

A Highly Sensitive Electrochemical Sensor For Cd (II) Ions By Anodic Stripping Voltammetry Using Carbon Nanotubes And Salicylidene-2-Aminobenzylalcohol (SABA) Modified Electrode

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Abstract: The aim of the present work is to develop a chemically modified electrode with carbon nanotubes (CNTs) and a Schiff base namely salicylidene-2-aminobenzyl alcohol (SABA) for determination of Cd (II) ions using square wave anodic stripping voltammetry. The ligand, SABA has been characterized by Ultraviolet-Visible (UV-VIS) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, Nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). It has been found that the electrode coated with CNT and Schiff base ligand has shown a better performance than the mere CNT coated electrode. Operational parameters such as supporting electrolyte, pH and preconcentration time have been optimized for the anodic stripping analysis of Cd (II). The anodic stripping of Cd(II) ions was observed at - 0.7V. The stripping current was found to increase with increase in concentration of Cd(II) ions in solution. Under optimal conditions the linear range was from 3.7nM to 250nM and the limit of detection was 1.2nM ($S/N \geq 3$). This sensor was successfully applied to determine Cd(II) ions in real samples with good recovery ranging from 98 -103%. The analytical performance of the as-fabricated electrochemical sensor is superior to most of the existing sensors.

Keywords: Chemically modified electrode, Carbon nanotubes, salicylidene-2-aminobenzyl alcohol (SABA), Cadmium, anodic stripping voltammetry.

I. INTRODUCTION

Carbon nano tubes (CNTs) represents an increasingly important group of nano materials with fascinating structural and unique morphological, geometrical, mechanical, electrical and electrochemical properties [1, 2-7]. CNTs have been widely used for the development of chemically modified electrodes as it provides high electrical conductivity, chemical stability, mechanical strength and enhanced sensing capabilities of sensors and biosensors [8, 9]. Recently, numerous investigations have been carried out to find applications of CNTs for hydrogen storage [10], quantum wire [11], electron field emission sources [12], and electronic equipments. Moreover, in Electroanalytical methods, the use

of CNTs as the electrode material could greatly enhance the voltammetric response for determination of organic [13, 14] and inorganic analytes [15, 16]. CNT modified electrode arrays with bismuth has been employed as an excellent electrochemical sensing platform for voltammetric analysis [17].

Cadmium is known as an environmentally unfriendly material with toxic effects on living organisms due their non – biodegradability [18]. Long term intake of cadmium increases the risk of cancer, renal tubular dysfunction, bone degeneration and even cause an epidemic of bone diseases (itai – itai diseases) [19]. Heavy metals always coexist with Tibetan medicine which consists of herbs and minerals to treat sickness. The United Nations environment programme

proposed that the cadmium ranked first for its high toxicity which has been also reported to be a threat to the global safety [20].

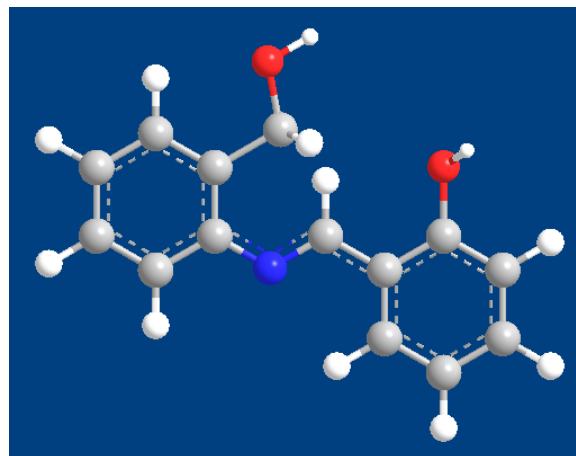
Various methods of heavy metals analysis include atomic absorption (AAS) [21, 22], inductively – coupled plasma atomic emission spectrometry (ICP-AES) [23], atomic fluorescence spectrometry [24] and inductively – coupled plasma mass spectrometry (ICP- MS) [25]. These methods provide excellent precision and good resolution, but they are more expensive, difficultly to handle and require high cost operations etc. Therefore, electrochemical methods are promising tools for their speed, low – cost, simplicity, high sensitivity and the capability of monitoring the environmental samples.

