

A Highly Sensitive Mercury(II) Sensor Using Zn/Al Layered Double Hydroxide-3(4-hydroxyphenyl)propionate Modified Multi-Walled Carbon Nanotube Paste Electrode

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A multi-walled carbon nanotube (MWCNT) modified with zinc/aluminium layered double hydroxide-3(4-hydroxyphenyl) propionate nanocomposite (Zn/Al-LDH-HPP) was employed to prepare a chemically modified carbon nanotube paste electrode (CMCNTPE) for Hg(II) determination by cyclic voltammetry. The results indicated that Zn/Al-LDH-HPP nanocomposite has enhanced the sensitivity of the voltammetric responses. Under optimum experimental conditions such as percentage of modifier, pH of solution, type of supporting electrolyte, scan rate and regeneration, a linear relationship between concentration and current was observed within the concentration ranges of $1.0 \times 10^{-9} - 1.0 \times 10^{-7}$ M and $1.0 \times 10^{-7} - 1.0 \times 10^{-3}$ M Hg(II). The detection limit was found to be 5.0×10^{-10} M. Interferences of several metal ions were studied and showed that they did not interfere in the determination of Hg(II). The proposed CMCNTPE was one of high sensitivity, selectivity, repeatability and reproducibility. It has been used for the determination of Hg(II) in real samples such as fish and shellfish with success.

Keywords: Chemically modified electrode, Cyclic voltammetry, Hg(II), Nanocomposite

1. INTRODUCTION

Mercury may exist in the environment as elemental mercury (Hg^0), inorganic mercury (Hg^+ and Hg^{2+}) and organic mercury (methylmercury and ethylmercury) [1]. It is recognized to be highly toxic

even at low levels because of its reactivity, volatility and solubility in water and living tissues [2]. Mercury is known to accumulate in human body via the food chain [3]. This will, eventually, affect human health in terms of defects during birth, skin rash [4] brain and nerve damage [5] and mental disabilities [6].

Nowadays, the available analytical techniques for determination of low levels mercury are mostly complicated, too costly and time consuming [7]. Such techniques include inductively coupled plasma - mass spectrometry (ICP-MS) [8], cold vapor atomic absorption spectrometry [9,10], gas chromatography [11] and atomic fluorescence spectrometry [12]. Although the potentiometric sensors are useful for the determination of mercury in the environment, mostly cannot be used at below nanolevel [13-18]. It is then crucial that sensitive and user-friendly techniques for determination of mercury in the environmental samples are used. The electrochemical techniques appear to be the option as they have the necessary advantages e.g. high sensitivity, good selectivity and ease of operation over the techniques mentioned earlier [19-21].

In the last few years, nanomaterials have been widely used in the fabrication of electrochemical sensors [22]. In particular is the carbon nanotube (CNT) which can be used in place of graphite to prepare a CNT paste electrode. CNT paste electrode demonstrates low background current, easy preparation and rapid renewal of the surface as is the graphite paste [23]. CNT offer advantages due to its unique structure, high mechanical strength, high surface area, high electrical conductivity and electrocatalytic activity [24-26] in comparison with graphite that has lower conductivity than CNT. It has been reported [27] that once incorporated with a chemical modifier this chemically modified carbon nanotube paste electrode (CMCNTPE) has its sensitivity and selectivity further improved. Numerous CMCNTPE have already been successfully examined for the detection of several species of inorganic [28, 29] and organic [30, 31] compounds. Among the chemical modifier used is synthetic anionic clay of layered double hydroxide [32, 33] which has been exploited for its electrocatalytic property through ion-exchange process [34].

In the current work, a nanocomposite Zn/Al layered double hydroxide-3(4-hydroxyphenyl)propionate modified multi-walled carbon nanotube paste electrode has been used to determine of mercury(II) in real samples by cyclic voltammetry.

2. EXPERIMENTAL

2.1. Chemicals and reagents

MWCNT (Timesnano) with purity more than 99.9%, were used without further purification. The Zn/Al-LDH-HPP nanocomposite was synthesized according to previous method [35]. Paraffin oil and sodium hydroxide were purchased from Sigma-Aldrich. All supporting electrolyte (potassium chloride, lithium chloride, sodium chloride and sodium acetate), acetic acid and nitric acid were supplied by Merck. Reagent grade mercury dichloride (Merck) and chloride salts of other cations (Merck and Sigma-Aldrich) were used as received.

2.2. Apparatus

Electrochemical data were obtained with a three-electrode system using a Gamry Potentiostat, Series-G750, USA. A saturated Ag/AgCl electrode, a platinum wire and carbon paste electrodes (unmodified and modified) were used as the reference, counter and working electrodes, respectively. All pH measurements were accomplished with a digital pH-meter, Orion model 720A, equipped with a glass electrode (916500). A mercury analysis system FIMS 100 of Perkin Elmer was used to analyse mercury(II) in real samples.

