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Original scientific paper

Determination of lead(II) and cadmium(II) in water lily stems using a bismuth film electrode

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Abstract

Mesoporous silica nanoparticles and chitosan were combined with ex-situ bismuth film modified glassy carbon electrode (NanoSiO$_2$–CTS/BiFE) for simultaneous determination of Pb(II) and Cd(II) in HCl/KCl pH 2.2. Differential pulse anodic stripping voltammetry (DPASV) measurements, based on formation of ion-associates between chlorocomplexes and protonated amino groups (–NH$_3^+$) of chitosan at the electrode surface, were explored. Under optimum conditions, the linear correlation coefficient was 0.998 for both Pb(II) and Cd(II) after 240 s of deposition time. The limits of detection (LOD) and quantification (LOQ) were 1.0 μg/L and 3.3 μg/L for Pb(II) and 0.5 μg/L and 1.6 μg/L for Cd(II), respectively. The method exhibited satisfactory reproducibility and the results comparable to ICP-OES. Also, DPASV at NanoSiO$_2$–CTS/BiFE was applied successfully in determining Pb(II) and Cd(II) in water lily stems in Thale Noi.

Keywords
Anodic stripping voltammetry; mesoporous silica nanoparticles; chitosan

Introduction

Thale Noi is a freshwater lake at the uppermost part of Songkhla Lake in the south of Thailand, between 7°45'-55' N and 100°05'-15 E. Its area is approximately 27 square kilometers and the depth 1.5 meters on average [1]. People around Thale Noi are living on crafts, especially handicrafts made from Krajood (*Lepironia articalata*). To make the products colorful, the plant needs to be dyed with the substances containing toxic heavy metals including lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu) and nickel (Ni) [2], and the resulting wastewater contaminated with heavy metals is usually released to water resources of Thale Noi.

Phytoremediation is direct use of plants to clean up contaminated water, soils and sediment. This technology is cost effective and environmentally friendly [3]. In addition, the roots of aquatic plants such as water lily (macrophytes) have an ability to absorb and accumulate heavy metal from polluted water resources [4].

Water lily *(Nymphaea lotus)* is an herbaceous water plant with widespread distribution in Thale Noi. One of the edible parts of water lily is a stem which can be used in cooking a variety of foods. Therefore, growing of water lily in the soil contaminated with heavy metals makes a possible risk to human health.

Previous researches concerning Thale Noi were addressed to determination of lead and chromium concentrations in water [5], as well as lead and arsenic in water, sediment and water plants, including esthwaite waterweed (*Hydrilla verticillata*), coontail hornwort (*Ceratophyllum demersum*), blue water lily (*Nymphaea stellata*) and water lily (*Nymphaea lotus*)[6]. According to the studies on heavy metal contents in water lily plants, high ability for uptake of heavy metals including lead (Pb), cadmium (Cd), iron (Fe), arsenic (As), copper (Cu), nickel (Ni) and mercury (Hg) was also found [7].

The techniques that have been used for heavy metal determination include atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and electroanalytical techniques. Although being commonly used, spectroscopic techniques have disadvantages of high cost and need for pre-concentrating and extracting steps, which are tedious with the risk of loss and contamination [8]. Electroanalytical techniques, in particular anodic stripping voltammetry (ASV) at modified electrodes, could be considered as a preferable choice due to more satisfactory detection limit, higher sensitivity, lower cost, faster operation, higher degree of simplicity and greater capability in simultaneous analysis [9].

A great variety of electrode materials have already been investigated due to their crucial role in improving analytical performances of the method. Compared with other materials, bismuth offers a number of superb characteristics covering sensitivity, low toxicity, simplicity in preparation, no oxygen interference and also, well-defined and well-separated analytical signals [10]. Application of Bi as a modifying agent started with detection of lead [11]. Its versatile applications have thoroughly been reviewed [12], whereas its few recent uses are also referred here. Particle sizes were found to play important role in thermodynamic properties of Bi nano-oxide which can be applied in a variety of areas including analysis and energy [13]. Despite specific treatment to form alloys, the nanoporous bismuth modified electrode was found to provide better life time and precision [14]. In forming thin film with tin, bismuth alloy electrodes with different compositions were studied in order to obtain greater accuracy in simultaneous trace metal analysis [15]. It was also shown that Bi nanoparticles decorated in graphene nanotubes in the screen-printed electrode form can be used for Hg detection [16]. More importantly, a mesoporous nano-silica modified bismuth film was found to increase the surface area and enhance the sensitivity [17].

An additional substance selected as an adhesion reagent for mesoporous nano-silica is chitosan. This natural product extracted from the shell of shrimps, crabs and insects has both hydrophilic and hydrophobic groups. The chitosan amino group has pK_a about 6.5 [18], suitable for its protonation under acidic or neutral conditions. These reasons prove chitosan as water soluble, bioadhesive and easily binding to negatively charged metal ion complexes. Since chitosan has special characteristics of biocompatibility, biodegradability, non-toxicity and adsorption properties, several reports have already been published, involving chemical modification of electrodes by chitosan [19] and their application in determination of various metals [20-22].

The principle of the method involving anodic stripping voltammetry (ASV) at a chitosan modified electrode is in accordance with that proposed by Khaled *et al.* [23] and involves attraction of MCl_4^{2-} to the electrode surface where metal ions are reduced by applying the negative potential. In the next step, the metal ions are re-oxidized, resulting in stripping current peaks as an analytical signal. Selective current enhancement could be explained by the electrostatic attraction between protonated amino groups ($–NH_3^+$) of chitosan and negatively charged metal chlorocomplexes. To picture the whole process, this enhancement starts with the protonation of amino groups to increase density of active sites on the electrode surface. Metal chlorocomplexes then attach to these positive sites to balance the charge. After that upon potential control, the metal ions are firstly reduced and finally stripped out of the surface in the form of chlorocomplexes once again.