In recent years, chemically modified electrodes have been developed for the electrochemical determination of toxic metal ions due to various advantages such as high sensitivity, low detection limits, renewable, fast response and high selectivity [26]. Therefore chemically modified electrodes have attracted much attention in field of electroanalytical technique for determination of heavy metal ions.

In stripping voltammetry, mercury has been widely used as the working electrode owing to its tendency to form amalgam with reduced metals. However, the toxicity of mercury excludes its application as working electrode in stripping analysis and hence attempts have been made to introduce mercury - free electrodes in stripping analysis. Anodic stripping voltammetry (ASV) is the most sensitive and selective method for determination of heavy metal ions. These techniques are based upon the accumulation step of the metal ions with suitable ligands and then stripping the metal anodically after reduction of metal ion at suitable potential. For stripping voltammetric determination of cadmium, various solid electrodes such as glassy carbon electrode [30], gold electrode [31], platinum electrode [32, 33] and graphite electrode [34] have been reported.

Salicylidene-2-amino benzyl alcohol (SABA) is a schiff base ligand prepared by condensation of salicylaldehyde and 2- amino benzyl alcohol. It has fluorescence properties and its biological activity has been reported for antimicrobial, antibacterial, antifungal, anti- inflammatory, anti –convulsant, antitumor and anti HIV activities [35].

In this work, we report the development of a chemically modified electrode (CME) consisting of carbon nanotubes and salicylidene-2-aminobenzylalcohol (SABA) ligand for the determination of Cd (II) ions by anodic stripping voltammetry (ASV). To the best of our knowledge, there is no report available on the carbon nanotube and salicylidene-2-aminobenzylalcohol (SABA) ligand modified electrode for the determination of Cd(II) ions. The modified electrode has shown better sensitivity and selectivity for determination of Cd (II) ions. The modified electrode has been successfully applied for determination of Cd (II) ions in real samples



Structure of the Salicylidene-2-aminobenzylalcohol (SABA) ligand

II. EXPERIMENTAL

A. CHEMICAL AND REAGENT

Graphite rods (3mm diameter), Carbon nano tubes (CNT) and 2-aminobenzylalcohol were all purchased from Sigma Aldrich. Salicylaldehyde, Cadmium acetate and Sodium nitrate were purchased from SRL. Stock solution of Cadmium acetate (0.001M) was prepared by directly dissolving Cadmium acetate in water. Sodium nitrate solutions (0.1M) with different pH values from 3.5 to 6.5 were prepared with sodium hydroxide and nitric acid. All other chemicals and reagents were of analytical grade and used as received. All the solutions were made with doubly distilled water.

B. INSTRUMENTATION

The voltammograms were obtained on a CHI 660B electrochemical workstation with a three electrode system. The bare / modified electrode was used as the working electrode, platinum electrode as counter electrode and SCE as the reference electrode. pH measurements were made with a Digital pH meter (Digisun electronic system). All the experiments have been carried out at ambient temperature. UV-Vis spectrometer (Diode Array 8453 Model) was used to record the electronic spectra of ligand. FT-IR (Agilent Model) was used for recording IR Spectrum of the ligand. NMR Spectra of the ligand was recorded using CDCl₃ NMR spectrometer (Bruker). The surface morphology of the electrodes was studied using SEM (Hitachi Sv-6600 microscope, Japan).

C. SYNTHESIS OF SALICYLALDEHYDE-2-AMINO BENZYLALCOHOL [SABA] LIGAND

The ligand was prepared as reported earlier [36] with a slight modification. An ethanolic solution (30ml) of 0.04mmol of salicylaldehyde was added with 0.04mmole of 2-aminobenzylalcohol drop by drop with stirring. The above mixture was stirred for 2hrs and the yellow greenish solid

obtained was filtered, washed thoroughly with ethanol, recrystallised from methanol and dried in vacuum.

