(II) measurement, and determination of Cd(II) in real sample.

Determination of optimum condition for Cd(II) detection using DPASV technique

The optimum condition for Cd(II) measurement using DPASV technique was performed in 0.1 M KCl. Several parameters were optimized during Cd(II) measurement using DPASV technique such as potential range, deposition potential and deposition time. The potential range was varied from -1200 to -500 mV vs (Ag/AgCl). Meanwhile the deposition potential was optimized in the range of -1000 mV to -1500 mV vs (Ag/AgCl). The time deposition was varied in the range of 60 s to 420 s.

Evaluation of GCE Performance in Cadmium(II) Measurement

The evaluation of GCE performance in Cd(II) measurement include linearity, precision, limit of detection, and limit of quantitation obtained at the optimum condition.

Linearity was determined by preparing the series of Cd(II) stock solution at concentration of 1 – 9 µM and measured with DPASV technique at optimum condition. The regression linear was then obtained by relating positive relationship between Cd(II) concentration (x-axis) vs current response (y-axis). Meanwhile, precision was determined by preparing Cd(II) in the concentration of 0.5 to 0.9 µM and measured in 6 times replicates. Precision is defined in the relative of standard deviation (%RSD) based on the value of current of Cd(II) response. Meanwhile, the limit of detection (LOD) and limit of quantitation (LOQ) were determined based on the value signal/noise (S/N) 3 and 10 at significance level of 99%, respectively.

Measurement of Cd(II) in the water spinach sample

Detection of Cd(II) in vegetable sample was initially with ashing process of water spinach sample. Then Cd(II) was determined from ash sample of water spinach using AAS and compared with DPASV technique using GCE as a working electrode. The ashing process of water spinach sample refers to the SNI 2354.5:2011.

Determination of Cd(II) in the ash from water spinach sample using AAS and DPASV technique

The obtained ash from water spinach sample was added with 10 mL HCl 6 M for the AAS measurement. The AAS parameters for Cd(II) measurement were wavelength as 228.8 nm with flame type of air-acetylene, slit of 0.7 nm, cathode lamp of 5 mA, and gas carrier as acetylene. Meanwhile, for Cd(II) measurement using DPASV technique, the ash from water spinach sample was diluted in 10 mL KCl 0.1 M and filtered into 25 mL volumetric flask. Then, the solution was diluted with aquabidest.

Data Analysis.

Voltammetric data was obtained using ECHEM software and displayed in voltammogram plot with potential (x-axis) vs current (y-axis). Then, the obtained data was further processed using Origin 7.0 dan Microsoft Excel software.

RESULTS AND DISCUSSION

Effect of the Deposition Potential

In order to develop a sensitive method for Cd(II) determination at a GCE, various experimental conditions were optimized. Firstly, the deposition potential of Cd(II) was varied from -1000 mV to -1500 mV vs (Ag/AgCl). The result (Figure 1) shows that the stripping peak currents of Cd(II) increase when deposition potential was increased from -1000 mV to -1100 mV vs (Ag/AgCl), but the peak currents decrease with further increasing from -1200 mV to -1500 mV vs (Ag/AgCl). This trend could be assigned to the hydrogen evolution phenomena was beginning significant in the medium at the negative potential (Sukeri, Jayaraman, & Phani, 2013; Huang, Chen, Liu, & Ma, 2014).

In addition, the Cd deposition on the GCE surface might be damaged by the hydrogen bubble and resulted to lowered in the current response of Cd(II) at the more negative potential (Bagheri, Afkhami, Khoshsafar, Rezaei, & Shirzadmehr, 2013). From the Figure 1, it is also clear that the highest sensitivity for Cd(II) measurement observed at the potential range of -1000 mV to -500 mV vs while Guo et al., 2021 reported the oxidation potential of Cd(II) at more negative potential in the range of -1000 mV to -700 mV. Therefore, in order to obtain the high sensitivity for Cd(II) measurement, the deposition potential of -1100 mV was chosen for the further work.