2.3. Preparation of the electrodes

The unmodified CNT paste electrode was prepared by mixing MWCNT and paraffin oil at weight ratio of 75:25 until a uniform paste. Nanocomposites LDH-HPP (modifier) in % weight ratios (w/w) of 2.5, 5.0, 7.5, and 10.0 were added to the pastes and mixed to produce the final CMCNTPE. Both unmodified and modified CNT paste electrodes were finally packed into Teflon tubes (i.d. 2.8 mm) with one end inserted with copper wires as the external electric contacts and the other end as electrode surface. The electrode surface was polished with filter paper prior to experiment.

2.4. Voltammetric detection of Hg(II)

For all measurements the three electrodes were immersed in a 50 mL Hg(II) solution and 0.5 M potassium chloride at room temperature (25°C), and with stirring using a magnetic stirrer. The solutions were degassed for 15 minutes before every measurement by bubbling with nitrogen gas. The pH of the solutions was adjusted at 5.0 by acetic acid and sodium hydroxide. Unless otherwise stated the voltammetric response of the paste electrodes were measured at applied potential of -0.6 to +0.6 V and scan rate of 100 mV s⁻¹.

2.5. Preparation of real samples

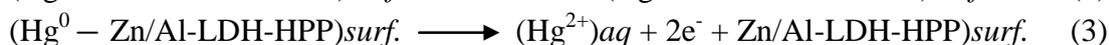
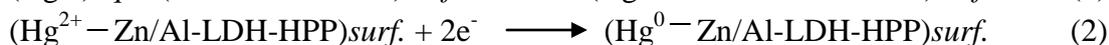
Marine animal samples including fish and shellfish purchased from local market in Tanjung Malim, Malaysia. For digestion of marine animal samples, 500 mg of dried sample was placed in a 50 mL beaker and 15 mL of HNO₃ (65%) was added. The digestion was done at 110 °C about 3 hours on the hotplate. After the beaker was sufficiently cool, the liquid sample was filtered by filter paper (Whatman No. 1) and the filtration was collected into a 100 mL volumetric flask. Supporting electrolyte was added into the volumetric flask and appropriate amounts of NaOH were added to adjust the pH. The solution was then diluted to the mark with deionized water.

For the recovery study, the waste water samples were spiked with 1.0 x 10⁻⁸ M Hg(II). The mean of the recovery was calculated as a percentage of the total mercury concentration founded and the mercury concentration added to the samples. The recovery study was performed by cyclic voltammetric measurement under optimum experimental conditions.

3. RESULTS AND DISCUSSION

3.1. Voltammetric behavior of Hg(II) at Zn/Al-LDH-HPP modified CNT paste electrode

Cyclic voltammograms (CV) of 2.0×10^{-4} M Hg(II) in potassium chloride (pH 5.0) on the unmodified (Figure 1a) and CMCNTPE (Figure 1b) show that the electrode process only occur at the CMCNTPE as the unmodified CNT paste electrode only shows background currents. This indicates the presence of the Zn/Al-LDH-HPP nanocomposite in the paste is vital for the response obtained. The anodic peak current (I_{pa}) observed at anodic peak potential (E_{pa}) of 93.9 mV corresponds to the oxidation of Hg to Hg(II). The cathodic peak current (I_{pc}) observed at cathodic peak potential (E_{pc}) of -37.9 mV corresponds to the reduction of Hg(II) to Hg. The peak separation (ΔE_p) of 131.80 mV involving two electrons suggests that the electrode process is one of quasi-reversible. The redox process takes place only after the accumulation of Hg(II) at the surface of CMCNTPE via complexation with Zn/Al-LDH-HPP nanocomposite [36]. The overall mechanism that gives rise to the voltammetric response is then suggested [37];



The SEM image of the CMCNTPE shows the incorporation of Zn/Al-LDH-HPP nanocomposites in the MWCNT (Figure 2).