D. FABRICATION OF CNT / SABA LIGAND MODIFIED ELECTRODE

Paraffin wax impregnated graphite electrodes (PIGE) have been used for electrode modification. The graphite rods have been impregnated with paraffin wax following the procedure developed by Scholtz et al. Soft graphite rods of 3mm diameter and 5cm length were put into molten paraffin under vacuum until air bubbles cease to evolve from the rods. After re-establishing the atmospheric pressure the rods were removed before the paraffin solidifies. The PIGEs were then polished to a mirror like finish by rubbing over a fine quality emery paper. The polished surface was then washed with methanol and rinsed thoroughly in distilled water. The electrodes were then polished with emery paper and then with 0.5 μ alumina silica washed with distilled water and dried in air. About 0.1mg CNT was dispersed in 1ml of ethanol and 10 μ l of dispersion was dropcasted on the electrode surface. Then, the SABA ligand was dissolved in ethanol and then 10 μ l of 1mM ligand was drop casted on the CNT modified electrode surface and dried in air.

E. ELECTROCHEMICAL MEASUREMENTS

Square wave anodic stripping voltammetry (SWASV) was employed for the successive determination of Cd(II) ions under the optimised conditions. A known amount of Cd(II) ions was first preconcentrated by immersing the electrode into 0.1M NaNO₃ solution containing 40nM Cd(II) ions under stirred condition for 4min. Then Cadmium was deposited at the potential of -1.2V for 60s in 0.1M NaNO₃ solution by reducing Cd(II) to Cd(0). The anodic stripping of electrodeposited Cd(0) was performed by the scanning the potential from -1.2 to -0.4V with optimized parameters (Frequency = 40Hz, amplitude=25mV, potential increment =4mV). The electrode was cleaned free of metal ion by immersing in 0.01M EDTA solution for 2min until the anodic stripping response disappeared.

III. RESULTS AND DISCUSSION

A. CHARACTERISATION OF CNT / SABA LIGAND

The synthesised ligand was characterised by UV-Vis, FT-IR and NMR spectroscopy. The Carbon nanotubes / Salicylaldehyde-2-aminobenzylalcohol [SABA] modified electrode was characterized by scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and Square wave anodic stripping voltammetry (SWASV). The UV-VIS spectra of the SABA ligand are shown in Fig.S1. The ligand shows three bands at 241, 270 and 341 which are assigned to π - π^* transitions of aromatic rings. The FT-IR of the ligand is shown in Fig.S2. The strong absorption at 3274 cm⁻¹ is attributed to the presence of hydroxyl group. The absorption peak at 1613cm⁻¹ is assigned to presence of C=N group. The proton NMR spectra of the ligand is shown in

Fig.S3. The spectroscopic results of ligand and metal complexes are in conformity with previous report [37]. The chemical shift for the OH proton is observed at 13.07ppm and aromatic protons appear in the range 6.87- 7.47 and a sharp singlet peak for CH=N proton is seen at 8.55ppm. The surface morphology of the CNT and ligand modified electrode was studied by SEM and the image obtained is shown in Fig.1. A flexible crystallite shaped structure was seen for the CNT and ligand on the modified surface and for the comparison CNT modified electrode structure is also shown which shows spherical surface.

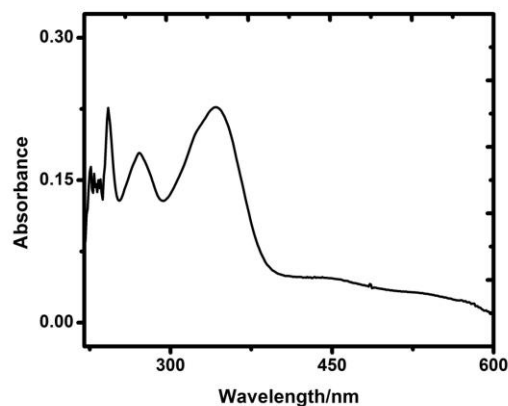


Figure S1: (a) UV-Vis spectra of Salicylidene -2-aminobenzyl alcohol (SABA) ligand

