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Determination of trace levels of Cd(II) in tap water samples by anodic stripping voltammetry with an electrografted boron-doped diamond electrode

Chalermpol Innuphat[a,*], **Pipat Chooto**[a]

[a] Department of Chemistry, Analytical Chemistry Division, Faculty of Science, Prince of Songkla University, Hatyai, Songkhla 90112 Thailand

*Corresponding author, e-mail: chalermpoli@hotmail.com

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ABSTRACT: A boron-doped diamond electrode modified by 0.5 mM 4-aminomethyl benzoic acid was used for electrochemical determination of Cd^{2+} in tap water samples by anodic stripping voltammetry. This method is based on the electrochemical reduction of 4-aminomethyl benzoic acid on the electrode followed by the determination of Cd^{2+} with a single well-defined reduction peak at −0.72 V versus Ag/AgCl in acetate buffer solutions at pH 6.0. Optimal conditions were established with respect to electrode pretreatment, time accumulation, potential accumulation, scan rate, and pH. Accurate ($r^2 = 0.9989$, $n = 6$) calibration curves were obtained for Cd^{2+} concentrations ranging between 2 ppb and 50 ppb. Other dissolved metals (Ca, Mg, Zn, Mn, Fe, Cu, Al, Co, Pb, and Ni) have no interference on the Cd^{2+} calibration curves. The achieved detection limit was 0.2 ppb. High accuracy and reproducibility of the results as well as excellent stability of the electrode material proves superb capabilities of this Cd^{2+} detection system. Recovery in the range of 97–102% further confirmed the usefulness of the proposed method to analyse Cd^{2+} in tap water samples. The results with SRM1640 were in good agreement with those by inductively coupled plasma optical emission spectrometry.

KEYWORDS: voltammetric analysis, ASV, Cd^{2+}

INTRODUCTION

The contamination of utility water with heavy metals such as Cd^{2+} is one of the most hazardous environmental and health problems. Those metals are highly toxic to certain organs of both humans and animals, including nervous, immune, reproductive, and gastrointestinal systems[1]. Ingestion of any significant amount of Cd^{2+} causes immediate poisoning as well as damage to the liver and the kidneys because of their tendency to accumulate in the body, toxicity, and low clearance rate. The biological half-life of Cd^{2+} is 10–30 years[2] and compounds containing Cd^{2+} are also carcinogenic[3]. Building up of Cd^{2+} levels in the water, air, and soil has been increasing, particularly in industrial areas. Workers can be exposed to Cd^{2+} in air from the smelting and refining of metals, or from the air in industrial plants that make Cd^{2+} products such as batteries, coatings, or plastics. Even cigarettes are a significant source of Cd^{2+} exposure. Although there is generally less Cd^{2+} in tobacco than in food, the lungs absorb Cd^{2+} more efficiently than the stomach[4]. Some sources of phosphate in fertilizers contain Cd^{2+} up to the amounts of 100 mg/kg[5,6], which can lead to an increase in the concentration of Cd^{2+} in soil as found in New Zealand[7]. In addition, Nickel-cadmium batteries are one of the most popular and most common cadmium-based products. Environmental exposure to Cd^{2+} has been particularly problematic in Japan where many people have consumed rice that was grown in Cd^{2+} contaminated irrigation water. This phenomenon is known under the name itai-itai disease[8]. The determination of trace level Cd^{2+} in water samples therefore plays an important role in the environmental pollution monitoring due to the cumulative toxicity of Cd^{2+}.

Sensitive methods to determine trace amount of Cd^{2+} have received much attention and many techniques have been developed. Typical methods of metal ion analysis include inductively coupled plasma-mass spectrometry[9], X-ray fluorescence spectrometry (XRF)[10], and atomic absorption spectrometry (AAS)[11]. However, these techniques use expensive and sophisticated instruments and are time consuming, which severely restricts their practical applications[1]. Anodic stripping voltammetry is a well established method for trace analysis of heavy metals. The equipment for ASV measurement is inexpensive because of its small size and does not demand a high power supply. This makes field deployment possible and constitutes a big advantage over AAS or ICP. Generally, the detection limit of ASV is not as low as the detection limit of the spectrometric measurements, but still adequate for most of the tasks mentioned above[12]. One of the extensively used electrode materials for ASV is mercury. Nowadays, however, mercury electrodes are considered undesirable due to the toxicity of both metallic mercury and mercury salts employed for its preparation. Alternative environmentally friendly electrode materials are therefore required[13]. Several new types of mercury-free electrodes have recently been developed for sensitive metal determinations, including bismuth film electrodes[13,14], gold-coated electrodes[15,16], silver electrodes[17,18], glassy carbon electrodes[19], carbon paste electrodes[20–22], carbon nanotube electrodes[23], or screen-printed carbon electrodes[24].