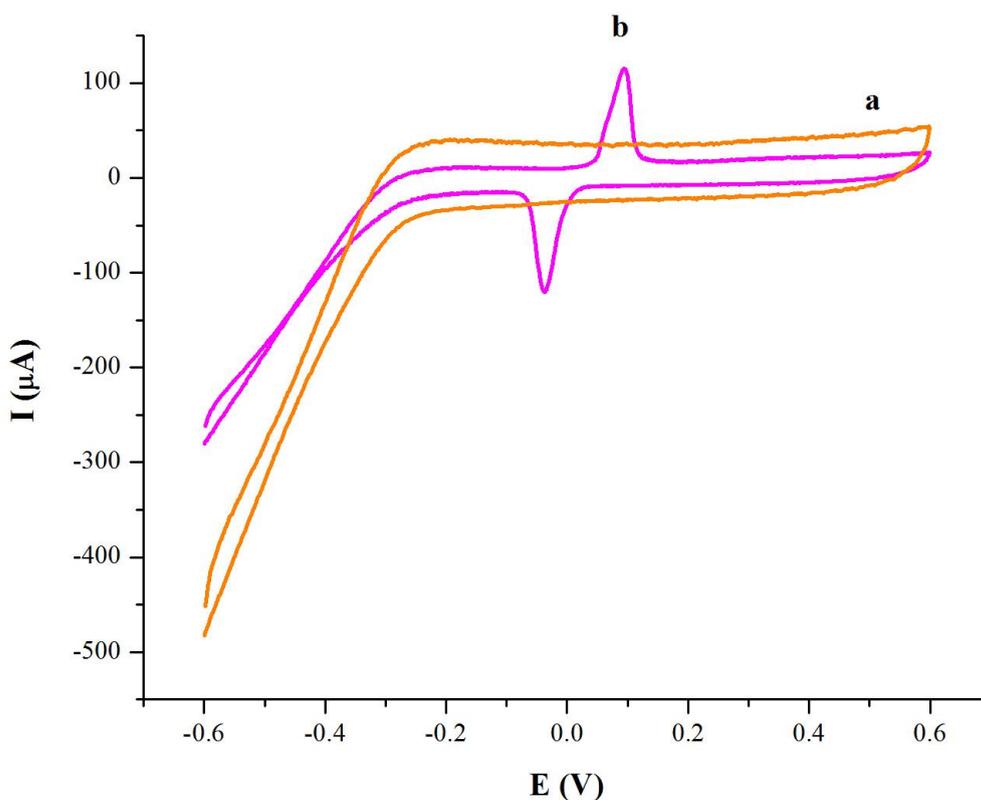


Figure 1. CV of (a) unmodified CNT paste and (b) Zn/Al LDH-HPP modified carbon nanotube paste towards 2.0×10^{-4} M Hg(II) in 0.5 M KCl buffered at pH 5.0 and scan rate 100 mV s^{-1} .

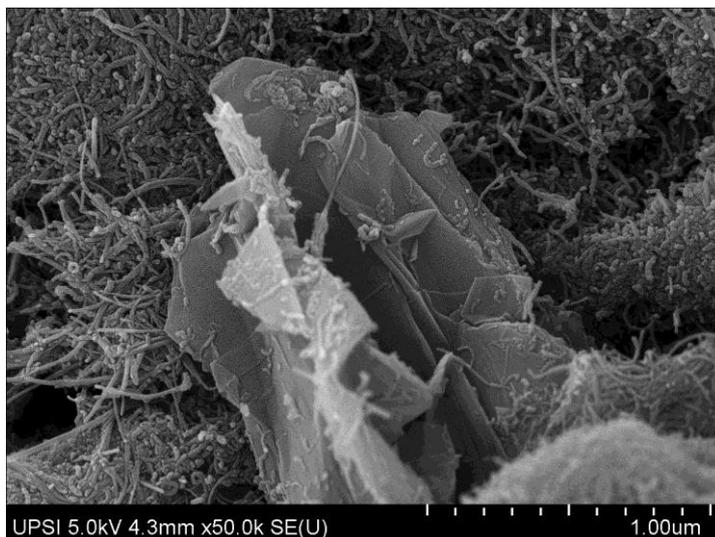


Figure 2. SEM image of Zn/Al LDH-HPP modified carbon nanotube paste electrode.

3.2. The effect of modifier

The nature and amount of the nanomaterial added in the CMCNTPE have been reported [21] to be significantly influence the sensitivity and selectivity of determination of mercury. Therefore, different compositions of Zn/Al-LDH-HPP nanocomposites in the preparation of CMCNTPE were investigated and the results are shown in Figure 3. It shows that maximum I_{pa} is obtained at 2.5% w/w Zn/Al-LDH-HPP. However, the continuous increase in the amount of modifier leads to a decrease in the I_{pa} which presumably due to the decrease in the CNT content of the paste, and as a result the conductivity of the electrode decreases [38].

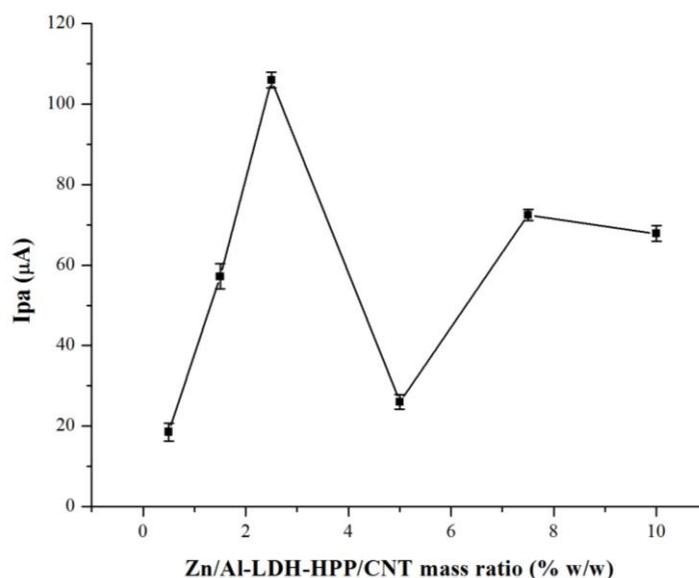


Figure 3. Effect of the amount of Zn/Al LDH-HPP nanocomposite in the CMCNTPE on the anodic peak currents obtained by cyclic voltammetry for 2.0×10^{-4} M Hg(II) in 0.5 M KCl buffered at pH 5.0 and scan rate 100 mV s^{-1} .