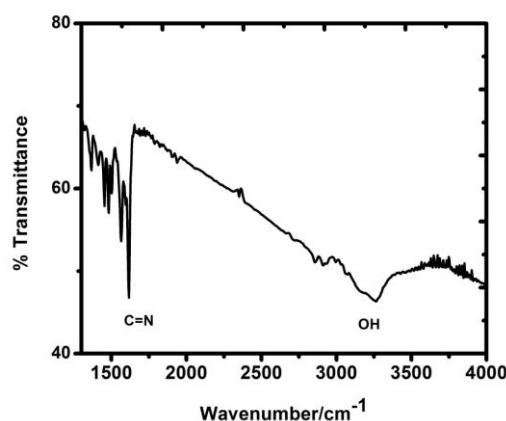


Figure S2: FT-IR Spectrum of Salicylidene -2-aminobenzyl alcohol (SABA) ligand

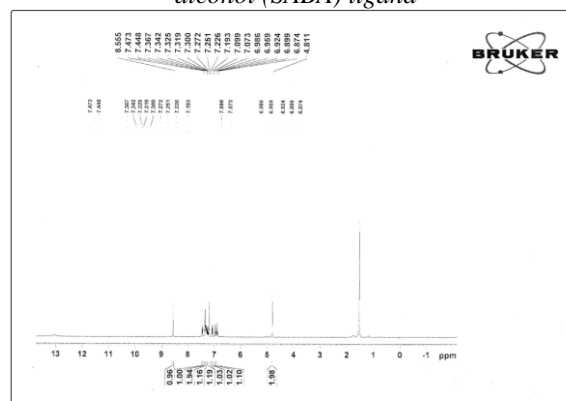


Figure S3: NMR spectrum of Salicylidene-2-aminobenzyl alcohol (SABA) ligand

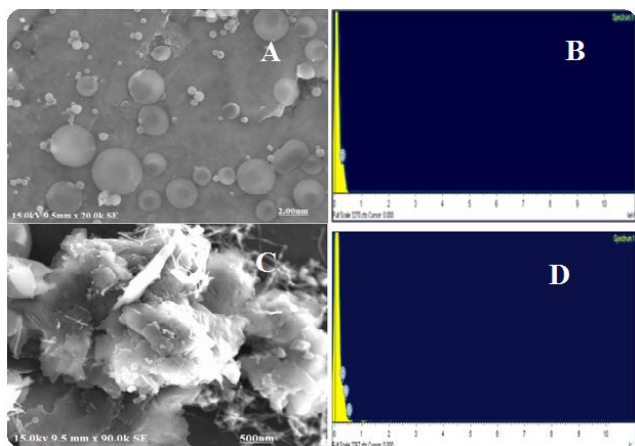


Figure 1: FESEM and EDAX image for bare electrode (A and B) and CNT and SABA ligand (C and D)

B. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDIES (EIS)

Electrochemical impedance spectroscopy (EIS) was used to investigate the surface of the modified electrode at the electrode-electrolyte interface. Fig.2. Shows the Nyquist plots of the electrochemical impedance study for the unmodified and modified electrode for 5mM $[Fe(CN)_6]^{3/4-}$ in 0.1M acetate buffer solution. A semicircular element with a large diameter, corresponding to the charge transfer resistance R_{ct} at the electrode surface was observed for the bare electrode in the frequencies ranging from 0.1Hz to 1.0MHz. However, the diameter of the semicircle diminished when modified electrode was employed. Further, the charge transfer resistance (R_{ct}) for mere CNT electrode was estimated to be $215 K\Omega cm^{-2}$ and for CNT and ligand coated electrode, the charge transfer resistance was $168 K\Omega cm^{-2}$. The schematic representation of the modified Randle's equivalent circuit for this CNT and SABA ligand modified electrode is shown in the inset. The impedance data obtained for modified electrode shows a lower resistance to the charge transfer kinetics which confirms that this modified electrode is a very attractive one for the electron transfer reactions.