Boron-doped diamond (BDD) electrodes can be applied in a variety of areas due to their superior properties, including extreme robustness with a low level of background interference, less adsorption of polar molecules, and wide potential window in aqueous media[2,25]. It has been used to quantify manganese in tea[26] as well as lead in tap water[27] and river sediment. Anodic stripping voltammetry BDD has been proved to possess outstanding features[28] to determine silver[29] and simultaneous detection of lead and copper[30].

This paper reports the detection of Cd^{2+} by ASV on BDD electrode based on simple and selective electrochemical reduction of Cd^{2+} on diazonium-modified electrode with interference study. The method was verified by analysing standard material and was then applied to the analysis of Cd in Hatyai tap water. The modification of carbon through the electrochemical or chemical reduction of aromatic diazonium derivatives has been extensively used for modification of various carbon materials, such as glassy carbon[31], graphite[32], graphene[33], and carbon nanotube[34]. It is well-recognized as a very versatile and simple way to graft a wide variety of functional groups onto carbon surfaces for various applications. Furthermore, the diazonium-modified electrode has been found to be stable to long-term storage in air and organic solvents. The high stability of the diazonium-modified electrode and the versatility of the diazonium modification method are particularly attractive for stripping analysis. Due to these characteristics, the method can therefore be applied well to Cd^{2+} analysis.

MATERIALS AND METHODS

Reagents and solutions

All reagents were used as received without any further treatment. Cd^{2+} standards were prepared in-house from Cd^{2+} nitrate Atomic Spectroscopy Standard Solution. KNO_3 as a supporting electrolyte was supplied by Ajax Finechem. All other reagents and the metal salts used for the interference experiments (all nitrates except $MnCl_2 \cdot 4\,H_2O$ and $MgCl_2 \cdot 6\,H_2O$) were of analytical-reagent grade with the highest purity commercially available. All subsequent solutions were prepared by using deionized water of resistivity not less than 18 MΩ cm (ELGA water purification system, England). Nitrogen gas (99.99%) was used to deaerate the testing solutions for 2 min. Laboratory glassware was kept overnight in 10% (v/v) HNO_3 solution and rinsed with deionized water before use. Standard solutions of Cd^{2+} were prepared by diluting the respective stock solutions with high purity deionized water and stored in polyethylene bottles before use.

The reference sample analysed was NIST (National Institute of Standards and Technology) SRM 1640 trace elements in natural water. NIST SRM 1640 is composed of natural fresh water from Clear Creek, Colorado, USA. The sample was filtered and stabilized with HNO_3 to a concentration of 0.5 M. The certified value of Cd^{2+} was 22.82 ± 0.96 ppb.

Sampling and digestion

Tap water samples were collected between August and September 2015 in different regions within the city of Hatyai, Songkhla, Thailand. An aliquot of 500 ml of tap water sample was digested by mixing with 2 ml of concentrated HNO_3 and 2 ml of KNO_3 and then placed in cleaned polyethylene bottles.

Instrumentation

Cyclic voltammetry (CV) and square wave anodic stripping voltammetry (SWASV) were performed with a Powerlab 2/20 with Potentiostat (ADInstrument, Australia) controlled by ECHEM. The three-electrode system consisted of an Ag/AgCl/3 M KCl reference electrode, a platinum counter electrode, and a BDD electrode with inner diameter of 3 mm (Windsor Scientific Ltd., UK) was used as a working electrode. All electrochemical measurements were carried out in a 50 ml cell and the pH of solutions were measured by pH meter Model 510 (Eutech instruments, USA).