The present research is focused on the use of bismuth film modified with mesoporous silica nanoparticles and chitosan for simultaneous determination of Pb(II) and Cd(II) ions by ASV technique. The modified electrode is applied to water lily stems to pave the way for monitoring the metals in local raw materials for food products.

Experimental

Reagents

All the reagents were of analytical reagent grade. Mesoporous silica nanoparticles were of 200 nm particle size and 4 nm pore size. Low molecular weight chitosan was purchased from Sigma-Aldrich. Standard solutions of Pb(II) and Cd(II) (1000 mg/L) were from Fluka. Bismuth salt ($Bi(NO_3)_3×5H_2O$) was dissolved to get 0.01 mol/L stock solution. A supporting electrolyte HCl/KCl was obtained by combining 0.1 mol/L HCl with 0.1 mol/L KCl and pH was adjusted to 2.2 by pH meter. Double deionised water (Milli-Q Millipore 18.2 MΩ cm was used in preparing all aqueous solutions. Before use, all glassware was soaked overnight in a 10 % v/v nitric acid and then rinsed with deionized water.

Instruments

All voltammetric experiments were conducted on a Powerlab 2/20 Potentiostat (ADInstrument, Australia) with Echem software version 2.1.16. A glassy carbon electrode (GCE) (diameter of 3 mm, BAS) was used as a working electrode, Ag/AgCl (3M KCl) as a reference electrode and Pt wire as a counter electrode. All electrodes were put in 50 mL cell for electrochemical measurements and the solution was stirred with a magnetic stirrer without any deaeration. pH of solutions was measured by pH meter Model 510 (Eutech Instruments, USA). ICP-OES (Perkin-Elmer, USA) was used to validate sample analysis by the proposed method.

Ex-situ preparation of bismuth film modified glassy carbon electrode (BiFE)

Glassy carbon electrode (GCE) was polished with 0.05 µm Al_2O_3 on a polishing kit to completely shiny surface. Then, the electrode was sonicated in distilled water to get rid of alumina and any other contaminants from the surface. The bismuth film was deposited on GCE surface without removing oxygen by immersing in 1 mol/L HCl solution containing 2 mmol/L Bi(III) ions and electrolyzed at -0.80 V *vs.* Ag/AgCl for 150 s while stirring the solution. After the electrode was modified with bismuth, it was rinsed with distilled water and dried.

Preparation of NanoSiO$_2$–chitosan/bismuth film modified glassy carbon electrode (NanoSiO$_2$–CTS/BiFE)

To obtain NanoSiO$_2$–chitosan as a modifying solution, 10 ml chitosan solution (0.2 % (w/v) in 2 mol/L acetic acid) was prepared and pH was adjusted to 6.0 with 1 mol/L NaOH. Then 2 mg NanoSiO$_2$ was added with mechanical stirring at room temperature to obtain a highly viscous solution. After that, 2 μL drop of NanoSiO$_2$–chitosan was placed with a micropipette (Brand, USA) onto the GCE modified with bismuth film and allowed to dry in the air.

Voltammetric procedure

Standard solutions of Pb(II) and Cd(II) were added into a three-electrode electrochemical cell containing HCl/KCl (pH 2.2), and stirred under -1.1 V for 240 s. After that, the stirring was stopped and 10 s of quiet time was spent before differential pulse anodic stripping voltammetry (DPASV) was applied with a potential scan from -1.1 to -0.4 V, pulse amplitude 50 mV, pulse duration 20 ms and step potential 5 mV. In order to obtain the best pulsing wave forms, square wave (SWASV) measurements were additionally performed.

Sampling, sample storage and pretreatment

Water lily samples shown in Figure 1 were collected from five sites in Thale Noi denoted in Figure 2. The stems of water lily samples were cut by using plastic-ceramic knife, kept in polyethylene resealable zipper plastic bags, labelled and later transported to the laboratory by keeping in the icebox. On arrival at the laboratory, the samples were cleaned with distilled water to eliminate any adhering soil or dust particles, stored in polyethylene resealable zipper plastic bags and then frozen at -5 °C.

Next, the samples were defrosted, rinsed three times with distilled water, cut by using plastic-ceramic knife and placed in different Petri dishes before being dried in an oven at 105 °C until reaching constant weights. The dried samples were ground to powder with non-metal mortar and pestle and finally collected in polyethylene bags before analysis.