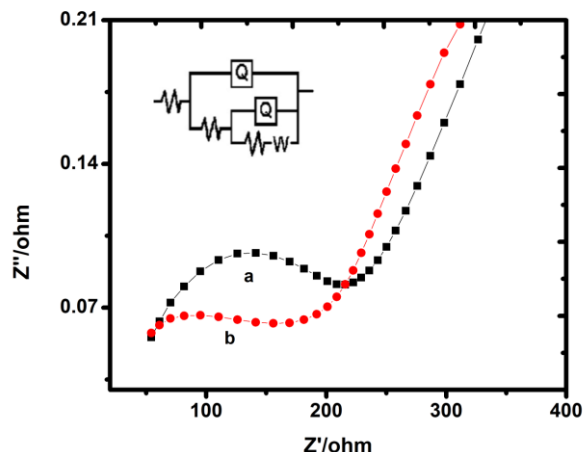


Figure 2: Impedance plots of bare electrode (a) and CNT and SABA ligand modified electrode (b) with 5mM $K_4[Fe(CN)_6]$ in 0.1M acetate buffer. Inset: Randles equivalent circuit

C. ELECTROCHEMICAL BEHAVIOUR OF CD(II) IONS

To study the effect of the modified electrode for the stripping analysis of Cd(II) ions comparing the bare electrode, experiments have been performed like preconcentration, reduction and stripping of 40nM of Cd(II) ions. The results obtained with the stripping analysis are shown in Fig.3. It is clearly seen from figure that an enhanced anodic current for the modified electrode is observed indicating that the presence of the CNT and SABA ligand enhances the amount of Cd(II) ions in the deposition steps, due to the complexation with the ligand than the unmodified electrode. Thus, it can be confidently stated that the ligand present on the electrode surface complexes with the metal ion in the deposition step and thus enhances the sensitivity of the method for the determination of the Cd(II) ions. The mechanism of Anodic stripping voltammetry for determination of Cd(II) ions with CNT and SABA ligand modified electrode is explained in the following steps:

- ✓ Preconcentration step (0.1M $NaNO_3$, for 4min pH-5.5)
 $CNT/SABA_{surface} + Cd(II)_{aqueous} = CNT/SABA-Cd(II)_{surface}$ [Complex formation]
- ✓ Reduction step (0.1 M $NaNO_3$, pH-5.5, -1.2V)
 $CNT/SABA_{surface} - Cd(II) + 2e^- = CNT/SABA-Cd(0)_{surface}$ [Reduction step]
- ✓ Stripping step (closed circuit, 0.1M $NaNO_3$, pH-5.5)
 $CNT/SABA-Cd(0)_{surface} - 2e^- = CNT/SABA - Cd(II)_{surface}$ [Stripping]

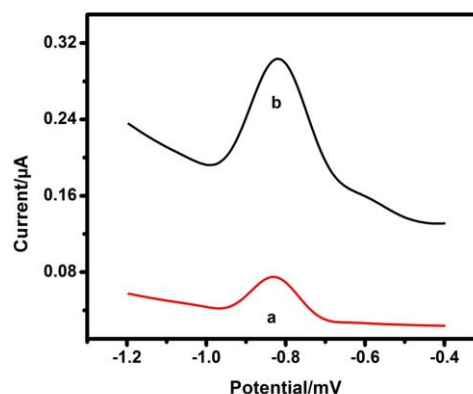


Figure 3: Stripping current of 40nM for Cd(II) ions at bare (a), modified electrode (b) in 0.1M $NaNO_3$. Preconcentration time: 240s, deposition potential: -1.2V, Amplitude: 50mV

D. OPTIMIZATION OF EXPERIMENTAL CONDITIONS

In order to obtain the highest sensitivity for the electrochemical determination of Cd(II) ions by CNT/SABA ligand modified electrode various parameters such as supporting electrolyte, effect of pH, preconcentration time and stripping medium were optimized.

a. EFFECT OF pH, SUPPORTING ELECTROLYTE AND PRECONCENTRATION TIME

The preconcentration of Cd(II) ions on the modified electrode was studied using different supporting electrolytes of

0.1M solution such as KNO_3 , NH_4NO_3 , $NaNO_3$ and acetate buffer. Fig.4 (A) shows the stripping voltammogram for Cd (II) ions which was preconcentrated from these different media. From the figure, it is found that 0.1M $NaNO_3$ is the most suitable medium for preconcentration of Cd (II).