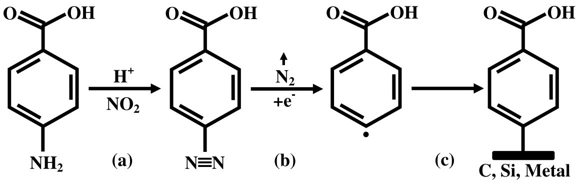

Fig. 1 Grafting process through the electrochemical reduction of diazonium salts. (a) Spontaneous diazotization, (b) electrochemical reduction, and (c) grafting on the electrode surface.

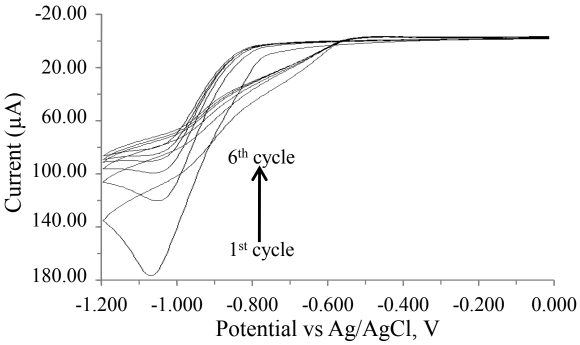

Fig. 2 Electrografting of BDD electrodes with 0.5 mM 4-aminomethyl benzoic acid in methanol with 10 mM $TBAPF_6$ as an electrolyte with the 1st, 2nd, 3rd, 4th, 5th, and 6th potential CV cycles for scan rate 100 mV/s.

Preparation of modified electrode

The modification of thin films by electrofunctionalization was electrochemically performed by the reductive electrolysis of diazonium salts on the electrode surface. Diazonium salts were directly generated in the electrochemical cell by the spontaneous diazotization method using an aromatic amine presenting an adequate substituent in the para-position relative to the amino group ($-NH_2$). The in situ transformation of the amine into a diazonium salt ($-N_2^+$) was carried out with an aqueous nitrite solution (10 mM tetrabutylammonium hexafluorophosphate, $TBAPF_6$) in acidic medium (HCl, pH = 2). Fig. 1 shows the electrochemical reduction of diazonium salts to immobilize organic layers on the electrodes surface. The electrochemical grafting was carried out under stirring (400 rpm) in a cyclic voltammetry mode (5 cycles) between 0.2 and −1.2 V versus Ag/AgCl at 100 mV/s. The aqueous electrolyte was composed of 10 mM $TBAPF_6$, 0.5 M HCl and 0.5 mM 4-aminomethyl benzoic acid.

Cd^{2+} determination procedure

Stripping voltammetric measurements were performed with a BDD electrode and the target metal Cd^{2+} in the presence of dissolved oxygen. Prior to its use, the BDD electrode was polished with a 0.05 µm alumina slurry. The three electrodes were immersed into a 50 ml electrochemical cell containing pH 6.0 acetate buffer solutions. A deposition potential of −1.10 V for measurements of Cd^{2+} was applied to the BDD electrode in the stirred solution. Following a preconcentration step of 120 s, the stirring was stopped; and after 30 s, the voltammogram was recorded by sweeping the potential from −1.0 to −0.3 V (with scan rate 10 mV/s, a frequency of 10 Hz, amplitude of 4 mV, and potential step of 25 mV). Aliquots of the Cd^{2+} standard solution were introduced after recording the background voltammograms. The peak currents were measured at −0.72 V. A 30 s conditioning step at +0.3 V (with stirred solution) was applied to fully oxidize all metal deposits prior to the next measurement. All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Electrografting BDD electrode with 4-aminomethyl benzoic acid

The reduction of diazonium salts was carried out in a narrow potential range between 0.2 and −1.2 V (Fig. 2). The broad reduction peak present in the first cycle (at −1.08 V) is presumably attributed to the reduction of the corresponding diazonium species to form an aryl radical which reacts with the electrode surface. It can therefore be assumed that the same phenomenon occurred in the current study, namely, is the covering of BDD electrodes by the corresponding aryl layers.

Evolution of the wettability

To characterize the wettability of the electrolyte on the BDD modified electrode, the droplets of distilled water after grafting with 4-aminomethyl benzoic acid were found to induce an increase in the contact angle from 22° to 68° (figure not shown), indicating that the hydrophobicity is greater with the presence of the aromatic ring.