Figure 1. *Water lily in Thale Noi showing stems, flowers and leaves*

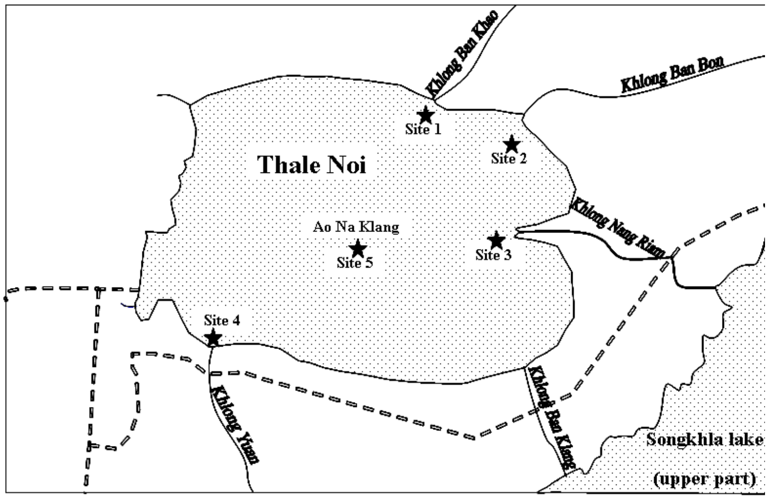

Figure 2. *Location of sampling sites within Thale Noi*

Sample digestion by water bath digestion method

Water lily stem samples were further digested using water bath digestion method [6]. 0.5 g dry sample was transferred to a test tube, followed by adding 2.0 ml of 65 % of nitric acid (HNO$_3$). The test tube was then placed in the water bath, heated at 95 °C about 1.5 hours and left to cool at room temperature. After that, 0.5 ml 30 % hydrogen peroxide (H_2O_2) was added, placed in the water bath, heated at 95 °C about 30 min, left at room temperature, filtered through Whatman No. 1 and diluted with ultrapure water to 10 ml and finally analyzed by ICP-OES. For DPASV, 1 ml of sample solution was added into the electrochemical cell and adjusted to 50 ml with HCl/KCl (pH 2.2).

Results and discussion

Optimization of voltammetric procedure

Table 1 shows the list of operating parameters for the comparison between the square wave (SWASV) and differential pulse (DPASV) anodic stripping voltammetry (ASV) modes in the analysis of 20 μg/L Pb(II) and Cd(II) at the modified GCE.

Table 1. *Comparison between operating parameters of square wave (SW) and differential pulse (DP) modes of ASV technique*

Parameter	SWASV	DPASV
Accumulation step		
Deposition potential, mV	-1000	-1000
Deposition time, s	180	180
Equilibration time, s	10	10
Measuring step		
Potential window mV	-1000 to -300	-1000 to -300
Frequency, Hz	25 Hz	-
Step potential, mV	5 mV	5
Amplitude, mV	25 mV	50

As shown in Figure 3 in terms of currents, DPASV exhibited higher sensitivity than SWASV mode, and therefore DPASV was selected for further experimentation.

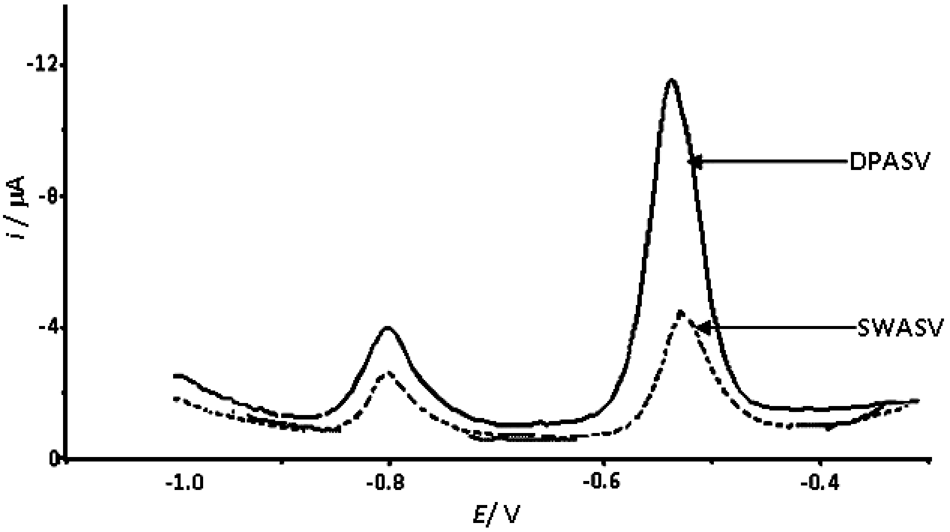

Figure 3. *Comparison of peak currents between SWASV and DPASV modes for 20 μg/L Pb(II) and Cd(II) in 0.1 mol HCl/KCl (pH 2.2).*

Potential and time of pre-plated bismuth film modified electrode

Bi film formation on GCE was optimized using 2 mmol/L Bi(III) solution in 1 mol/L HCl as a plating solution [24] and the effects of plating potential (from -0.6 to -1.0 V) on the electrochemical performance were investigated. At more negative deposition potentials, the peak currents of Pb(II) and Cd(II) increased as shown in Figure 4a. At the potential more negative than

-0.8 V, the electrode did not provide higher currents due to the overloaded bismuth. Therefore, -0.8 V *vs*. Ag/AgCl was selected as the optimum plating potential.

The plating time is crucial in controlling bismuth film thickness. Its effect was studied in the range of 60–300 s. As shown in Figure 4b, Pb(II) and Cd(II) peak currents increased with longer bismuth deposition time up to 150 s and after that, peak currents were lowered due to the film saturation for both metals. The plating time of 150 s was therefore chosen for further investigations.