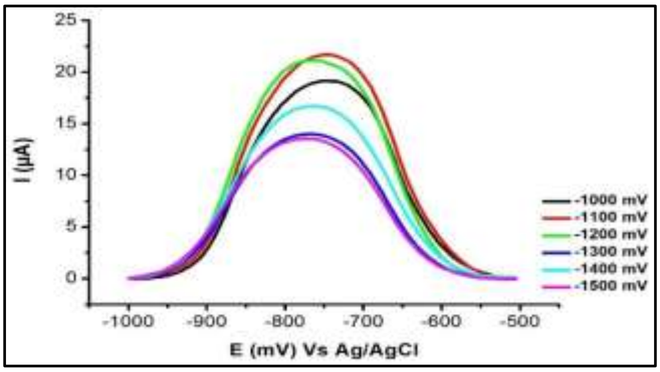

Figure 1. Voltammogram of 1 mM Cd(II) in 0.1 M KCl at various deposition potential from -1000 mV to -1500 mV vs (Ag/AgCl) and deposition time of 180 s with scan rate of 10 mV s^{-1}.

Effect of Deposition Time

The effect of deposition time on the stripping response of Cd(II) was studied from 60 s to 420 s. From Figure 2, it has been found that the anodic current of Cd(II) peak increase with the increase of deposition time from 60 s to 360 s. This is due to the fact that as the deposition time longer caused more Cd(II) get accumulated at the interface of GCE/solution and thus current increases. After 360 s, the anodic current of Cd(II) becomes decreased, it is due to the saturation of electrode surface with the deposited cadmium which may be lead to the cadmium removal from electrode surface. Therefore, a deposition time of 360 s has been used in all further studies.

In order to fully optimize of time deposition, it was prepared the series of Cd(II) stock solution in the concentration range of 1 x 10^{-5} M to 9 x 10^{-5} M and measured in optimum parameters with two different time accumulation, as shown in Figure 3. It is meant to investigate the sensitivity for Cd(II) detection in the different time deposition.

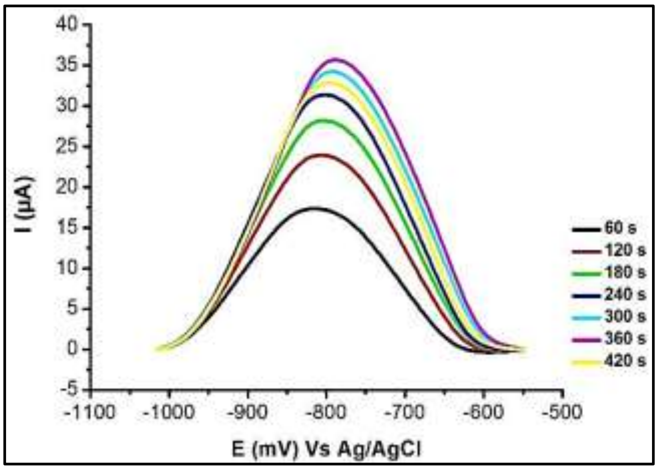

Figure 2. Voltammogram of 1 mM Cd(II) in 0.1 M KCl at various deposition time from 60 s to 240 s with scan rate of 10 mV s^{-1}.

Both deposition time (60 s and 360 s) giving a linear relationship in respect to the Cd(II) concentration (x-axis) vs peak current (y-axis), but with 360 s provides higher coefficient of determination and sensitivity (inset of Figure 3B). Thus, it can be concluded that the optimum time for the saturation of Cd(II) concentration at the electrode surface as 360 s and used for all further studies.

Effect of Scan Rate

The scan-rate effect on the voltammogram of 1 mM Cd(II) in 0.1 M KCl was investigated at various scan rate with deposition potential of -1100 mV (vs Ag/AgCl) and deposition time of 360 s. When the scan rate was increased from 10 to 100 mV s^{-1}, the anodic current of Cd(II) increased. Higher scan rate (above 100 mV s^{-1}) causes losses in peak definition and thus lowering the sensitivity for Cd(II) measurement using DPASV technique. Therefore, the scan rate of 100 mV s^{-1} was chosen for further analysis because it presented the highest sensitivity for Cd(II) analysis and a relatively faster analysis.