Cyclic voltammogram of Cd^{2+}

The overlay of CV voltammograms for 30.0 mg/l Cd^{2+} in the absence (curve a) and presence (curve b) of electrografted BDD electrode is shown in Fig. 3. The deposition peak was observed at −0.92 V versus Ag/AgCl corresponding to preconcentration of Cd^{2+} onto a BDD electrode surface at negative

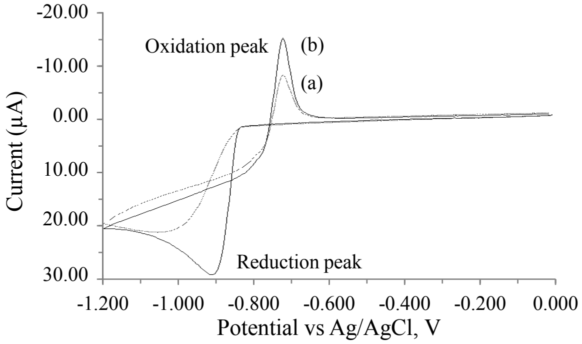

Fig. 3 Cyclic voltammogram of 30.0 mg/l Cd^{2+} at (a, dashed line) bare BDD electrode and (b, solid line) the modified electrode in pH 6.0 acetate buffer solutions with scan rate of 100 mV/s.

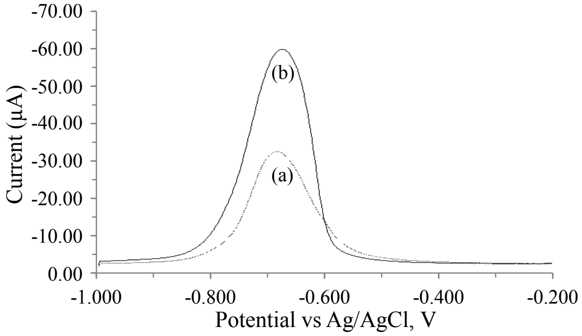

Fig. 4 SWASV of Cd^{2+} at (a, dashed line) bare BDD electrode and (b, solid line) the modified electrode. Experimental conditions: deposition/measurement solution, pH 6.0 acetate buffer solutions containing 30.0 mg/l Cd^{2+}; deposition time, 120 s, potential 1.0 V, frequency 10 Hz, amplitude of 4 mV, and potential step of 25 mV.

potentials. On the reverse scan, the single well defined stripping peak appeared at potential around −0.72 V versus Ag/AgCl with electrografted BDD electrode surface.

The electrochemical response of Cd^{2+} stripping on bare and benzoic acid-modified BDD electrode

Fig. 4 shows square wave anodic stripping voltammograms (SWASV) of Cd^{2+} at bare and benzoic acid-modified BDD electrode, both reflecting well-defined peak at 0.72 V. The anodic peak current of Cd^{2+} at the benzoic acid-modified BDD electrode (58.5 μA) was about twice of that at the bare BDD electrode (32.0 μA). The increases in anodic peak current are attributed to the electrostatic interaction between the negatively charged electrografted BDD electrode and the positively charged metal ions that facilitates the preconcentration of Cd^{2+} which are beneficial for Cd^{2+} determination.

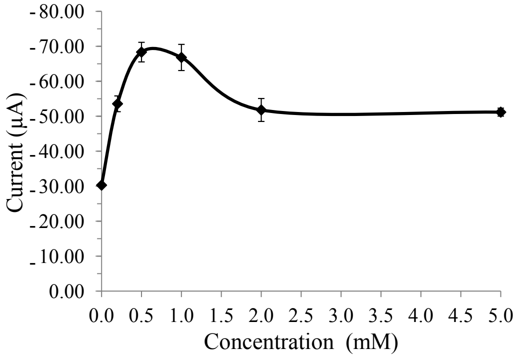

Fig. 5 Peak currents from BDD electrode at concentration of 30.0 mg/l Cd^{2+} with various concentrations of 4-aminomethyl benzoic acid 0.0, 0.2, 0.5, 1.0, 2.0, and 5.0 mM in acetate buffer solutions pH 6.0 with scan rate of 100 mV/s.