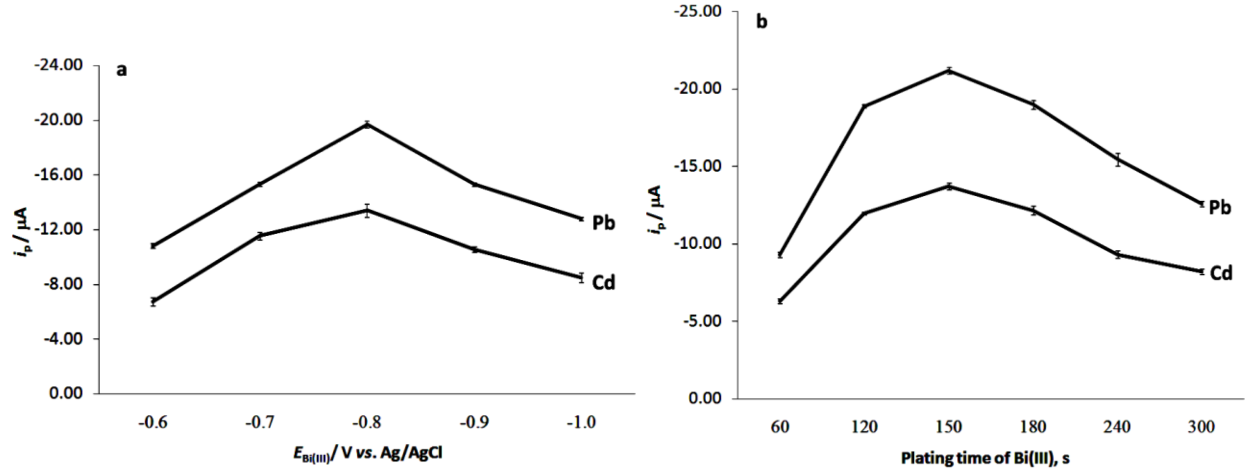

Figure 4. *Influence of plating potential (180 s of deposition time) (a) and plating time (deposition potential -1.0 V) (b) of bismuth film formation upon DPASV signals of 20 μg/L Pb(II) and Cd(II) in 0.1 M HCl/KCl (pH 2.2). Other DPASV parameters as in Table 1.*

Effect of chitosan

The effectiveness of modification by chitosan was investigated by varying its concentration in the modifying solution with a fixed content of mesoporous silica nanoparticles (NanoSiO$_2$) of 2 mg. Figure 5 shows that the peak currents of both metals were higher with increasing concentration of chitosan and reached the maximum at 0.20 % (w/v).

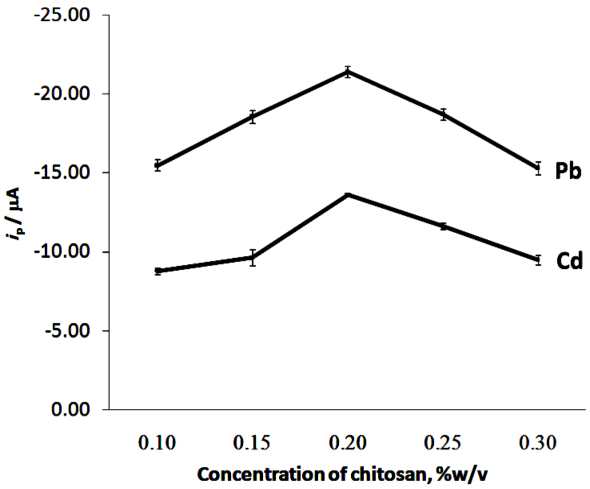

Figure 5*. Effect of concentration of chitosan upon DPASV signals of 20 μg/L Pb(II) and Cd(II) in 0.1 M HCl/KCl (pH 2.2) and other parameters as in Table 1.*

Further increase of the concentration of chitosan suppressed both peak heights, probably due to lower conductivity of chitosan. Therefore, 0.20 % (w/v) of chitosan in the modifying solution was chosen in all subsequent work.

Effect of HCl/KCl solution pH

pH of HCl/KCl solution is an important parameter in supporting the deposition of Pb(II) and Cd(II) on NanoSiO$_2$-CTS/BiFE. As shown in Figure 6, by varying pH from 1.7 to 2.4 for 20 µg/L Pb(II) and Cd(II), both metal ions seem to remain in the form of MCl_4^{2-} in HCl/KCl pH 2.2 which is suitable for sorption on protonated amino groups (NH_3^+) in chitosan through anion exchange/ electrostatic attraction. Thus, 0.1 M HCl/KCl pH 2.2 was selected for further experiments.

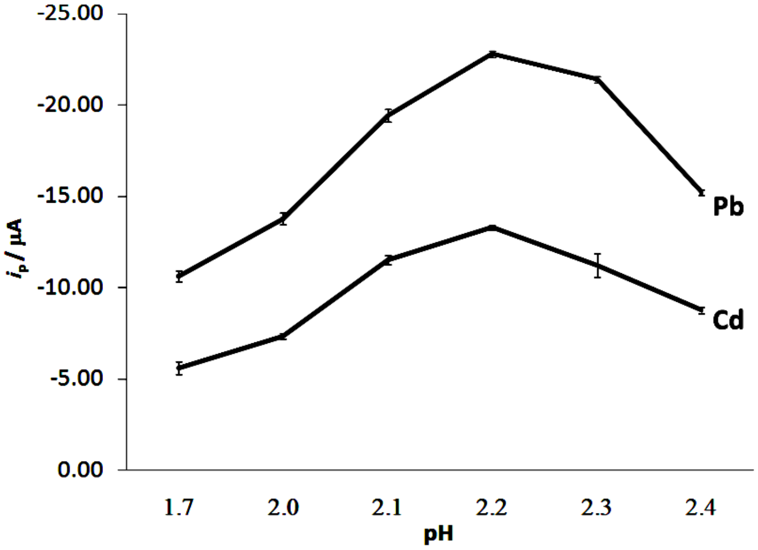

Figure 6. *Effect of pH upon DPASV signals of 20 µg/L Pb(II) and Cd(II) in 0.1 M HCl/KCl with other conditions specified in Table 1.*

Optimization of voltammetric parameters

Due to the fact that ASV is mostly based on the electrolytic deposition of analytes onto the electrode for preconcentration, the operational parameters such as optimum deposition potential and optimum deposition time that would result in the best current response need to be investigated. The deposition potential was varied between -0.8 to -1.3 V with 180 s deposition time with the results shown in Figure 7a. At deposition potentials from -0.8 to -1.1 V, the currents increased for both analytes and then decreased due to hydrogen evolution at higher negative potentials. Consequently, the deposition potential of -1.1 V was selected for the following experiments.

