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Synthesis of Nickel Nitroprusside Coordination Nanoparticles by Simple Means: Its Characterization and Use as Electrochemical Sensor for Sulfide Estimation in Sewage and Water Samples

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Nickel nitroprusside (NiNP) complex has been synthesized from two procedures i.e. drop by drop (DbD) and bulk mixing methods. Surface morphology, size and shape of the complex resulted from the two procedures has been compared using scanning electron microscopy (SEM) images. X-ray diffraction (XRD) patterns were used to understand the phase purity and particle size of the complex particles obtained from two procedures. Presence of characteristic functional groups in the complex was examined using IR spectroscopy. From the studies it was clear that, size of the complex particles (n-NiNP) prepared from DbD method was considerably reduced. Carbon paste electrodes (CPEs) were constructed using NiNP complex prepared from DbD and bulk mixing methods to examine their electrocatalytic activity for the oxidation of sulfide. Obviously n-NiNP modified CPE showed enhanced electrocatalytic activity toward the oxidation of sulfide. Attempt has been made to use the n-NiNP modified CPE as an electrochemical sensor for sulfide estimation. It showed a linear response over 2 – 14 $\times 10^{-5}$ M and 0.2 – 1.4 mM of sulfide. Limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.1 $\times 10^{-5}$ M and 0.43 $\times 10^{-4}$ M sulfide respectively for the lower end calibration graph. Interference of various cations and anions generally present along with sulfide in water matrices was studied. Proposed electrochemical sensor has been applied for the estimation of sulfide in sewage and water samples. Good agreement between the results obtained from the proposed electrochemical sensor and standard Methylene blue method was observed.

Keywords: Nickel nitroprusside, drop by drop method, cyclic voltammetry, sulfide, sewage and water samples.

1. INTRODUCTION

The advancement of nanoscience provided ample opportunities for analytical chemists. Metal nanomaterial with interesting size dependent electrical, optical, magnetic, and chemical properties, as a kind of modish materials, have been frequently prepared. Size, shape, morphology are the principle factors in revealing, determining and enhancing the properties of the nonmaterials [1-3]. On the other hand making use of nanomaterials for the development of sensor technology is an evolving interdisciplinary field in which the inherent characteristics of analytical techniques blend with unique electronic, optical, magnetic, mechanical, and catalytic properties of nonmaterials [4, 5]. Metal nanomaterials are widely used in electroanalytical chemistry because of their good potential for constructing electrochemical sensing systems with high sensitivity and selectivity to sense wide range of analytes [6]. It is obvious that metal nanomaterials are highly conductive and provide larger electrochemically active surface area for the adsorption of analytes and hence exhibit improved analytical performance [7, 8].

One important group of inorganic compounds utilized for electrode modification and used for electrocatalytic purposes are the metal pentacyanonitrosylferrates. Pentacyanonitrosylferrate, $[Fe(CN)_5NO]^{3-}$ have been intensively persued, not only for its ability to form complex with series of transition metals like Co, Pb, Sn, Cd, Zn etc but also for its excellent electrocatalytic properties [9-13]. Nickel pentacyanonitrosylferrate (NiPCNF) is one such compound which has been extensively studied in an electroanalytical chemistry domain. Different strategies have been developed for the modification of electrode with NiPCNF. Electroless procedure, sol-gel technique and the electrochemical modification are well known among the reported strategies [14-17]. NiPCNF has been extensively used as an electrocatalyst for the quantification of various analytes such as ascorbic acid, hydrazine, sulphur compounds etc.

Detection of sulfur compounds is very necessary in various matrices because of its toxicity [18-20]. When sulfur compounds enter into the environment they react with oxygen to from sulfur dioxide, which causes respiratory problems in the persons allergic to it. Sulfur dioxide is responsible for acid rain when it get oxidizes to sulfur trioxide [21, 22]. In aqueous solution, sulfur exists in different chemical forms such as sulfide, sulfite, sulfate and thiosulfate, and frequently these are present in natural waters and industrial effluents [23]. Oxidation of organic matter and the reduction of sulfate ions are responsible for the origin of sulfide in natural waters [24, 25]. The sulfide anion is an important constituent of aqueous systems wherever microbial colonies flourish, whether in environmental or in physiological contexts [26, 27]. Some of the main industrial sources of hydrogen sulfide are kraft-pulp mills, petroleum refineries, gasification of coal, meat processing plants, sewage treatment plants, leather and paper processing industries [28-30]. Detection of dissolved sulfide or hydrogen sulfide has gained significance within the analytical community as a consequence of its high toxicity to human beings and aquatic life [31].

Recently we have reported the synthesis, characterization of cobalt pentacyanonitrosylferrate nanoparticles and there application as electrochemical sensor for sulfite quantification in various food samples [32]. Synthesized nanoparticles showed considerably enhanced analytical performance. Those results encouraged us to continue the work on metal nitroprusside nanoparticles. Because of the presence of sources which are continuously adding sulfide to the environment and its adverse effect, there is a great need for the development of sensitive method for its quantification. Hence we considered sulfide as a model system for examining the elecrocatalytic activity of synthesized n-NiNP.