Analytical Performance of Cd(II) Measurements using DPASV Technique

Linearity

The selected optimum parameters for Cd(II) measurement using DPASV technique have been applied to construct a calibration curve as shown in the inset of Figure 4. The calibration graph is: y = 0.51x + 0.426 (y = peak current (I_p) in μA, x = Cd(II) concentration in M, R^2 = 0.996). From the Figure 4, a linear response from Cd(II) measurement in the concentration range of 1 to 9 x 10^{-5} M was obtained.

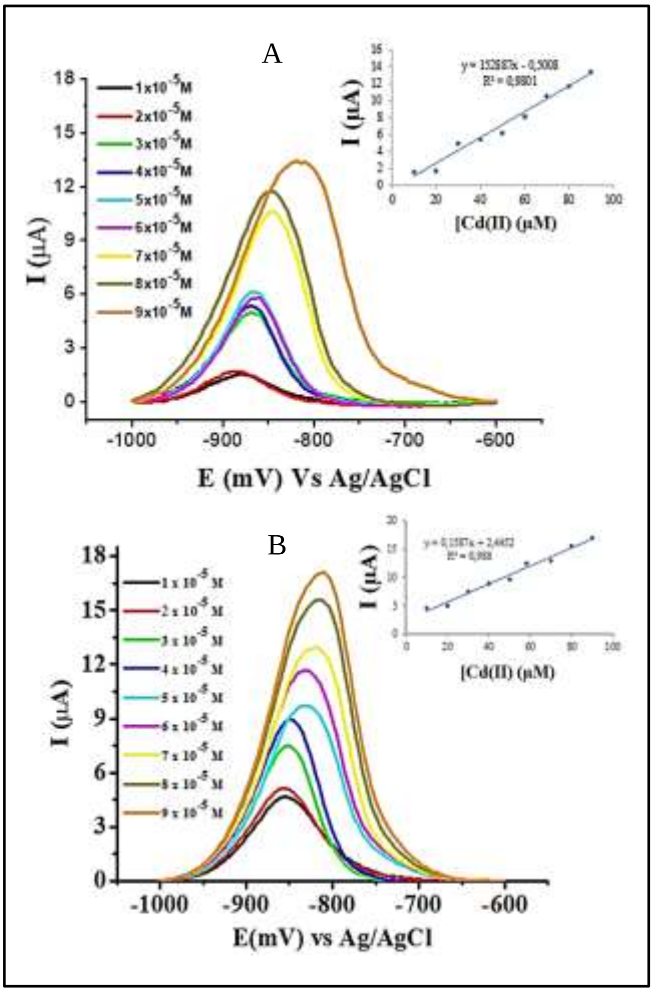

Figure 3. Voltammogram of Cd(II) at concentration range of 1 – 9 x 10^{-5} M in 0.1 M KCl measured at deposition potential of -1100 mV (vs Ag/AgCl) and scan rate of 10 mV s^{-1} with different deposition time of (A) 60 s and (B) 360 s.

This result shows the sensitive measurement of Cd(II) using GCE with DPASV technique and possibly could be used for quantitative analysis. In addition, the employment of differential pulse anodic stripping voltammetry (DPASV) for Cd(II) measurements provides a higher sensitivity and low background in current via charging current than cyclic voltammetry (Lai et al., 2020). Thus, it can be used in the determination of Cd(II) at GCE surface and estimating a lower limit of detection and limit of quantification.

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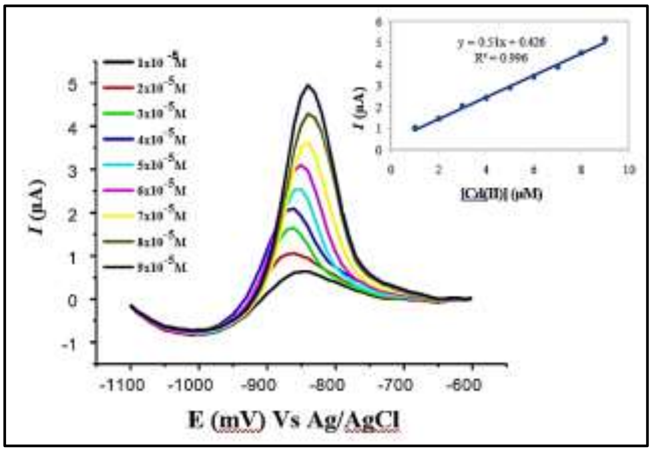

