

## Sensory Measurement of Mercury and Cadmium Ions in Water Using Silicon Nanowires-Modified Screen Printed Carbon Electrode

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Modified screen printed carbon electrode (SPCEs) with silicon nanowires (SiNWs) were used as working electrode for the simultaneous detection of Hg(II) and Cd(II) ions in water. Linear sweep with anodic stripping voltammetry with optimum conditions of 0.05 M HCl as the supporting electrolyte,  $-1.2$  V deposition potential and 150 s deposition time were applied. The formed electrode material was thoroughly investigated for the morphology, effects of supporting electrolyte, deposition time and potential were well calibrated for the detection of Hg(II) and Cd(II) ions. The interference studies in the presence of other competitive ions in waste water such as Ni(II), Al(III),  $\text{SO}_3^-$ ,  $\text{SO}_4^{2-}$ , Mg(II), As(III), Zn(II) and Pb(II) indicated no significant interference, which reflects the availability of these species in the sample solution that did not affect the detection and measurement of Hg(II) and Cd(II) ions. However, Cu(II) presence found to affect the detection of Hg(II) or Cd(II) ions to some extent by suppressing the peak current. Further, the efficiency of the prepared electrode investigated by the testing of sea water samples and comparing its results against ICP-MS and AAS indicated that the screen printed carbon electrode can well be suited for the non-destructive measurement of Hg(II) and Cd(II) ions in real-time samples.

**Keywords:** Screen printing, Carbon electrode, Silicon nanowires, Mercury, Cadmium, Wastewater analysis.

### INTRODUCTION

In recent years, the increased level of heavy metals pollution in air, water and soil are mainly due to the rapid industrialization and the disposal of ever using consumer products filled with toxic metal contaminants. This includes the waste from industrial treatment processes such as the ceramics, semiconductors, metallurgical, pharmaceutical, agriculture and petrochemicals [1-3]. The toxic metal ions released from these industries such as mercury, arsenic, lead, cadmium, *etc.* are posing serious problems to the environment as well as to human health. The common problems associated with these heavy metal ions include the skin irritation, bone marrow suppression, chronic heart and lung diseases, neurological disorders and birth defects in newly born, to mention some. Considering the human targeted toxic reactions into account, the development of novel chemical/biosensors that can detect as well as measure even trace amounts of heavy metal contaminants in air, water and biological samples is of utmost importance.

Currently available spectroscopic techniques for heavy metal ion detection includes the inductively coupled plasma-mass spectrometry (ICP-MS) [4], surface-enhanced raman

scattering (SERS) [5] and cold vapour atomic fluorescence spectroscopy [6]. However, the high costs associated with the maintenance, expensive instrumental handling and the requirement of specialized personnel for the analysis *etc.* are especially limiting the frequent use of these techniques for day to day analysis [7,8]. For those means, developing a screen printed electrode (SPE) for the electro-analysis of heavy metal ion detection is of priority to many researchers in the past few years. This is due to the fact that the SPE has potentials to serve as an alternative to traditional electrodes in the development of analytical methods that respond to perform rapid *in situ* analyses. The other attracting features of SPE technique includes the low cost, ease of handling and sample preparation, avoiding the needs of surface cleaning, problems of memory effects and reliability of the measures without compromising the sensitivity or selectivity [9].

For the development of screen printed electrode, nano-materials offer unique features which influence the sensor performance and selectivity towards a specific group. The unique features offered by the nanomaterials for such applications include their chirality, size and composition. Thus, the SPE technique showed greater promises towards the detection of pollutants by amplifying the signals through the incorporation

of surface active nanomaterials for chemical marker analysis [10]. It was also observed that the modification of SPE with active surface plasmon resonance material such as gold nanoparticles proven to increase the sensitivity of detection system. Based on these factors, the present work is aimed to employ silicon nanowire (SiNW)-based SPE technique for the simultaneous detection and measurement of Hg(II) and Cd(II) ions. The superior features of silicon nanomaterial such as their stability, availability, easy preparation, electron mobility, voltage tunable behaviour, compatibility with other semiconductor/metal oxide materials are making us to choose this as a base material. Further, in this report, we discussed about the preparation and characterization of the developed chemical sensor of silicon nanowire/3-aminopropyl-triethoxysilane/screen printed carbon electrode (SiNWs/APTES/SPCE) for detection and measurement of Hg(II) and Cd(II) ions using linear sweep with anodic stripping voltammetry.