Effect of concentration of 4-aminomethyl benzoic acid

The dependence of the peak Cd^{2+} currents on the concentration of 4-aminomethyl benzoic acid is depicted in Fig. 5. It is apparent that 4-aminomethyl benzoic acid film can increase peaks height of Cd^{2+} oxidation, a sharp increase in the response signal can be observed with increasing concentration of 4-aminomethyl benzoic acid from 0.0–0.5 mM followed by a decrease from 1.0–5.0 mM. When the concentration of 4-aminomethyl benzoic acid was very high, the formation of a thick layer probably partially blocked the conductive surface of the electrode, resulting in a decrease of electrodeposition sites. The optimum concentration with the highest current was 0.5 mM, which was selected for further experiments.

Electrolyte and pH dependence for film formation

Since the electrografting on electrode surfaces depends mainly on acidity, pH can be one of the effective parameters strongly influencing the peak current. The pH range of 1.0–8.0 (data not shown) was investigated using cyclic voltammetry in 10 mM $TBAPF_6$ as an electrolyte. With the increase of pH from 1.0–2.0, the peak current continuously increases due to greater extent of complex formation of Cd^{2+} with 4-aminomethyl benzoic acid at the electrode surface. However, with pH values higher

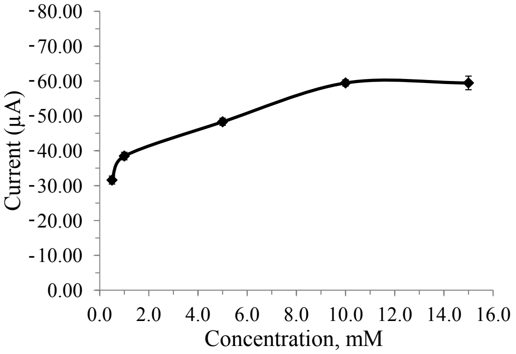

Fig. 6 Peak currents from BDD electrode at concentration of 30.0 mg/l Cd^{2+} in various concentrations of $TBAPF_6$ 0.5, 0.1, 5.0, 10.0, and 15.0 mM (pH 2, as an electrolyte for film formation) in acetate buffer solutions pH 6.0 with scan rate of 100 mV/s.

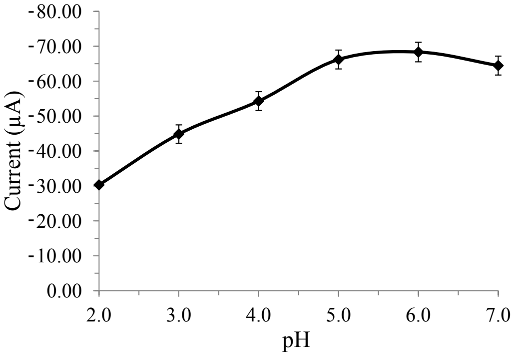

Fig. 7 Peak currents of 30 mg/l Cd^{2+} in acetate buffer at different pH values.

than 2.0 the peak current decreased drastically possibly due to the formation of insoluble metal hydroxide complex, $Cd(OH)_2$. Thus pH 2.0 was selected as an optimum condition in order to obtain maximum sensitivity in quantitative analytical measurements. The effects of electrolytes concentration at 0.5, 1.0, 5.0, 10.0, and 15.0 nM $TBAPF_6$ on the peak currents of Cd^{2+} were also carefully investigated. It was found that Cd^{2+} had the best electrochemical responses in 10 mM $TBAPF_6$ (Fig. 6), which was chosen as a supporting electrolyte for voltammetric determination of the Cd^{2+} for further experiments.

Effect of pH on Cd^{2+} determination

The effect of pH 1.0–7.0 on the peak current of Cd^{2+} in SWASV is shown in Fig. 7. The results indicate a rapid enhancement of the peak current of Cd^{2+} with ascending of pH to a maximum approximately at pH 6.0 and then a progressive decrease. This might result from the higher pH value, at which the metal ion easily hydrolyses[35]. At lower pH value, hydrogen ion are reduced more easily[36], which in turn interfere with Cd^{2+} deposition. pH 6.0 was therefore chosen for further studies.