Figure 4. Voltammogram of Cd(II) at concentration range of 1 – 9 x 10^{-5} M in 0.1 M KCl measured at deposition potential of -1100 mV (vs Ag/AgCl) and scan rate of 100 mV s^{-1} with deposition time 360 s. Inset: calibration curve: y = 0.51x + 0.426, $R^2 = 0.996$.

Limit of Detection, Limit of Quantitation, and Precision

The limit of detection (LOD) and limit of quantification (LOQ) value obtained from Cd(II) measurement displayed of 0.4206 µM and 0.5525 µM, respectively. The analytical performance of this method provides comparable in terms of deposition time although other methods displayed higher sensitivity and lowered linear range (Table 1). Beside LOD and LOQ, the precision value has been determined by measuring 0.5 µM Cd(II) in 6 replicates and can be reported as the value of percentage of relative standard deviation (%RSD). Based on the calculated results, %RSD value for Cd(II) measurements using DPASV technique was reported as 0.66% and can be considered as good precision due its value lower than 5% (Perelonia et al., 2021). From these values, it is clear that this developed method has a good analytical performance and can be potentially used for Cd(II) measurement in the real sample such as in water spinach.

Cadmium Content in Water Spinach

In order to illustrate the application of the developed method in real sample analysis, it was employed to detect Cd(II) in water spinach sample. For the real sample analysis, water spinach was bought from a local market. Water spinach sample was dried, dry ashed, and determined its water content and ash content. From the experiment refers to the AOAC standard, it was obtained high water content in water spinach as 89.11 ± 0.32%. Most of water contents in the water spinach sample are physically bound to the material networks such as membrane, capillary, and fiber. These water contents are easily evaporated during drying and ashing process. Meanwhile, the ash content in water spinach sample was obtained as 2.07 ± 0.06%. This value reflects the total amount of minerals in the water spinach sample and sometimes used to retard the growth of certain microorganisms.

Table 2. A comparison of Cd(II) content measured with DPASV and AAS technique

Method	Concentration (mg/kg)	Maximum concentration (BSN 2009, mg/kg)
DPASV	0.2399	0.25
AAS	0.0814	0.25

Determination of Cd(II) in the water spinach sample was performed using standard addition method and investigated by DPASV technique. Results of Cd(II) detection from DPASV was then compared with the results from AAS technique. Table 2 shows the Cd(II) measurements obtained using DPASV and AAS technique. As seen in the table, the concentration detected for cadmium is higher to the value obtained by AAS. This might be due to the non-homogeneity of the assay when measurements were taken. Although, there is a disagreement in result between both methods, however DPASV could be used as an alternative for cadmium detection in vegetables sample.

Other work reported by Palisoc, Estioko, & Natividad, 2018 revealed that the cadmium concentration in several vegetables obtained from AAS and anodic stripping voltammetry were comparable. By comparing these obtained values with the acceptable international standard for cadmium (SNI, 2011 and Codex General Stan Tox,1997) for leafy vegetables as 0.25 mg/kg), it is obvious that the water spinach sample is considered to be contaminated by Cd(II) and not safe for human consumption. It is probable that any metals that could have been detected in the vegetable samples from the accumulation process through the soil and nearby waters (Palisoc et al., 2018). The concentration of cadmium(II) is not only coming from soil and water but might be due to the transportation, handling, and storage of water spinach samples.

CONCLUSION

A simple and cost effective for quick assessment of Cd(II) was developed using DPASV technique at a glassy carbon electrode. The developed method was successfully applied on vegetable samples in particular water spinach, which the cadmium concentration was 0.24 mg/Kg. The results of this study indicated that level of Cd(II) in analyzed water spinach samples were found within maximum acceptable levels which could be dangerous for human consumption. Therefore, attention to the quality of vegetable samples for human needs with regard to level of toxic metals is very necessary.

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