## EXPERIMENTAL

All chemicals used were of analytical reagent grade. Aqueous solutions were prepared with deionized water and the working solutions were prepared by dilution with ultrapure water obtained from a Milli-Q (Millipore) system. The poly-dispersed silicon nanowires (SiNWs) and 3-aminopropyl-triethoxysilane (APTES) were obtained from Sigma Aldrich (USA), while Cd(II) and Hg(II) standard solutions ( $1000 \text{ mol L}^{-1}$ ) were obtained from Fluka. The  $0.05 \text{ mol dm}^{-3}$  HCl solution, which served as a supporting electrolyte was prepared by the dilution of concentrated HCl (analytical grade, 37 %,  $1.19 \text{ g cm}^{-3}$ , Merck) with milli-Q water.

Linear sweep with anodic stripping voltammetry (LSASV) was carried out by using a computerized hand-held, battery-powered PalmSens portable electrochemical analyzer (Palmsens BV, The Netherlands) interfaced with a computer. The whole analytical procedure is controlled by the PalmSens PC software, including stirring of the samples by a hot plate magnetic stirrer. Screen-printed carbon electrode (SPCE) with three electrode strips were purchased from DropSens (Spain). These devices consist of a working electrode (4 mm diameter), a carbon auxiliary electrode and a silver pseudo-reference electrode printed on ceramic substrate. The metal ion concentration of a solution was determined using Inductively Coupled Plasma Mass Spectrometry, ICP-MS (ELAN DRC-e) Perkin-Elmer SCIEX and Atomic Absorption Spectroscopy, AAS (S Series GE712405 v1.30). The field emission scanning electron microscopy (FESEM) images were obtained by using Nova NanoSEM 230 with sputter coating and EDX analysis with Jeol JSM 7600F instrument.

**Preparation of modified electrode:** The SPCE was pretreated by dropping KOH (1 %) solution onto SPCE for 5 min and washed with deionized water to form hydroxyl groups on the electrode surface. About 3 mg of polydispersed SiNWs with 1 mL of 2 % APTES was sonicated for 60 min to get a homogenous mixture and the mixture was stable for several hours. However, overnight incubation led to the precipitation of the modified SiNWs solution. Then,  $2 \mu\text{L}$  of SiNWs and APTES mixture was dropped on the SPCE and dried at room temperature for 24 h. Later, the modified electrode was washed

with 95 % ethyl alcohol and baked in the furnace at  $75^\circ\text{C}$  for 30 min.

**Voltammetry technique:** The analysis of Hg(II) and Cd(II) using LSASV (linear sweep anodic stripping voltammetry) was carried out in a 10 mL of supporting electrolyte of 0.05 M with Hg(II) and Cd(II) analytes respectively. The following steps are applied for analyzing the sample: (a) in pre-conditioning step, a potential of 0.500 V *vs.* Ag/AgCl was applied for 5 s before each measurement to ensure the dissolution of remaining deposits on the surface of the modified electrode; (b) then the step proceed to deposition potential at  $-1.200 \text{ V vs. Ag/AgCl}$  for 150 s; at the end of the deposition time, stirring was stopped and a 5 s rest period was allowed for the solution to become quiescent; (c) the linear sweep with anodic stripping voltammograms were recorded when the potential was swept from  $-0.500$  to  $+0.500 \text{ V vs. Ag/AgCl}$ . In the deposition processes, the detection solutions were stirred with a magnetic stirrer and the experiments are carried out at ambient temperature ( $25 \pm 1^\circ\text{C}$ ).