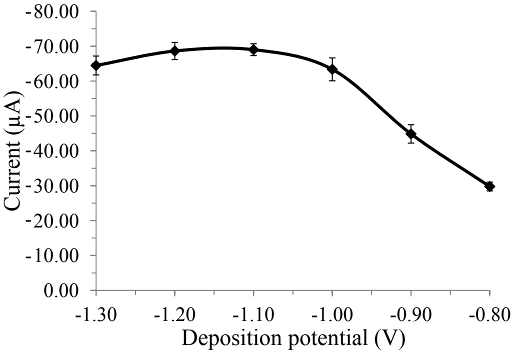

Fig. 8 Effect of deposition potentials on the SWASV peak currents. Conditions: 30.0 mg/l Cd^{2+} in 50 ml acetate buffer pH 6.0.

Deposition potential

The effect of deposition potentials on the stripping peak currents of 30.0 mg/l Cd^{2+} was studied in the potential range from −0.80 to −1.30 V (Fig. 8). The negative shifts of deposition potential can clearly improve the extent of Cd^{2+} reduction on the surface electrode and increase the peak current. The peak current however does not change significantly with the deposition potentials to values more negative than −1.10 V. Moreover, the background current increased when the potentials were more positive than −1.10 V. The results reflect an optimum deposition potential of −1.10 V at which further experiments were then performed to achieve high sensitivity and better response.

Deposition time

For the effect of the deposition time screened within a range of 1–8 min on the stripping currents of 20.0 µg/l Cd^{2+}, longer deposition times should increase the peak current because more Cd^{2+} could be deposited (Fig. 9). When the deposition time increases, the stripping peak currents increase greatly and are almost constant beyond 6 min which reflects surface saturation. Thus 6 min was chosen for all subsequent analysis.

Scan rate

The scan rate was screened from 10–200 mV/s. As shown in Fig. 10, the peak height was small at lower

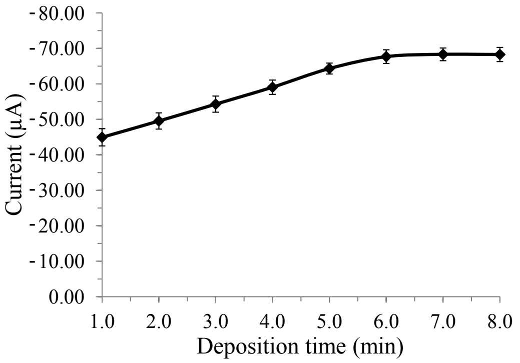

Fig. 9 Effect of deposition time on the SWASV peak currents. Conditions: 30.0 mg/l Cd^{2+} in 50 ml acetate buffer pH 6.0.

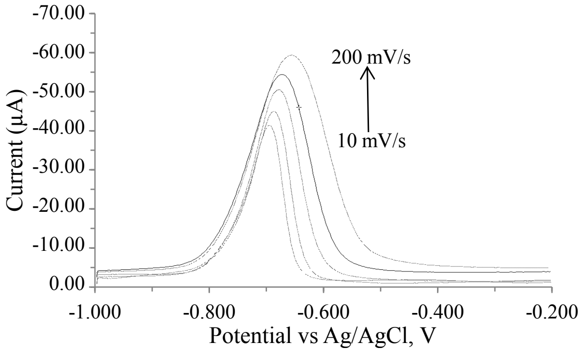

Fig. 10 Effect of scan rates 10, 20, 50, 100, and 200 mV/s on the stripping voltammograms. Conditions: 30.0 mg/l Cd^{2+} in 50 ml acetate buffer pH 6.0, 0.5 mM 4-aminomethyl benzoic acid; deposition potential, −1.1 V versus Ag/AgCl; deposition time, 6 min; pulse amplitude, 4 mV.

scan rate and increased rapidly at higher scan rate with the best result of better current and greater stability of peak potential at a scan rate of 100 mV/s. At more than 200 mV/s, the signal peak becomes broader and shifts to much more positive stripping potentials. A scan rate of 100 mV/s was therefore selected for further experiments.