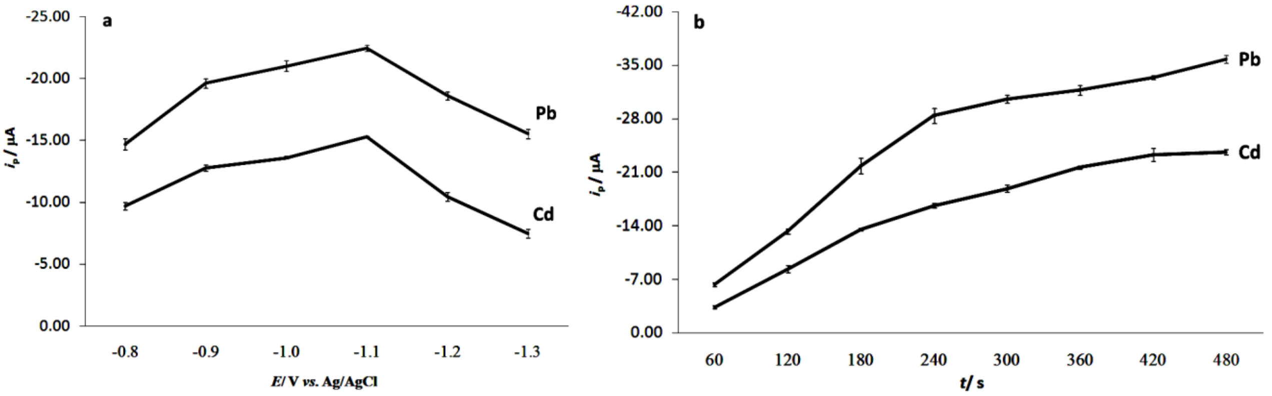

Figure 7. *Influence of deposition potential (a) and deposition time (b) on DPASV signals of 20 µg/L Pb(II) and Cd(II) in 0.1 M HCl/KCl (pH 2.2) with other conditions specified in Table 1.*

The effect of Pb(II) and Cd(II) deposition time was investigated within 60-480 s at deposition potential of -1.1 V as shown in Figure 7b. At longer deposition time, higher sensitivity was obtained, as expected due to a greater amount of analyte deposited on NanoSiO$_2$-CTS/BiFE. At times longer than 240 s, however, the sensitivity did not increase much because of the saturated electrode surface. The deposition time of 240 s was therefore chosen as the optimum value. For further optimization, DPASV operating parameters including step potential and pulse amplitude, were varied to observe the stripping response of 20 μg/L Pb(II) and Cd(II). The best results were obtained for the step potential of 5 mV and pulse amplitude of 50 mV, which were taken as optimum values.

The optimum operation conditions

All studied parameters affecting analytical performance and the optimum conditions for Pb(II) and Cd(II) determination by DPASV using NanoSiO$_2$-CTS/BiFE as the working electrode are collected in Table 2.

Table 2. *Optimized operating conditions for DPASV at NanoSiO$_2$-CTS/BiFE*

Parameter	Optimum value	Studied Range
Plating potential for ex-situ BiFE formation, V	-0.8	-0.6 – -1.0
Plating time for ex-situ BiFE formation, s	150	60–300
Deposition potential for Pb^{2+} and Cd^{2+} detection, V	-1.1	-0.8 – -1.3
Deposition time for Pb^{2+} and Cd^{2+} detection, s	240	60 – 420
pH of 0.1 mol/L HCl/KCl	2.2	1.7 – 2.4
Chitosan concentration, % (w/v)	0.20	0.10–0.30
Equilibration time, s	10	0–40
Step potential, mV	5	1–20
Pulse amplitude, mV	50	50–150

Interference studies

The effect of other metal ions on the peak currents of Pb(II) and Cd(II) was evaluated under optimized conditions by detecting 20 μg/L Pb(II) and Cd(II) in presence of interfering ions and the results are listed in Table 3.

Table 3. *Interference from other metal ions (200 μg/L) on stripping peak currents of 20 μg/L Pb(II) and Cd(II)*

Interference	Contribution, % (i_p Pb(II) = 100 %)	Contribution, % ($i_{p.}$Cd(II) = 100 %)
Ca^{2+}	0	0
Mg^{2+}	0	0
Zn^{2+}	-7.08	-5.40
Ni^{2+}	-5.03	-7.27
Cu^{2+}	-31.00	-42.97
Hg^{2+}	-5.95	-6.02
Fe^{3+}	+2.84	+0.35

i_p: peak current

Most metal ions under study provided less than 10 % current response change and they considered to be not interfering. Presence of Cu(II), however, contributed more than 30 % change for both Pb(II) and Cd(II) signals. To improve the sensitivity by eliminating Cu(II) interference in ASV, 0.01 mmol/L of ferrocyanide can be added as a masking agent acting *via* complex formation with Cu(II).