The effect of pH on the preconcentration of Cd(II) ions on the modified electrode in 0.1M $NaNO_3$ medium solution was studied in the pH range 3.5 to 6.5 and the result obtained are shown in Fig.4(B). It seen from the figure that a pH 5.5 is most suitable for the preconcentration of Cd (II) ions of the electrode surface.

The preconcentration time was optimized by complexing Cd (II) ions on the electrode surface from 0.1M $NaNO_3$ solution of pH 5.5. Preconcentration have been carried out at different time intervals from 60 to 300 sec and the results obtained are shown in Fig.4(C). It is seen from the figure that as the preconcentration time increases the stripping current also increases indicating that the metal ions are complexed more with the ligand on the electrode surface as the time increases. The stripping current reaches a maximum value at 180 sec and then remains more or less same up to 300 sec. Hence an optimum time of 240 sec has been chosen for subsequent experiment.

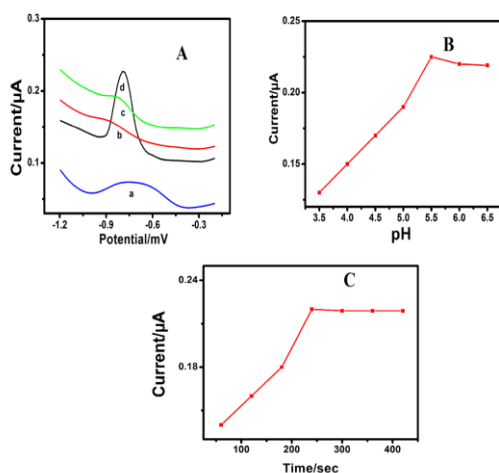


Figure 4: (A) The Effect of supporting electrolytes :0.1M solutions of a) Acetate buffer b) KNO_3 , c) NH_4NO_3 , and d) $NaNO_3$, (B) Effect of pH and (C) Preconcentration Time for Cd(II) ions containing 40nM at modified electrode

E. LINEAR RANGE, CALIBRATION PLOT AND DETECTION LIMIT

Under optimized experimental conditions, the linear range, limit of detection, and reproducibility were investigated by square wave anodic stripping voltammetry (SWASV). Fig .5 shows the square wave anodic stripping voltammetry of various concentrations of Cd(II) ions at the CNT / SABA ligand modified electrode. It is seen from the figure that the oxidation peak current of Cd(II) ions increases linearly with the increase of the concentration of Cd(II) ions by SWASV. A calibration graph has been drawn by plotting the stripping current vs concentration of Cd (II) ions taken and is shown as inset in the Fig.5. A linear range was observed from 3.7 to 250nM with a correlation coefficients of 0.996. The linear

regression equation is expressed as $i/\mu A = 0.008x + 0.047$ nM and the limit of detection (LOD) was 1.2nM for the determination of Cd(II) ions. Thus, a sensitive anodic stripping method has been proposed for the determination of Cd(II) ions.

Furthermore, the linear range and the detection limits obtained with the CNT/SABA ligand modified electrode compares favourably with previously reported modified electrodes (Table.1). It can be seen clearly from the table that the proposed method is better or comparable to these previous reported methods in terms of detection limit and linearity range.