## RESULTS AND DISCUSSION

The morphology of the SPCE before and after the modification was thoroughly characterized with FESEM. Fig. 1 shows the SEM images of unmodified (a) and SiNWs/APTES-modified (b) SPCE. From the comparison of both the images, one can clearly see the successful attachment of nanoparticles on the working area of SPCE with that of SiNWs and the bonding is assumed to be a covalent. Fig. 1(b) also shows that the randomly decorated silicon particles on the SPCE provide the information that the SiNWs are falling within the nanosized range.

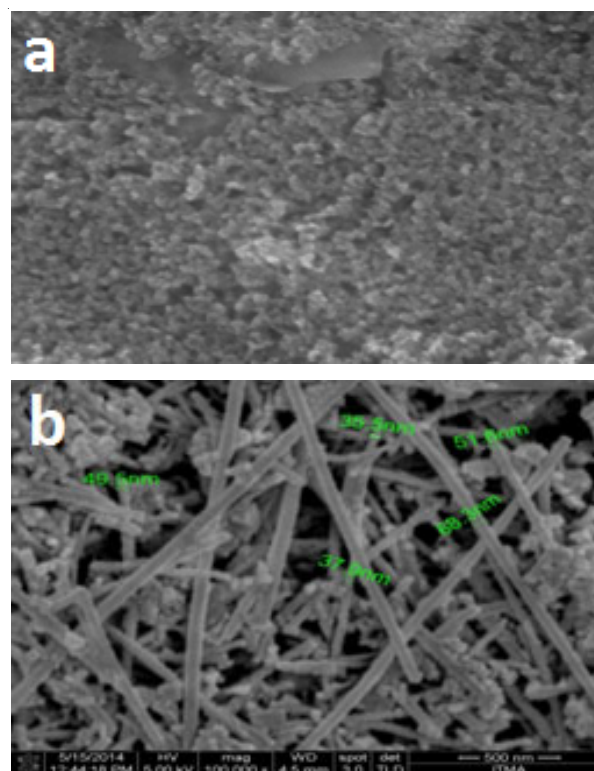


Fig. 1. FESEM images of (a) unmodified and (b) SiNWs/APTES-modified SPCE

**Effect of supporting electrolyte:** Preliminary experiments were carried out with four different supporting electrolytes: HCl,  $\text{KNO}_3$ , acetic buffer and KCl. It was observed among those four solutions that the highest peak currents and well-defined peak shapes were obtained for only HCl solution. Hence, HCl was chosen as ideal for all our subsequent studies and is also widely recommended electrolyte solution for heavy metal detection in the majority of studies elsewhere [11]. Fig. 2 shows the effect of varying HCl concentration on the current signals obtained for Hg(II) and Cd(II) ions when evaluated in the range of 0.01-0.1  $\text{dm}^{-3}$  HCl.

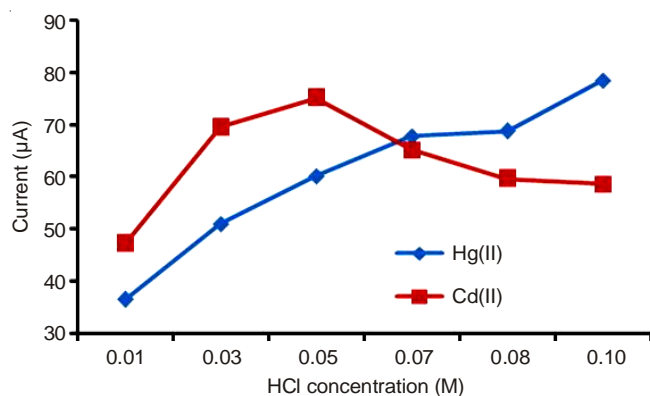


Fig. 2. Effect of HCl concentration on the peak current of Hg(II) and Cd(II) in the solution of 100 ppm each of Cd(II) and Hg(II). Deposition time: 120 s; Deposition potential: -1.2 V