Analytical characteristics of the method

Calibration curve

The calibration curve was obtained using DPASV at NanoSiO$_2$-CTS/BiFE performed under optimized experimental conditions in HCl/KCl, pH 2.2 solution, containing 2-40 μg/L Pb(II) and Cd(II) and shown in Figure 8. As shown in Figure 9, the linear correlation coefficient (R^2) of 0.998 was achieved for both Pb(II) and Cd(II) after 240 s of deposition time. Slight difference of the slopes for two ions revealed minor matrix effect and suggested the use of standard addition.

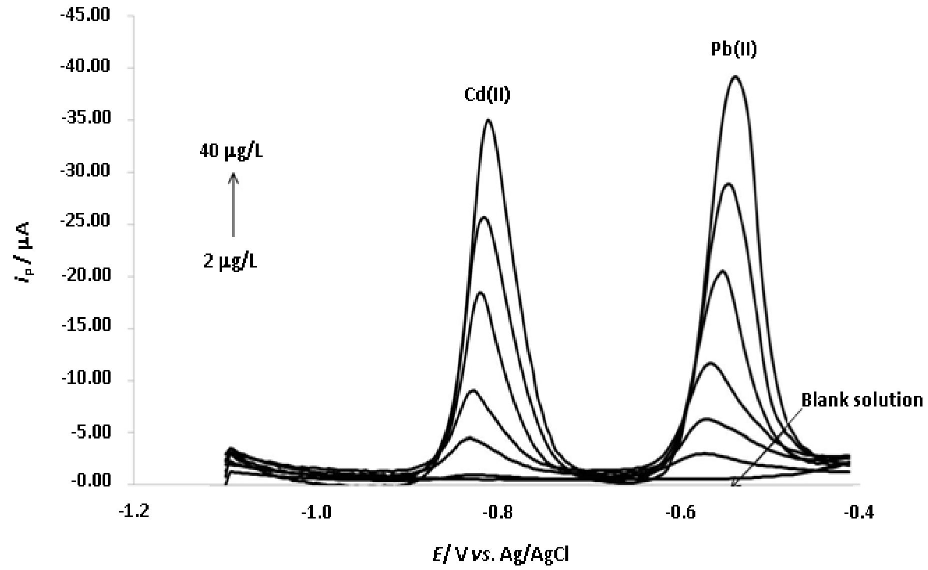

Figure 8. *DPASVs obtained upon increasing of Pb(II) and Cd(II) in HCl/KCl (pH 2.2): 0.0, 2.0, 5.0, 10.0, 20.0, 30.0 and 40.0 μg/L at optimized measurement parameters listed in Table 2*

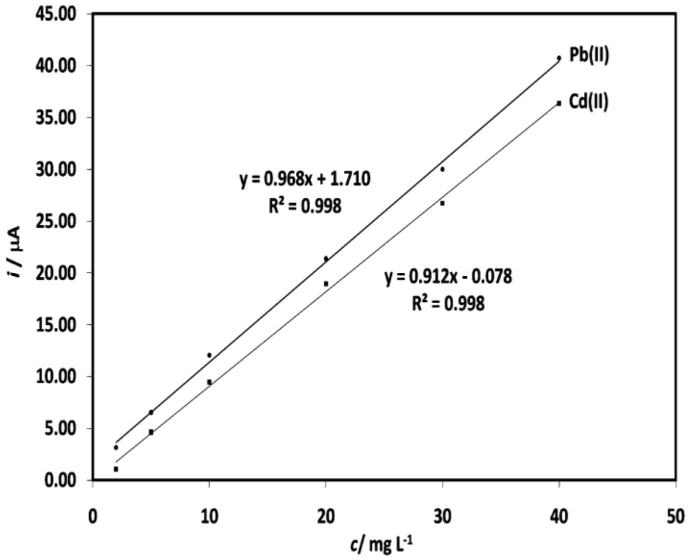

Figure 9. *Calibration graphs for Pb(II) and Cd(II) determinations*

Limit of detection (LOD) and limit of quantification (LOQ)

For the blank solution spiked with 2.0 μg/L of Pb(II) and Cd(II) standard solution, the limit of detection (LOD) and limit of quantification (LOQ) of 0.3 μg/L and 1.1 μg/L for Pb(II) as well as 0.1 μg/L and 0.4 μg/L for Cd(II), respectively, were obtained.

Reproducibility

The reproducibility of the developed NanoSiO$_2$-CTS/BiFE electrode was investigated by measuring ten replicates of 20 μg/L Pb(II) and Cd(II) in 0.1 mol/L HCl/KCl (pH 2.2). The relative standard deviations (RSD) for Pb(II) and Cd(II) currents were found to be 2.26 and 1.71 %, respectively.