3.3. The effect of solution pH

The effect of solution pH was studied in the pH range of 2.0 – 8.0. As shown in Figure 4, the maximum I_{pa} is obtained at pH 5.0. The decrease in I_{pa} at pH < 5.0 is due to interference of H^+ competing with Hg(II) in the complexation with Zn/Al-LDH-HPP. Meanwhile, the decrease in I_{pa} at pH > 5.0 is due to the hydrolysis of cation, so will diminish the soluble Hg(II) in the solution [39]. It was found that solution pH strongly affect the voltammetric response. Therefore, pH 5.0 was used as optimum pH.

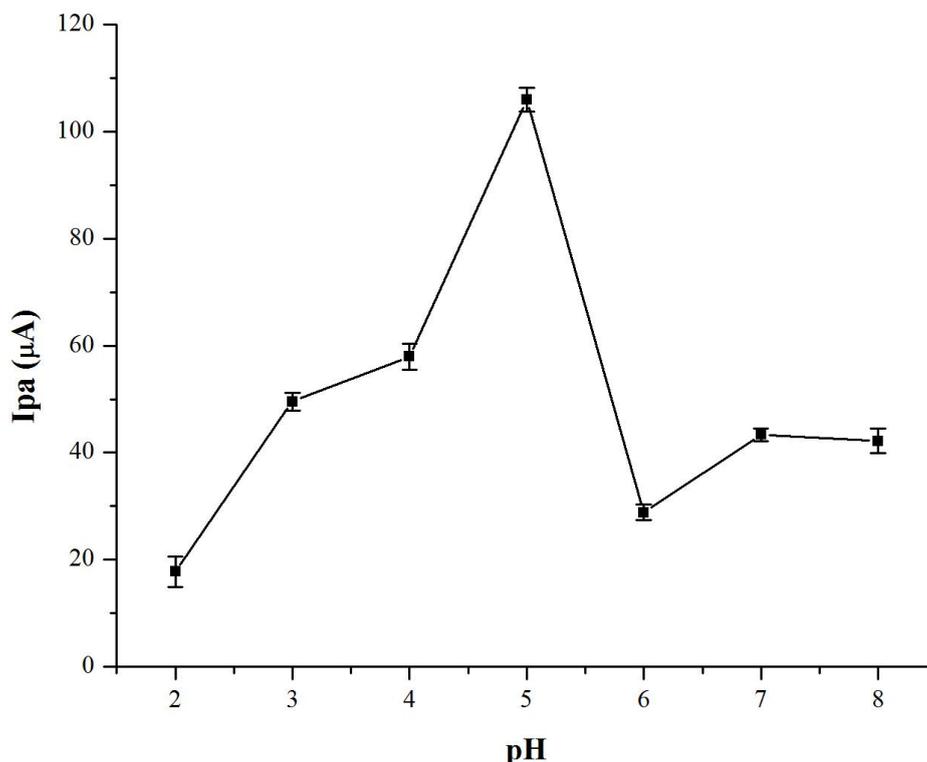


Figure 4. Effect of pH on the anodic peak currents obtained by cyclic voltammetry for 2.0×10^{-4} M Hg(II) in 0.5 M KCl and scan rate 100 mV s^{-1} at CMCNTPE.

3.4. Type of supporting electrolyte

Different supporting electrolytes will have different properties that will affect the voltammetric measurement. The effect of different supporting electrolyte, such as KCl, NaCl, LiCl and CH_3COONa , on the voltammetric behaviour of the CMCNTPE was investigated. There are distinct differences in E_{pa} of supporting electrolytes used but much less on the E_{pc} i.e. at -40 mV (Figure 5). The best ΔE_p at 120 mV is observed when 0.5 M KCl is being used as supporting electrolyte, due to the most quasi-reversible response. The highest I_{pa} was also obtained in 0.5 M KCl. Types of anion available affect the redox process. The acetate in 0.5 M CH_3COONa appears to cause an irreversible electrode process. Furthermore, the presence of a number of Cl^- ions enhances sensitivity for detection of Hg(II) [40]. Therefore, KCl was chosen as supporting electrolyte.