From Fig. 2, it can be seen that the trend for Hg(II) ions is proportionally increased with regards to an increase in HCl concentration. In general for many electrochemical systems, it is desirable to have excessive non-conductive ionic species so as to increase the conductivity of the electrolytes and also to decrease the electrical drifts of the electroactive species. However, the increased concentration of HCl also contributed for an increased current to some extent only for Cd(II) and further increase of HCl levels gave rise to a drop-down in the sensitivity of Cd(II) ionic current. The occurrence of this phenomenon can be explained with an assumption that there exists a reduction in the bond strength between the metal and substrate by means of over increased chloride ion levels [12-14]. At upper concentrations of HCl, the excess  $\text{Cl}^-$  ions would form coordinate complexes with Cd(II) ions, resulting in a decrease of its peak current. Hence, for further studies, the optimum concentration of HCl selected are 0.05 M for the simultaneous analysis of Hg(II) and Cd(II); consequently, a 0.05  $\text{mol dm}^{-3}$  HCl was selected as optimum supporting electrolyte.

**Deposition potential:** Anodic stripping voltammetry involves the analytes that are pre-concentrated on the working electrode during a deposition step and then oxidized at the electrode in the stripping step. In this way, the pre-concentration conditions have a significant impact on the analyte stripping signals. Fig. 3 shows the effect of deposition potential on the stripping peak currents of the solution of 100 ppm each of Hg(II) and Cd(II) ions in 0.05 M HCl when studied in the range -1.0 to -1.4 V vs. Ag/AgCl. From the graph shown in Fig. 4, the current seems to be increased with an increase of the negative deposition potential; however, at more negative

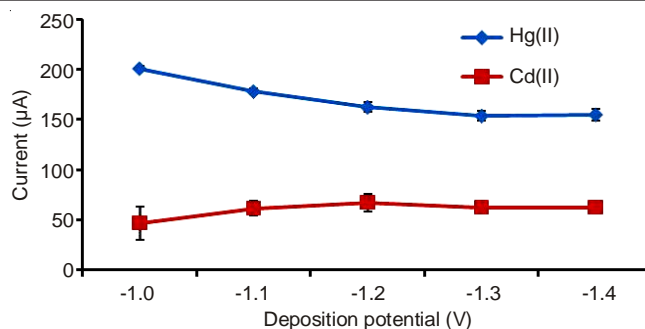


Fig. 3. Effect of deposition potential on the peak current of Hg(II) and Cd(II) in the solution of 100 ppm each of Cd(II) and Hg(II)

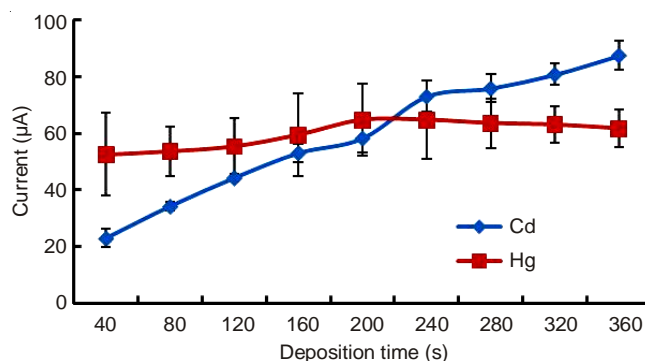


Fig. 4. Effect of deposition time on the peak current of Hg(II) and Cd(II) (5 ppm each of solution). Deposition potential: -1.2 V

direction, this reduction in current is less because of the hydrogen evolution and the deposition of metals on the electrode surface [15].

**Deposition time:** The effect of peak current as a function of deposition time for the Hg(II) and Cd(II) solutions are shown in Fig. 4. It is observed that the peak current is increasing with an increased order of deposition time as expected to the influence of accumulation time when studied from 40-360 s, the stripping peak currents increased greatly for the Hg(II) ions than the corresponding Cd(II). However for the purpose of applications, the short time analysis is much preferred and thus, a 150 s time period was selected as standard for all the subsequent analyses. The other reason for choosing the 150 s period is that for the studies where the deposition time is longer than 150 s, the amount of Hg(II) deposited on the electrode is not getting completely removed during the stripping step and this further responsible for the worsening in the repeatability of subsequent analyses [16].