Recoveries

As shown in Table 4, the recovery range obtained by spiking both metal ions in the extracted solution were 93.3 –101.9 % for Pb(II) and 99.3 –103.7 % for Cd(II)

***Table 4.** Recovery test for the studied method using water lily stem samples (n = 3) spiked with 2.0, 20.0 and 40.0 μg/L of Pb(II) and Cd(II)*

	$c_{\mathrm{Pb(II)}}$ / μg L^{-1}	Recovery, %	$c_{\mathrm{Cd(II)}}$ / μg L^{-1}	Recovery, %
Sample	ND	-	ND	-
Sample + 2.0 μg/L	1.9	93.3	2.1	103.7
Sample + 20.0 μg/L	20.4	101.9	19.9	99.3
Sample + 40.0 μg/L	40.1	100.3	40.1	100.2

***Table 5.** Comparison of the proposed method with recent literature data of Pb(II) and Cd(II) analysis*

	Electrode	Method	Deposition time, s	Linear range, μg L^{-1}		LOD, μg L^{-1}		Ref
				Pb(II)	Cd(II)	Pb(II)	Cd(II)	
1	Bi/GCE	SWASV	250	5-150	5-150	1.9	3.2	[25]
2	Bi/OMC-MW/GCPE	SWASV	150	1-70	1-70	0.08	0.07	[26]
3	BiOCl/MWCNT/GCE	SWASV	120	5-50	5-50	0.57	1.2	[27]
4	L-cys/GR-CS/GCE	DPASV	120	1.04-62.1	0.56-67.2	0.12	0.45	[28]
5	MWCNT/poly(PCV)/GCE	DPASV	420	1.0-200.0	1.0-300.0	0.4	0.2	[29]
6	Bi$_2$O$_3$/GCE	SWASV	60	2-250	1-150	0.26	0.52	[30]
7	SPCE–Bi$_2$O$_3$–PSS–CnP	DPASV	420	15-45	15-45	0.10	0.27	[31]
8	Bi/MWCNT-EBP-NA/GCE	SWASV	120	1–50	1–50	0.08	0.06	[32]
9	Bi/MGF-Nafion/GCE	DPASV	360	0.5-110	2-70	0.1	0.5	[33]
10	PA-PANI/GCE	DPASV	120	0.1-60	0.05-60	0.05	0.02	[34]
11	NanoSiO$_2$-CTS/BiFE	DPASV	240	0-40	0-40	0.3	0.1	This work

Bi/OMC-MW/GCPE:	Bismuth Film/Ordered Mesoporous Carbon Molecular Wire Modified Graphite Carbon Paste Electrode
BiOCl:	Bismuth-Oxychloride
L-cys:	L-cysteine
GR-CS:	Graphene-Chitosan
MWCNT:	Multiwall Carbon Nanotube
Poly(PVC):	Poly(pyrocatechol violet)
Bi$_2$O$_3$/GCE:	graphite-composite electrodes bulk modified with Bi$_2$O$_3$
SPCE–Bi$_2$O$_3$–PSS–CnP:	Screen-printed carbon electrodes-Bismuth Oxide-polystyrene sulfonate carbon nanopowder
MWCNT-EBP-NA:	Multi-walled carbon nanotube-emeraldine base polyaniline-Nafion
MGF-Nafion:	Mesoporous graphene framework-Nafion
PA-PANI:	Phytic acid-polyaniline nanofibers
CTS:	Chitosan

Analytical characteristics of the proposed method in comparison with other recent studies are compared in Table 5. The present method is proved to have comparable deposition time and linear ranges, but relatively better LOD and LOQ for both metals. With simplicity, speed and cost-effectiveness, the developed method is a good alternative for metal ion analysis, especially in further continuing research and development.

Analytical application

The NanoSiO$_2$-CTS/BiFE was applied to determine the Pb(II) and Cd(II) in water lily stems samples by DPASV under optimum conditions. As shown in Table 6, with standard addition, the method provided well analytical performance and gave results comparable to those measured by ICP-OES, proving thus satisfactory accuracy and reliability. Therefore, the NanoSiO$_2$-CTS/BiFE is found effective in determining Pb(II) and Cd(II) at trace levels in real samples.

Table 6. *Concentration of Pb(II) and Cd(II) in water lily stems (mg/kg) determined by DPASV and ICP-OES methods (n = 3)*

Sites	Sampling site	Longitude and latitude	$c_{\mathrm{Pb(II)}}$ / mg kg^{-1}		$c_{\mathrm{Cd(II)}}$ / mg kg^{-1}	
			DPASV	ICP-OES	DPASV	ICP-OES
1	Khlong Ban Bon	E 100° 7′ 40″ N 7° 47′ 21″	0.11	0.10	< LOQ	< LOQ
2	Khlong Na Lam	E 100° 9′ 33″ N 7° 48′ 07″	< LOQ	< LOQ	< LOQ	< LOQ
3	Khlong Nang Riam	E 100° 11′ 6″ N 7° 47′ 05″	< LOQ	< LOQ	< LOQ	< LOQ
4	Khlong Yuan	E 100° 7′ 58″ N 7° 46′ 14″	0.29	0.28	0.10	< LOQ
5	Ao Na Klang	E 100° 7′ 40″ N 7° 46′ 43″	0.16	0.16	0.07	< LOQ

Conclusions

A simple and accurate electrochemical method to determine Pb(II) and Cd(II) was proposed using the NanoSiO$_2$-CTS/BiFE combined with DPASV technique, giving well-defined stripping peaks for both metals. The chitosan selected as strong adhesion reagent for silica nanoparticles coating is also cheaper than the normally used Nafion. Under optimized conditions, the linear correlation coefficient (R^2) was 0.998 for both metals with 240 s deposition time. The limit of detection (LOD) of 0.3 μg/L was obtained for Pb(II) and 0.1 μg/L for Cd(II). The method was successfully applied for determination of Pb(II) and Cd(II) in water lily stems with the results in good agreement with those obtained by ICP-OES.