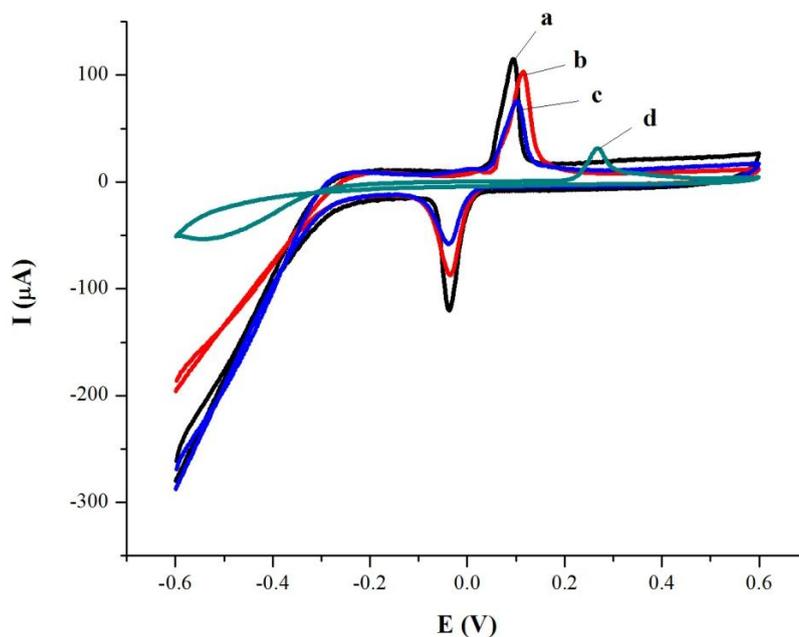


Figure 5. CV of 2.0×10^{-4} M Hg(II) in (a) 0.5 M KCl, (b) 0.5 M LiCl, (c) 0.5 M NaCl and (d) 0.5 M CH_3COONa at pH 5.0 and scan rate 100 mV s^{-1} at CMCNTPE.

3.5. The effect of scan rate

Figure 6 shows that the I_{pa} increases linearly with ν , confirming that the electrode process is quasi-reversible (see Section 3.1) and with an adsorption-controlled process. Plot of I_{pa} vs. ν has the regression equation of $I_{pa} = 1.2544\nu - 6.167$ with correlation coefficient (R^2) 0.9972. As the I_{pa} is proportional to scan rate, hence, an adsorption-controlled process is anticipated [41]. Although the peak current increased with the increase of scan rate, separation of anodic and cathodic peak leads to quasi-reversible process. Hence, the scan rate of 100 mV s^{-1} was used for this study.

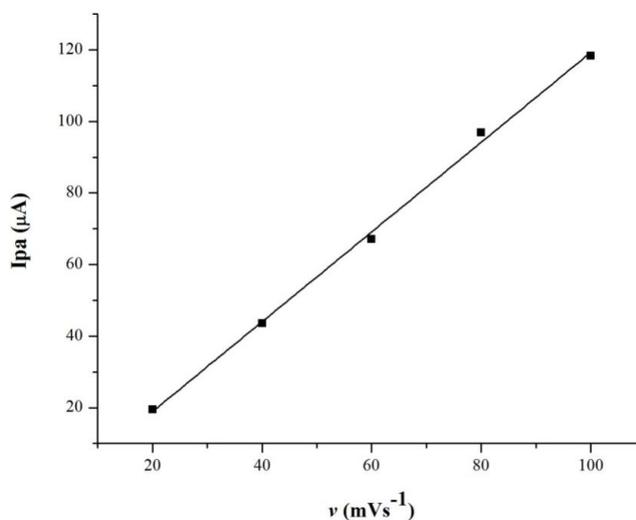


Figure 6. Effect of scan rates on the anodic peak currents obtained by cyclic voltammetry of 2.0×10^{-4} M Hg(II) at CMCNTPE in 0.5 M KCl buffered at pH 5.0.

3.6. The effect of regeneration of the CMCNTPE

The regeneration of the electrode surface was carried out using either several cleaning solutions *viz.* HCl, HNO₃, NaNO₃, NH₄Cl, H₂O and mechanical polishing. The electrode surface was cleaned every time after used. Table 1 indicates that mechanical polishing was superior in cleaning the adsorbed material as the decrease in *I*_{pa} was much less. Under normal conditions, the electrode can be used for about 10 weeks. Regeneration using cleaning solution was not completely clean the surface electrode and give rise to memory effects, causing the decrease in *I*_{pa} [42].

Table 1. The regeneration condition of CMCNTPE.