Limits of detection and quantitation

Fig. 11a shows square wave voltammetry measurements of water with different concentrations of Cd^{2+} with the optimum conditions to obtain the calibration curve and detection limit. The calibration curve shows linearity within the range of 2–50 ppb with a correlation coefficient of 0.9989 with the linear regression equation of Cd^{2+} of $i_p = 4.458x - 11.73$ (i_p: μA, x: μg/l).

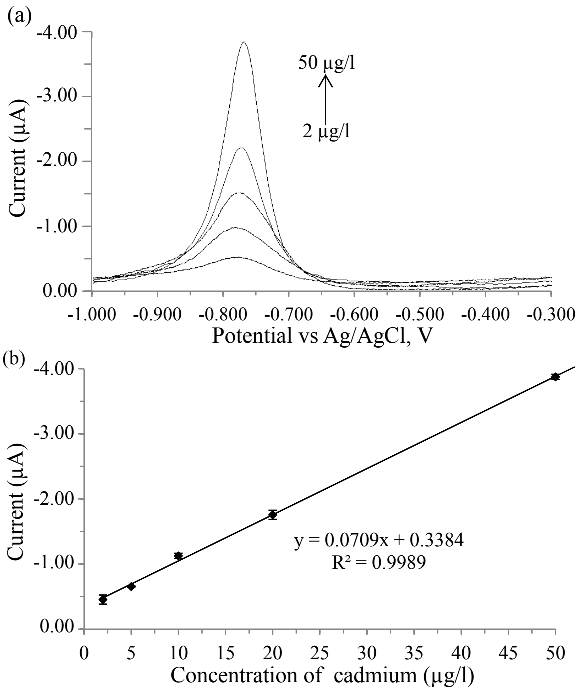

Fig. 11 SWAS voltammograms of water sample. After spiking with 2.0, 5.0, 10.0, 20.0, and 50.0 μg/l of Cd^{2+} standard solution. Conditions; accumulation potential, −1.10 V; accumulation time, 6 min; acetate buffer pH 6.0, 0.5 mM 4-aminomethyl benzoic acid; scan rate, 100 mV/s.

The limit of detection of Cd^{2+} was calculated by $\text{LOD} = 3N/m$[36], where N is the standard deviation of replicate blank responses ($n = 9$) and m is the slope of the calibration curve to obtain its value of 0.2 μg/l. The limits of quantification defined as $10N/m$, were found to be 0.6 μg/l. The relative standard deviation was 3% ($n = 10$) for repetitive determinations of 20.0 μg/l of Cd^{2+}. The results demonstrate that the proposed technique was reproducible and reliable for the detection of Cd^{2+} at trace level and can be used for real samples analysis.

Certified reference materials and real sample analysis

The accuracy of the proposed method was tested by determining the Cd^{2+} content of certified reference materials, natural water SRM 1640 from NIST. Stripping peaks for Cd^{2+} in the NIST sample occur at potentials of −0.72 V versus AgCl. The certified value (22.82 ± 0.96 μg/l) and the analytical results (22.72 ± 0.90 μg/l, $n = 5$) gave a satisfactory recovery of 99.02% ($n = 5$), proving that the proposed method is suitable for analysing tap water sample.

Table 1 Determination of Cd^{2+} in tap water samples ($n = 4$) spiked with 5, 10, and 20 µg/l of Cd^{2+}.

Sample	Spiked (µg/l)	Present method (µg/l)[b]	Recovery (%)	ICP-OES method (µg/l)	Difference (%)
Tap water 1[a]	0	ND[c]	–	ND	–
	5	5.56 ± 0.35	–	5.25 ± 0.65	6.2
	10	10.65 ± 0.52	101.8	10.35 ± 0.45	3.0
	20	20.35 ± 0.24	97.0	20.78 ± 0.32	2.2
Tap water 2[a]	0	ND	–	ND	–
	5	5.28 ± 0.25	–	5.58 ± 0.48	6.0
	10	10.35 ± 0.58	101.4	10.14 ± 0.65	2.1
	20	20.20 ± 0.68	98.5	20.25 ± 0.56	0.2

[a] Water sample 1st and 2nd region was selected for standard addition test

[b] Mean ± Standard deviation ($n = 4$)

[c] Not detected

Table 2 Comparison of the proposed method to determine Cd^{2+} in water sample with other anodic stripping voltammetric methods.