**Comparison study:** Fig. 5 shows the comparison of the LSASV voltammograms for the unmodified (a) and modified (b) SPCE of the Hg(II) and Cd(II) ions, respectively. From the Fig. 5A, the peak appeared in the LSVAS is due to an anodic process of Hg(II); the deposition of mercury was observed at -1.2 V for a 150 s period in 0.05 M HCl by the reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  and further oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  at a potential of +0.104 V. Similarly, Fig. 5B shows a peak in the LSVAS due to an anodic process of Cd(II). The deposition of cadmium was observed at -1.2 V for a 150 s period in 0.05 M HCl by the reduction of  $\text{Cd}^{2+}$  to  $\text{Cd}^0$ , then further oxidation of  $\text{Cd}^0$  to  $\text{Cd}^{2+}$  at a potential of -0.816 V. The redox reaction involved during the stripping analysis is given by the eqns. 1 to 4 for the formation of Hg(II) and Cd(II) ions.

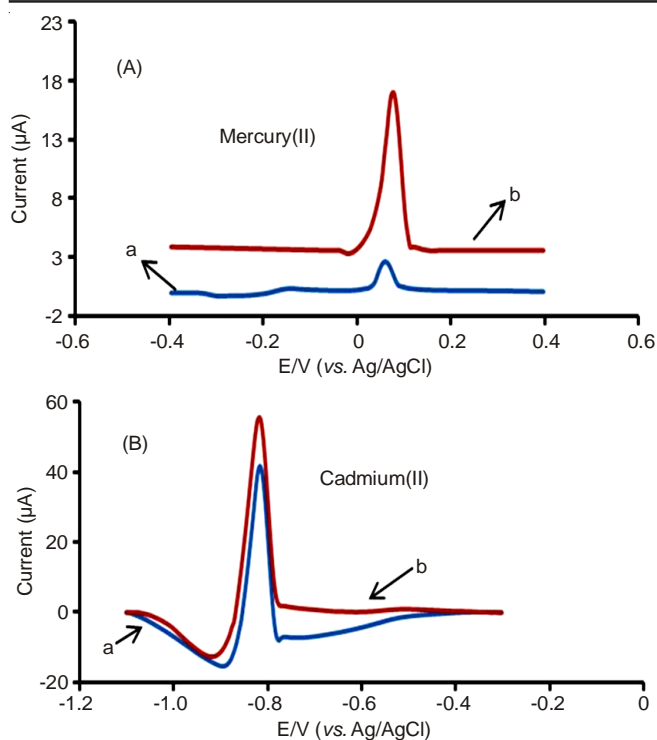
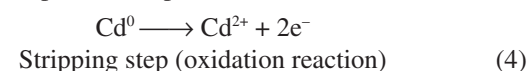
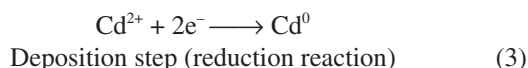
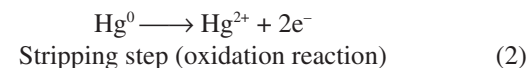
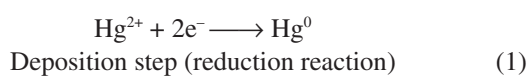


Fig. 5. Comparison of LSASV voltammograms for (a) unmodified and (b) SPCE/SiNWs modified in 10 mg/L of (A) Hg(II) and (B) Cd(II) at 0.05 M HCl concentration, deposition potential: -1.2 V, deposition time: 150 sec, potential scanning in positive direction from -1.1 V to -0.3 V vs. Ag/AgCl at a scan rate 100 mV s<sup>-1</sup>