Regeneration condition	<i>I</i> _{pa} /μA		<i>I</i> _{pa} loss (%) ^a
	Before regeneration	After regeneration	
NH ₄ Cl (0.1 M)	139.7	115.3	17.47
HCl (0.1 M)	138.3	103.0	25.52
HNO ₃ (0.1 M)	133.2	84.1	36.86
NaNO ₃ (0.1 M)	138.7	130.3	6.06
H ₂ O	138.0	134.7	2.39
Mechanical polishing	137.7	136.6	0.80

$$^a \text{Ipa loss (\%)} = \frac{\text{Ipa}(\text{before}) - \text{Ipa}(\text{after})}{\text{Ipa}(\text{before})} \times 100$$

3.7. Chronocoulometry studies

A double step chronocoulometry to the 2.0 × 10⁻⁴ M Hg(II) and 0.5 M KCl (pH 5.0) was studied with initial potential steps ranging from -1.1 to +1.1 V. According to Anson's equation [43]:

$$Q = 2nFAcD^{1/2}\pi^{-1/2}t^{1/2} + Q_{dl} + Q_{ads} \quad (4)$$

where *n* is the number of electron transferred, *F* (C mol⁻¹) is the Faraday constant, *A* (cm²) is the area of the electrode, *c* (mol cm⁻³) is the concentration of Hg(II), *D* (cm² s⁻¹) is the diffusion coefficient, *Q*_{dl} (C) is the double layer charge and *Q*_{ads} (C) is the adsorption charge, other symbols have their usual significances. *D* and *Q*_{ads} of CMCNTPE can be determined based on Equation 4. In our work, the plots of charge (point-by-point background subtraction) against the square root of time (*t*^{1/2}) show straight lines (Figure 7). From the plot of *Q* versus *t*^{1/2}, the values of *D* and *Q*_{ads} can be estimated (*Q*_{dl} is assumed not changed) from the slope and intercept, respectively. As *n* = 2, *c* = 2.0 × 10⁻⁷ mol cm⁻³ and *A* = 0.0616 cm² determined above, it was calculated that *D* = 8.185 cm² s⁻¹ and *Q*_{ads} = 5.1758 × 10⁻³ C. According to the equation: *Q*_{ads} = *nFAΓ*, the surface coverage (*Γ*) for CMCNTPE can be obtained as 4.3535 × 10⁻⁷ mol cm⁻², which has larger than the previous reported value of 4.93 × 10⁻¹¹ mol cm⁻² [41]. This indicates that CMCNTPE has a rather high sensitivity towards Hg(II).

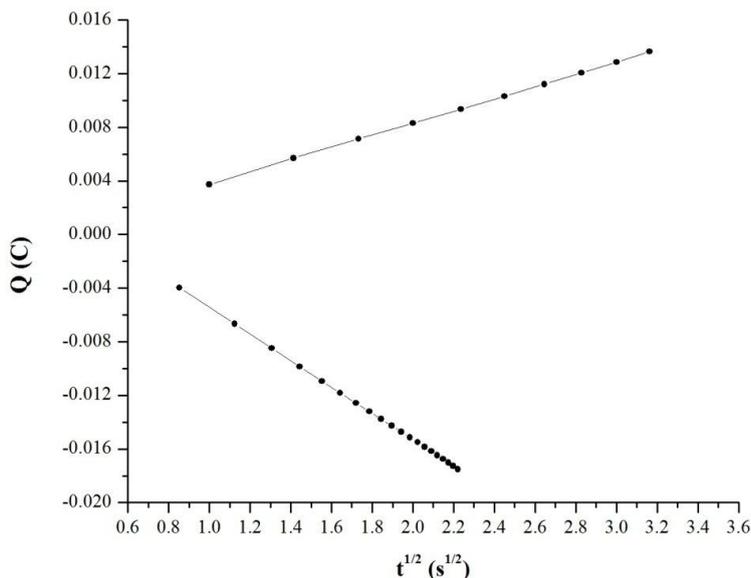


Figure 7. Double step chronocoulograms of 2.0×10^{-4} M Hg(II) at CMCNTPE in 0.5 M KCl (pH 5.0) at scanning potential of -1.1 to +1.1 V.

3.8. Interference studies

The selectivity of CMCNTPE was investigated by determining 2.0×10^{-4} M Hg(II) in the presence of various interfering metal ions in 0.5 M KCl at pH 5.0. Figure 8 indicates that 25-folds of Ni(II), Ba(II), Ca(II), Cd(II), Mn(II), Sr(II), Co(II) and Mg(II) did not interfere on the determination of Hg(II). So CMCNTPE can be determined selectively with the proposed method when these interferences are coexisted.

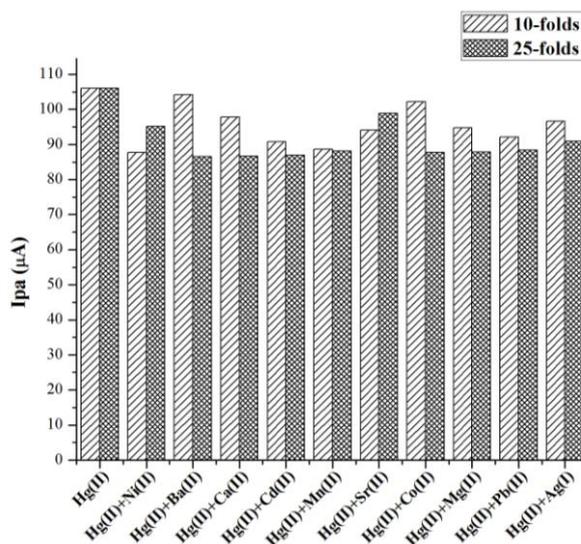


Figure 8. Effect of 10-fold and 25-fold concentrations of interfering ions on the voltammetric determination of 2.0×10^{-4} M Hg(II) at CMCNTPE in 0.5 M KCl, pH 5.0 and scan rate 100 mV s^{-1} .