Modified electrode	Method	Deposition time (s)	Linear range (µg/l)	Detection limit (µg/l)	Reference
(Bi/MCNTs-CPE)	SWASV	7200	1–60	0.3	Ref. 37
Sb nano/BDD	LSASV	120	50–500	38.10	Ref. 38
Bi/CNT/GCE	SWASV	300	2–100	0.70	Ref. 39
0.2 M 4-aminomethyl benzoic acid/BDD	SWASV	360	2–50	0.2	This work

The proposed technique was applied to the analysis of Cd^{2+} in tap water sample collected from 11 sites in Hatyai city, 500 ml for each. The standard addition method was performed by spiking a tap water sample with different concentrations of Cd^{2+} with the results in Table 1. The recoveries values were between 97 and 102%. The results obtained by the proposed method were compared with those obtained by the inductively coupled plasma optical emission spectrometry (ICP-OES). Statistical analysis of the results by the Student's t-test and variance ratio F-test (Table 1) revealed that factors calculated did not exceed the theoretical value (95% confidence limits for three degrees of freedom) or there was no significant difference between the proposed methods and the standard method. Thus the technique provides a good alternative for the determination of Cd^{2+} in tap water sample. Compared with other ASV techniques using modified electrodes, the proposed method exhibits better figures of merit (Table 2), revealing that this technique is among those with the highest sensitivity.

Effect of other ions

To study the selectivity of the proposed method, some metal ions were tested to evaluate the possible interference with the detection of Cd^{2+}. The ions were considered to interfere seriously when they gave a current signal change of more than 5%. The experimental results for typical ions present in tap water samples are given in Table 3. The peak current of Cd^{2+} was not significantly affected by substantial excess of Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, and Al^{3+}. However, Co^{2+}, Pb^{2+}, and Ni^{2+} significantly influenced the stripping response. These ions not only compete with Cd^{2+} for the substitution on the surface electrode but can also form intermetallic compounds with Cd^{2+} to prevent its accumulation on the electrode[13]. However, the influence of weakly interfering ions can be corrected by standard addition method. Thus the results demonstrate sufficient selectivity of the proposed method.

Table 3 Potential ion interference on the voltammetric response of 20.0 µg/l Cd^{2+} under optimum conditions.

Foreign ions	Concentration (µg/l)	Signal change (%)
Ca^{2+}	2600	−5.56
Mg^{2+}	1000	−5.35
Zn^{2+}	1000	−5.89
Mn^{2+}	400	−5.36
Fe^{2+}	200	−5.56
Cu^{2+}	200	−5.98
Al^{3+}	80	−5.89
Co^{2+}	40	−5.78
Pb^{2+}	40	−5.96
Ni^{2+}	20	−5.75

CONCLUSIONS

A simple and accurate method was developed for the analysis of trace Cd^{2+} in drinking water using the BDD electrode in combination with SWASV. The electrode exhibited a single stripping anodic signal at −0.72 V, of which the intensity increased linearly with Cd^{2+} concentration range of 2–50 µg/l. The detection limit achieved with 0.2 M 4-aminomethyl benzoic acid-modified BDD electrode for Cd^{2+} was 0.2 ppb. Good repeatability (recoveries between 96 and 102%, $n = 4$) and reproducibility (recovery of 99.02%, $n = 5$) in the measurements were also obtained. The method was applied with tap water samples to reveal better sensitivity, simpler sample preparation, shorter analysis time and easier operational processing. The accuracy of the proposed method was verified by analysing the SRM 1640 natural water standard with the certified value of 22.82 ± 0.96 µg/l yielded Cd^{2+} concentration of 22.72 ± 0.90 µg/l ($n = 3$). The recoveries of the method by spiking were in the range of 85–105%. The results of Cd^{2+} in natural water samples analysed by the developed method (FI-DPASV) were in good agreement with those obtained by Inductively Coupled Plasma-Optical Emission Spectrometry. The concentration of Cd^{2+} in tap water samples were found to be lower than the drinking water contamination standard limited level 3.0 µg/l issued by the World Health Organization and Provincial Waterworks Authority of Thailand.

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