Further, Figs. 5(A-B) showed a significant increase in the current from the voltammograms of SPCE/SiNWs modified SPCE than that of the unmodified one. Also, for both the solutions, the LSASV of bare SPCE (curve a) showed a low oxidation peak as compared against the modified electrode of SPCE with SiNWs (curve b). Eqn. 5 was used to calculate the enhancement factor for the modified and unmodified SPCE. From the analysis, the SPCE/SiNWs showed a 4.4 times increment for Hg(II) and 1.12 times for Cd(II).

$$\text{Enhancement factor} = \frac{\text{pa (modified)}}{\text{pa (unmodified)}} \quad (5)$$

**Calibration study:** Calibration graphs were constructed under the optimum conditions described earlier using SPCE/SiNWs: LSASV with deposition potential: -1.2 V, deposition time: 150 s and a scan rate 100 mV s<sup>-1</sup> in 0.05 M HCl as the supporting electrolyte. Figs. 6 and 7 show the voltammograms for different concentrations of Cd(II) and Hg(II), respectively obtained under the optimum conditions and the characteristics of calibration graphs are given in Table-1. The limit of detection (LOD) is defined as LOD = 3 Sb/m, where Sb and m are the

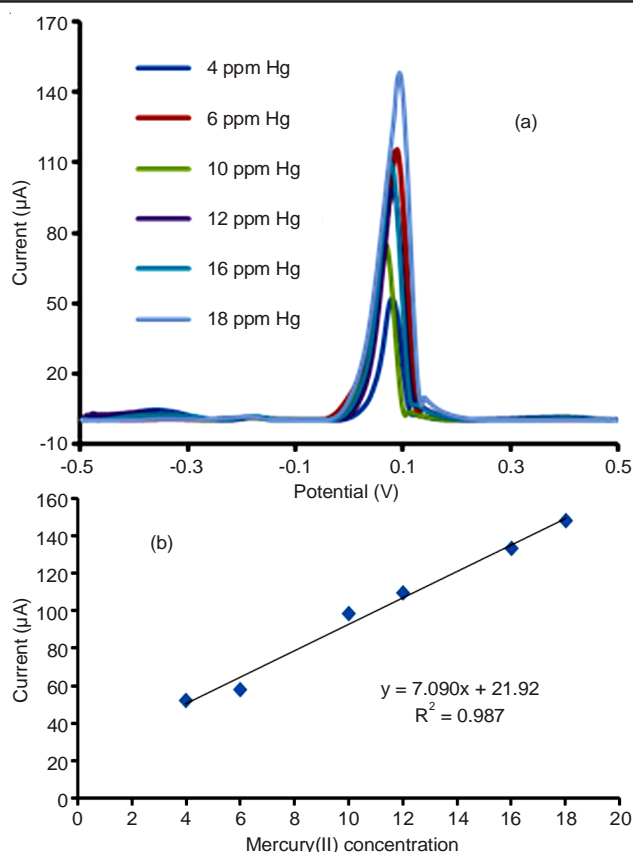


Fig. 6. (a) Voltammogram of linear sweep with anodic stripping voltammetry of Hg(II) and (b) current versus concentration of Hg(II) in range of 4-18 ppm under optimum conditions