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References

[1] H. Segers, P. Pholpunthin, *International Journal of Limnology* **33** (1997) 13-21.
[2] B. Vipul, K. Paresh, S. Gaurav, *International Journal of Scientific & Engineering Research* **5** (2014) 664-666.
[3] V. T. Bieby, R. S. A. Siti, B. Hassan, I. Mushrifah, A. Nurina, M. Muhammad, *International Journal of Chemical Engineering* **2011** (2011) 1-31.
[4] Z. A. Mohamed, M. S. Serag, *Journal of Materials and Environmental Science* **26** (2003) 1-20.
[5] K. Arnop, Lead and Chromium contamination of useless water from krajut dyeing at Talenoi. Research work, Department of Chemistry, Faculty of Science, Thaksin University, Phatthalung, Thailand, 1999, p. 68
[6] T. Phojanaluk, C. Sommai, P. Siriporn, The 11th Naresuan Research Conference: Research & Innovation, Concentration of arsenic and lead in water, sediment and some aquatic plants in Thale Noi lake, Naresuan University, Phitsanulok, Thailand, 2015, p. 456

[7] N. S. B. A. Rahim, Preliminary study of heavy metals in water lily plants around Kota Samarahan area. Research work, Bachelor of Science with Honours, Programme of Aquatic Resource Science and Management, Department of Aquatic Science, Faculty of Resource Science and Technology, University Malaysia Sarawak, Sarawak, Malaysia, 2014, p. 1

[8] G. Somer, A. C. Çalskan, O. Sendil, *Turkish Journal of Chemistry* **39** (2015) 639-647.

[9] K. Kaewkim, S. Chuanuwatanakul, O. Chailapakul, S. Motomizu, *Food Control* **31** (2013) 14-21.

[10] R. I. L. Catarino, M. F. C. Leal, A. M. Pimenta, M. R. S. Souto, J. R. T. Lopes, *Journal of the Brazilian Chemical Society* **25** (2014) 961-968.

[11] F. Arduini, J. Q. Calvo, G. Palleschi, D. Moscone, A. Amine, *TrAC Trends in Analytical Chemistry*, **29** (2010) 1295-1304.

[12] N. B., M. Sajid, T. A. Saleh, *TrAC Trends in Analytical Chemistry*, **111** (2019) 47-61.

[13] Q. Zhang, A. Yan, Z. Cui, Y. Xue, *The Journal of Chemical Thermodynamics*, **130** (2019)154-162.

[14] J.-H. Hwang, X. Wang, D. Zhao, M. M. Rex, H. J. Cho, W. H. Lee, *Electrochimica Acta* **298** (2019) 440-448.

[15] M. Finšgar, B. Petovar, K. Vodopivec, *Microchemical Journal* **145** (2019) 676-685.

[16] N. Jeromiyas, E. Elaiyappillai, A. S. Kumar, S.-T. Huang, V. Mani, *Journal of the Taiwan Institute of Chemical Engineers*, **95** (2019) 466-474.

[17] D. Yang, L. Wang, Z. Chen, M. Megharaj, R. Naidu, *Electrochimica Acta* **132** (2014) 223-229.

[18] K. Eunkyoung, X. Yuan, C. Yi, W. Hsuan-Chen, L. Yi, H. M. Brian, B.–Y. Hader, G. Reza, W. R. Gary, S. Jana, E. B. William, S. Xiaowen, F. P. Gregory, *Polymers (Basel)* **7** (2015) 1-46.

[19] A. Z. Karim, A. Mozhdeh, *Portugaliae Electrochimica Acta* **32** (2014) 369-379.

[20] Y. Xianzeng, Y. Qinghua, W. Yan, L. Nanqiang, *Talanta* **47** (1998) 1099-1106.

[21] L. Guanghan, Y. Xin, W. Xiaogang, Z. Tong, *Microchemistry Journal* **69** (2001) 81-87.

[22] C. A. M. Huitle, N. S. Fernandes, M. C. Lopes, M. A. Quiroz, *Portugaliae Electrochimica Acta* **28** (2010) 39-49.

[23] E. Khaled, H. N. A. Hassan, A. Girgis, R. Metelka, *International Journal of Electrochemical Science* **5** (2010) 158-167.

[24] T. T. Lemma, S. Khalid, R. S. Tesfaye, *Russian Journal of Electrochemistry* **49** (2013) 59-66.

[25] S. M. Rosolina, J. Q. Chambers, C. W. Lee, *Analytica Chimica Acta* **893** (2015) 25-33.

[26] G. Zhao, H. Wang, G. Liu, Z. Wang, *Electroanalysis* **29** (2017) 497-505.

[27] S. Cerovac, V. Guzsvany, Z. Konya, *Talanta* **134** (2015) 640-649.

[28] W. Zhou, C. Li, C. Sun, *Food Chem*istry **192** (2016) 351-357.

[29] M. A. Chamjangali, H. Kouhestani, F. Masdarolomoor, *Sensor and Actuators B: Chemical* **216** (2015) 384-393.

[30] J. Z. Marinho, R. A. B. Silva, T. G. G. Barbosa, *Electroanalysis* **25** (2013) 765-770.

[31] R. María-Hormigos, M. J. Gismera, J. R. Procopio, M. T. Sevilla, *Journal of Electroanalytical Chemistry,* **767** (2016) p. 114–122.

[32] G. Zhao, Y. Yin, H. Wang, G. Liu, Z. Wang, *Electrochimica Acta* **220** (2016) 267-275.

[33] L. Xiao, B. Wang, L. Ji, F. Wang, Q. Yuan, G. Hu, A. Dong, W. Gan, *Electrochimia Acta* **222** (2016) 1371-1377.

[34] H. Huang, W. Zhu, X. Gao, X. Liu, H. Ma, *Analytica Chimica Acta* **947** (2016) 32-41.