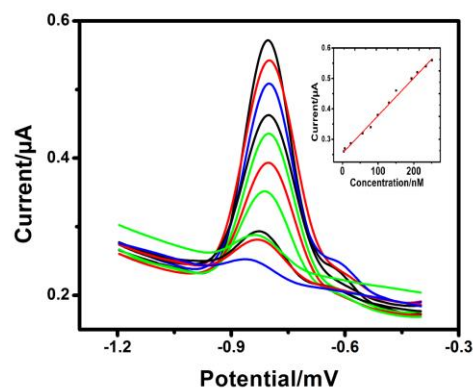


Figure 5: Anodic stripping voltammograms of different concentrations of Cd (II) ions in the range from 3.7nM to 250nM on CNT and SABA modified Electrode in 0.1 M $NaNO_3$ solutions Inset: calibration plot

Modifier	Method	Linear range nM	LOD nM	Reference
AllyICA-GCE	ASV	10 -300	2.2	[38]
G/PANI/PS	SWASV	10- 500	4.4	[39]
NCF-MCPEs	DPASV	150-650	8.8	[40]
CPCA-CPEs	DPASV	40-160	9.8	[41]
CNT and SABA	SWASV	3.7-250	1.2	This work

Table 1: Comparison of different electrodes for determination of Cadmium

F. REPRODUCIBILITY, INTERFERENCES STUDIES AND STABILITY

The stability of the prepared electrode was evaluated by storing the electrode in air for 30 days, and then the SWASV were recorded and compared with the ASV obtained previously. The electrode showed 100.1% of their initial peak current responses for five successive measurements in the presence of 40nM Cd (II) ions ion standard solution respectively. In order to study the reproducibility of the prepared electrode, five modified electrodes based on the same procedure and applied to the determination of 40nM Cd (II) ions. The RSD for the modified electrode was calculated to be 1.7%, indicating good reproducibility of the electrode preparation procedure. In order to evaluate the selectivity of the metal ions on the determination of 40nM Cd (II) ions was investigated. Experimental results have indicated that no interference was observed when determinations were carried

out in the presence of 10 fold concentration of Cu^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} , Hg^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} . These results indicate that they have no influence on the signals of 40nM Cd (II) ions with deviation below 5%. Due to the excellent reproducibility, stability and the result of interference tests, CNT and SABA ligand electrode can be used in practical analytical applications.

G. APPLICATION

The use of the CNT / SABA ligand modified electrode for the determination of Cd (II) ions in real samples, experiments have been carried out with sea water (Sample-1) and lake water (Sample-2) and ground water (Sample-3). A known amount of Cd (II) ions to the water samples were analysis three times and the anodic stripping current was measured. The results obtained are shown in Table.2. It is clearly seen from the table that the recovery of the added metal ion is from 98% to 103% indicating a good recovery for the added metal by the proposed method and hence this method can be employed for the determination of Cd (II) ions in real samples.

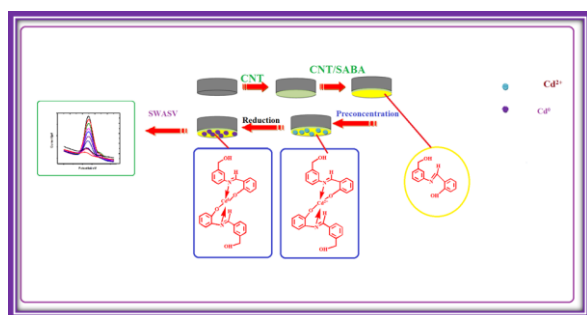
Water Samples	Added nM	Found nM	Recovery (%)
Sample -1	23	23.3±0.3	101.3
	46	45.2±0.2	98.2
Sample -2	51	51.4±0.4	101
	120	122.1±0.03	102
Sample -3	34	34.1±0.1	100.2
	68	68.4±0.2	101

Table 2: Determination of Cadmium in real samples

IV. CONCLUSION

In this paper we have demonstrated a simple and sensitive electrochemical method for the determination of Cd(II) ions using ASV based on the CNT/SABA ligand as the modifier material which was used to fabricate the modified electrode. The modified electrode showed an excellent selectivity and sensitivity for the determination of Cd (II) ions. Low limit of detection (LOD) of 1.2 nM Cd(II) ions was achieved using SWASV. Finally, this method was successfully applied for the electrochemical determination of Cd (II) ions in different water samples.

GRAPHICAL ABSTRACT



Mechanism of Cd(II) ions detection using CNT and SABA ligand

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