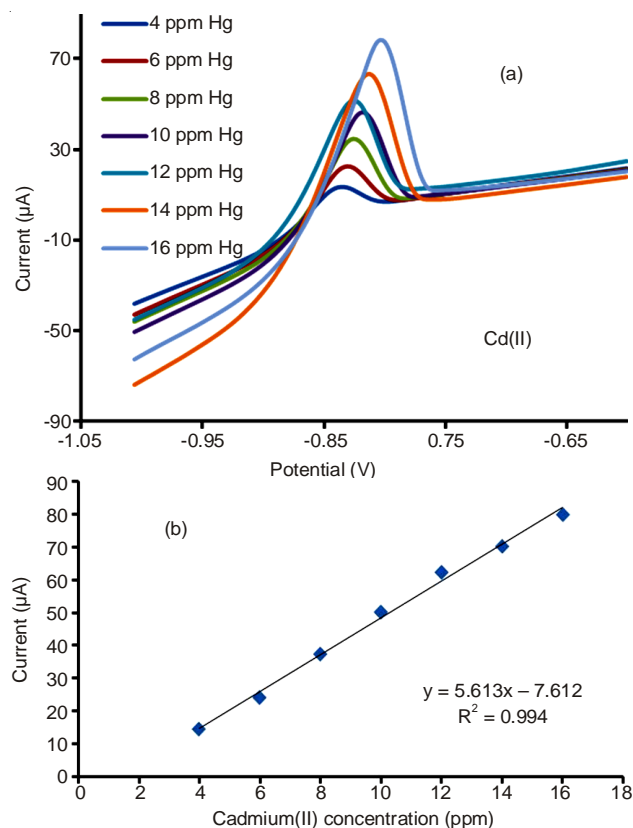


Fig. 7. (a) Voltammogram of linear sweep with anodic stripping voltammetry of Cd(II) and (b) current versus concentration of Cd(II) in range of 4-18 ppm under optimum conditions



TABLE-1  
SUMMARY OF DETECTION LIMIT FOR Hg(II) AND Cd(II) FOR MODIFIED SiNWs/SPCE UNDER OPTIMUM CONDITIONS WITH LSASV

Electrode	Analyte	R <sup>2</sup>	Detection limit (µg L <sup>-1</sup> )
SiNW's/SPCE	Hg <sup>2+</sup>	0.987	42.59
	Cd <sup>2+</sup>	0.994	25.17

standard deviation of blank and the slope of calibration graph, respectively. Sb was estimated by 3 replicate determinations of the blank signals.

The linear sweep with anodic stripping voltammetry of Hg(II) at various concentrations in the range of 4-18 ppm is shown in the Fig. 6a. The figure showed, it can be seen that the current is getting increased with an increase of Hg(II) concentration. Also from Fig. 6b, the correlation coefficient obtained to be 0.987 with the detection limit of 42.59 µg L<sup>-1</sup>. Similarly, the linear sweep with anodic stripping voltammetry for Cd(II) ions at various concentrations (4-16 ppm) is shown in Fig. 7a and 7b, the correlation coefficient obtained to be 0.994 with the detection limit of 25.17 µg L<sup>-1</sup>.

Fig. 8 shows the voltammograms of the metallic mixture of 10 ppm of Cd(II) and varying concentrations of Hg(II) ions (10-20 ppm range). From the figure, the graph represents a well-developed, separated stripping peaks for Hg(II) ions in accordance with the concentration even in the presence of Cd(II) ions. From the analysis, the characteristic peaks of Cd(II) and Hg(II) were observed at -0.816 V and +0.104 V, respectively.

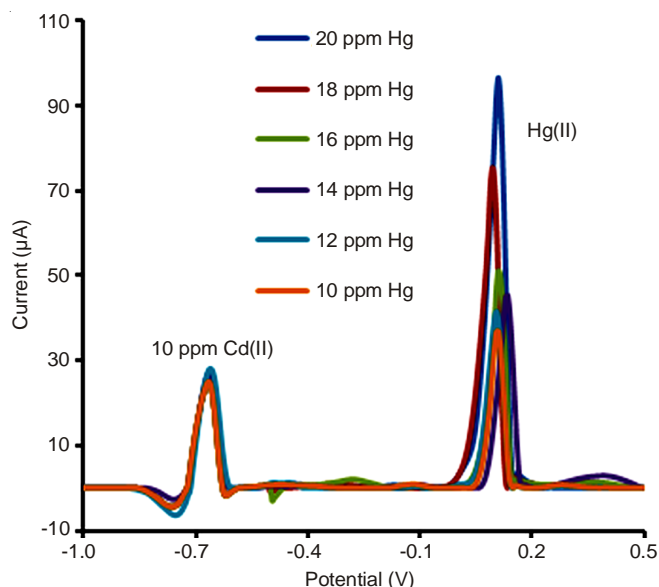


Fig. 8. Voltammogram of simultaneous detection of Cd(II) and Hg(II) ions when used a mixture containing the constant concentration of Cd(II) (10 ppm) and varying concentrations of Hg(II) ions (10-20 ppm)