3.9. Analytical parameters

Figure 9 is the calibration plot of Hg(II) solutions at the CMCNTPE at optimum conditions. It shows a linear relationship between current and concentration in the ranges of $1.0 \times 10^{-9} - 1.0 \times 10^{-7}$ M Hg(II) and $1.0 \times 10^{-7} - 1.0 \times 10^{-3}$ M Hg(II) with correlation coefficients of 0.9926 and 0.9963, respectively.

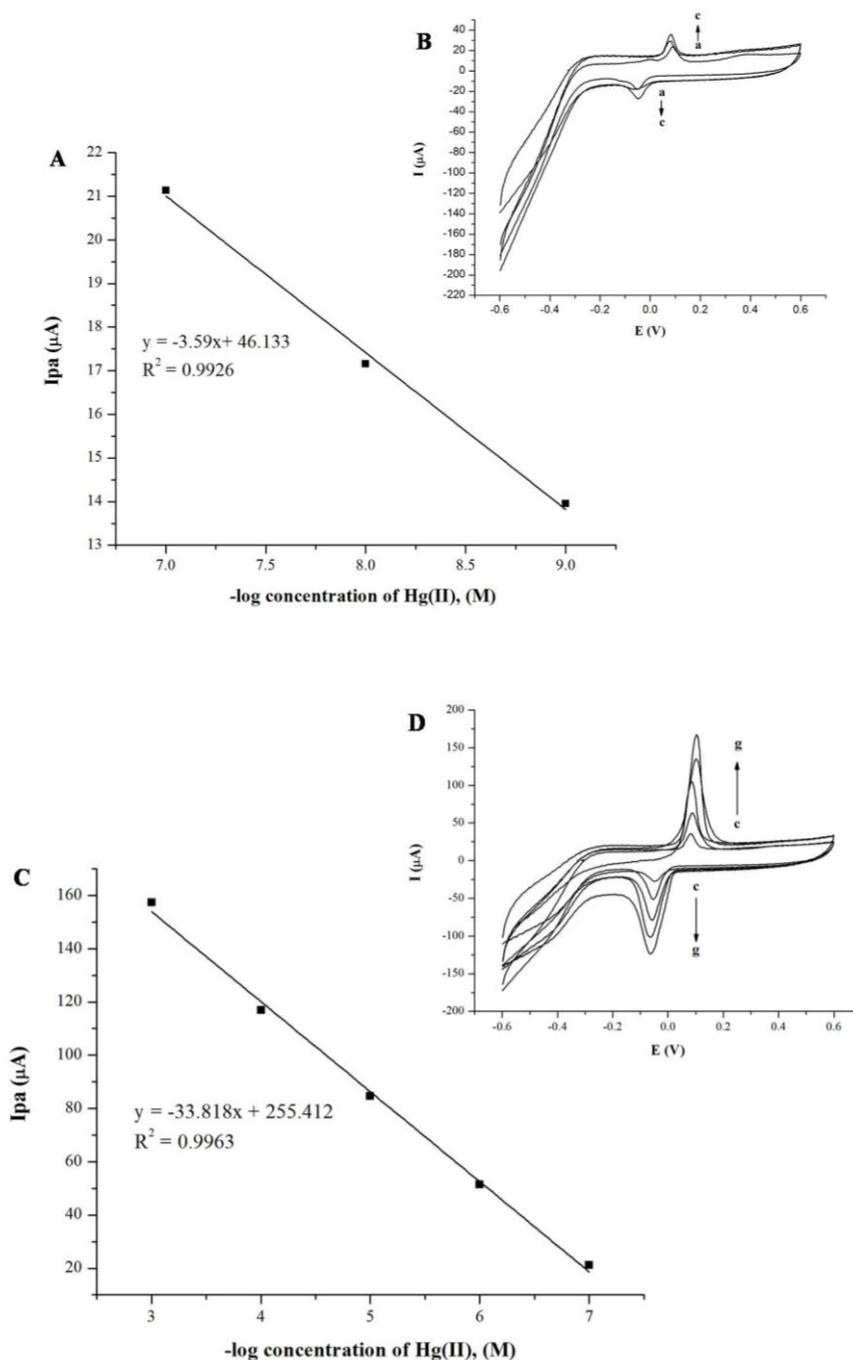


Figure 9. (A) Plot (1) of I_{pa} vs. $-\log$ [Hg(II)]; (B) CV (1) of (a) 1.0×10^{-9} M, (b) 1.0×10^{-8} M, (c) 1.0×10^{-7} M Hg(II) in 0.5 M KCl (pH 5.0), scan rate 100 mV s^{-1} at CMCNTPE; (C) Plot (2) of I_{pa} vs. $-\log$ [Hg(II)]; (D) CV (2) of (c) 1.0×10^{-7} M, (d) 1.0×10^{-6} M, (e) 1.0×10^{-5} M, (f) 1.0×10^{-4} M, (g) 1.0×10^{-3} M Hg(II) in 0.5 M KCl (pH 5.0), scan rate 100 mV s^{-1} at CMCNTPE.

It was not show a linear relationship after the concentration of 1.0×10^{-9} M Hg(II). The limit of detection (LOD) obtained is 5.0×10^{-10} M Hg(II). Table 2 is the comparison of some of the parameters of the CMCNTPE with some of other relevant electrodes. It can be seen from Table 2 that the LOD of the proposed method is comparable or better than other electrodes in the previous studies.

Table 2. Comparison of some of the parameters between the different paste electrodes in the determination of Hg(II).

Modifier	Electrode	Method	Concentration range (M)	Limit of detection (M)	Ref.
Nitro benzoyl diphenylmethylene-phosphorane (N-BDMP)	MCPE ^a	SWASV ^b	$4.98 \times 10^{-8} - 9.97 \times 10^{-6}$	4.09×10^{-8}	[4]
Crosslinked chitosan	MCNTPE ^c	LSASV ^d	$6.7 \times 10^{-9} - 8.3 \times 10^{-8}$	2.4×10^{-9}	[21]
Hybrid mesostructured silica nanoparticles	MCPE	SWASV	$2.5 \times 10^{-8} - 1.0 \times 10^{-6}$	2.3×10^{-8}	[44]
MWCNT and Schiff base	MCPE	SWASV	$2.0 \times 10^{-9} - 7.0 \times 10^{-7}$	9.0×10^{-10}	[45]
Nano-silica and Schiff base	MCPE	SWASV	$2.49 \times 10^{-9} - 4.98 \times 10^{-6}$	2.49×10^{-10}	[38]
Zn/Al-LDH-HPP	CMCNTPE	CV ^e	$1.0 \times 10^{-9} - 1.0 \times 10^{-7}$ $1.0 \times 10^{-7} - 1.0 \times 10^{-3}$	5.0×10^{-10}	This work

^aModified carbon paste electrode.

^bSquare wave anodic stripping voltammetry

^cModified CNT paste electrode