**Interference study:** Studies of the possible interference from foreign ions that exists in natural water have been carried out as these interfering ions can deposit on the modified electrode. The possible interfering ions such as Ni(II), Mg(II), Cu(II), Zn(II), Pb(II), Al(III), As(III), SO<sub>4</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> are chosen based on their abundance in environmental samples. For the analysis, the effect of various foreign ions during the determination of 10 ppm each of Hg(II) and Cd(II) was studied by using SiNWs/SPCE in 0.05 M HCl. The degree of interference was studied at 1:1 concentration of Hg(II)/Cd(II) : foreign substances and the results are given in Table-2. The presence of Cu(II) in sample solution was found to completely suppress the peak current and is probably due to the formation of an intermetallic compound between copper and cadmium or mercury deposited on the electrode in accordance with eqns. 6 and 7 [17]. The interference of Cu(II) with the stripping analysis of Cu(II) or Hg(II) is due to the formation of mercury film during the reduction step. However, the presence of other competitive metal ions such as Ni(II), Al(III), SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, Mg(II), As(III), Zn(II) and Pb(II) indicated no significant interference, means that the availability of these species in the sample solution did not affect the determination of Hg(II) and Cd(II) ions [18].

TABLE-2  
INTERFERENCE STUDY IN PRESENCE OF VARIOUS COMPETITIVE FOREIGN IONS

Foreign metal ions	Interference (%)	
	Hg(II)	Cd(II)
Ni(II)	6.94	27.13
Al(III)	8.50	46.48
SO <sub>3</sub> <sup>2-</sup>	15.82	11.70
SO <sub>4</sub> <sup>2-</sup>	37.74	25.23
Mg(II)	54.06	-3.53
As(III)	0.53	36.60
Cu(II)	288.24	100.00
Zn(II)	34.97	57.35
Pb(II)	49.43	31.40

**Analytical application of developed electrode:** The applicability of SiNWs/APTES/SPCE for the analysis of real sea water samples were tested and the results are summarized in Table-3. The samples collected for the analysis were tested without any further treatment. From the table, the results obtained by this method show a good agreement with those obtained by AAS for the Cd(II) sample and ICP-MS for the Hg(II) sample. The results therefore confirming the applicability of the proposed method during the determination of Cd(II) and Hg(II) ions in real water samples.

## Conclusion

In conclusion, we reported that the modified screen printed electrode was successfully applied for the determination of

TABLE-3  
DETERMINATION OF Hg(II) AND Cd(II) ION CONCENTRATION IN SEA WATER USING SiNWs/SPCE IN 0.05 M HCl AS SUPPORTING ELECTROLYTE

Sample	Analyte	Added (ppm)	Found	Recovery (%) (Developed method)	Detection
Sea water	Cd(II)	0.8	0.89 ± 0.09	111.00 ± 11.54	0.800 ± 0.03 (AAS)
Sea water	Hg(II)	0.4	0.47 ± 0.10	119.45 ± 23.09	0.476 ± 0.03 (ICP-MS)

Hg(II) and Cd(II) ions. The optimum conditions for the electrode include the 0.05 M HCl as the supporting electrolyte, –1.2 V deposition potential at a deposition period of 150 s. The interference studies carried with the prepared electrode gives a proof for the detection of Cd(II) and Hg(II) ions even in the presence of other competitive ions in water samples such as Ni(II), Al(III),  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , Mg(II), As(III), Zn(II) and Pb(II), with an exception to only Cu(II) ions. Also, the electrode is no way lesser to other instrumental analysis such as ICP-MS and AAS in terms of efficiency towards the detection of the same Cd(II) and Hg(II) ions, meaning that one can achieve the same results even with the use of our simple, fast, portable and economical electrode. Thus the easily prepared modified electrode, has an extra edge than the conventional electrodes and proved to be a selective electrode for Hg(II) and Cd(II) ions in linear scan anodic stripping voltammetry with satisfactory results.

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