^dLinear sweep anodic stripping voltammetry

^eCyclic voltammetry

The repeatability of the response of the electrode was evaluated by performing five determinations in 2.0×10^{-4} M of Hg(II). The relative standard deviation (RSD) obtained for I_{pa} was 1.71 %. The reproducibility of the electrode was studied using four electrodes prepared in the same manner and they were then investigated for their responses in 2.0×10^{-4} M of Hg(II). The RSD of the responses between electrodes was 1.36 %. These RSD values indicate small relative errors in the measurements and the worthiness in the fabrication of the CMCNTPE developed.

3.10. Application on real samples

The Hg(II) in waste water samples was determined by standard addition method (Table 3). The recoveries in the range of 98.30 – 99.57 % indicate that the sensor is reliable for the determination of

trace amount of Hg(II) in waste water samples. The fabricated sensor was also assessed for Hg(II) content in fish and shellfish, result of which is compared with standard method (Table 4). There is no significant difference between results obtained by the two methods indicating the fabricated sensor is also suitable for the determination of trace amounts Hg(II) in marine animal samples.

Table 3. Recovery of Hg(II) in waste water samples (n = 3).

Sample	Measured (nM)	Added (nM)	Found (nM)	Recovery (%)
Waste water 1	8.80	10.0	18.63	98.07
Waste water 2	11.41	10.0	21.32	99.21
Waste water 3	8.12	10.0	17.81	96.18

Table 4. Validation of results by the proposed method to the standard method on the determination of Hg(II) in marine animal samples (n = 3).

Sample	Proposed Method	Mercury Analyzer
Fish 1	4.235 ± 0.077 µg/g	4.274 ± 0.078 µg/g
Fish 2	5.491 ± 0.025 µg/g	5.599 ± 0.041 µg/g
Shellfish	3.908 ± 0.053 µg/g	3.982 ± 0.083 µg/g

4. CONCLUSION

The developed CMCNTPE is useful for determination of Hg(II) at trace levels. It showed high selectivity for mercury in the presence of common potential metal ions, except Zn(II). The developed sensor is simple to prepare, sensitive, accurate and reliable which make it a strong choice as the alternative method for the determination of Hg(II) in real samples.

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