2. EXPERIMENTAL PART

2.1. Apparatus

Electrochemical experiments were performed using CH Instruments electrochemical work station (model CHI 660D, CH Instruments, Texas, USA) in a standard three electrode cell. Modified carbon paste electrode as a working, Pt wire as the counter and Ag/AgCl as the reference electrodes. All the samples were characterized by X-ray diffraction (Bruker aXS Model D8 Advance powder X-ray diffractometer, Cu Kα source $\lambda = 1.5418$ Å, Θ - 2Θ geometry). IR spectra were recorded using a Bruker Alpha-T FTIR spectrometer (Diamond crystal ATR mode, resolution 4 cm^{-1}, 400–4000 cm^{-1}). Scanning electron micrographs were obtained using Quanta-200 scanning electron microscope by dispersing sample conducting carbon tape.

2.2. Chemicals and reagents

Nickel chloride hexahydrate $NiCl_2$ $6H_2O$, Sodium sulfide nanohydrate Na_2S $9H_2O$, Sodium nitroprusside dihydrate $Na_2[Fe(CN)_5NO]$ $2H_2O$, Potassium nitrate, KNO_3 (0.5 M) were all analytical grade and were used as received. Potassium nitrate, KNO_3 (0.5 M) was prepared by using pH 5 buffer solution. Buffer solution was prepared using 0.02 M solutions of sodium acetate and acetic acid. All solutions were prepared using double distilled water.

2.3. Procedures

2.3.1. Synthesis of nickel Pentacyanonitrosylferrate

NiNP was synthesized by two different protocols: Drop by drop (DBD) and bulk mixing methods

DBD method: Nickel Pentacyanonitrosylferrate particles have been prepared by drop wise mixing. 10 ml aqueous solution of nickel chloride (0.02 M) is taken in a beaker which was thermostated at 5-10 °C under vigorous stirring, to that 10 ml aqueous solution of sodium nitroprusside (0.01 M) was added dropwise. The resulted complex is referred as n-NiNP in all further studies.

Bulk mixing method: Nickel Pentacyanonitrosylferrate particles have been prepared by direct mixing 10 ml of aqueous solutions of 0.01 M sodium nitroprusside and 0.02 M cobalt chloride which were maintained at 5-10 °C at once in a beaker. The resulting compound is referred as b-NiNP.

To avoid the formation of metal hydroxides, pH of both the resulting mixtures were adjusted to 3 using 1N HCl and the precipitates were left overnight without disturbing. After rejecting the supernatant liquid, residue was centrifuged. The residue i.e. NiNP was initially washed with ample quantity of water and finally with alcohol. The residue was collected in a petridish and dried at room temperature. The resulted NiNP particles from both the approaches were used as a modifier in fabricating carbon paste electrodes.

2.3.2. Electrode preparation

The modified carbon paste electrode was prepared manually by thorough mixing of graphite powder and n-NiNP in a 15:1 mass ratio and subsequently adding 38% m/m of mineral oil acts as binder. The resultant mixture was ground in an agate mortar for 10 to 15 min. The obtained paste was packed into the capillary tube from the wider end. A copper wire was inserted from the opposite end of the capillary to obtain the electrical contact. Similarly b-NiNP CPE electrode and bare CPE were prepared using graphite powder and mineral oil. All these electrodes were dried for 24 h at room temperature and the resistivity was measured using a multimeter and it was found to be 10 - 12 ohms.

3. RESULTS AND DISCUSSION

3.1. FTIR study

Infrared spectral studies have been carried out to confirm the presence of functional groups in nano and bulk Nickel nitroprusside complex prepared using drop by drop and bulk method. The prepared complexes were separately mixed with KBr in 1:100 ratio to make the pellet and it has been exposed to infrared radiation in the range 1000 to 4000 cm^{-1}.

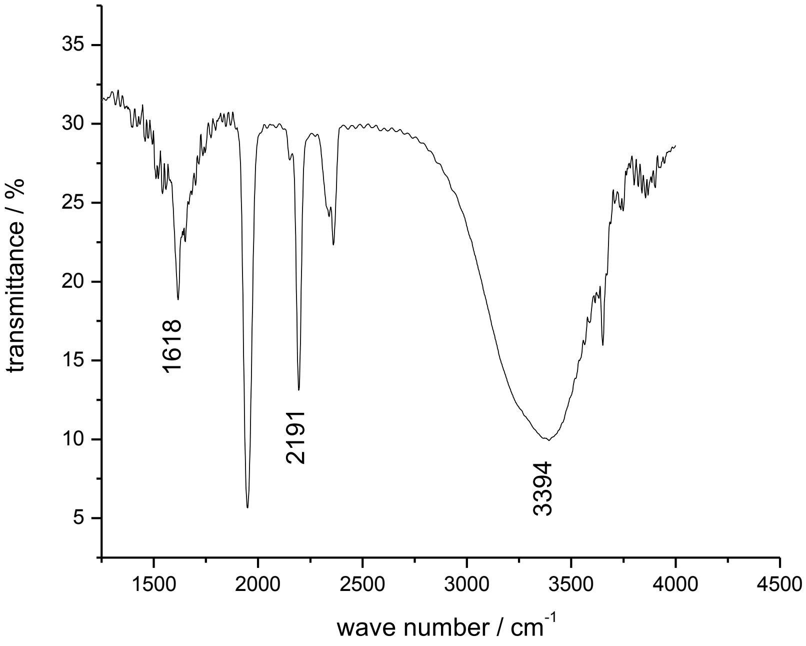


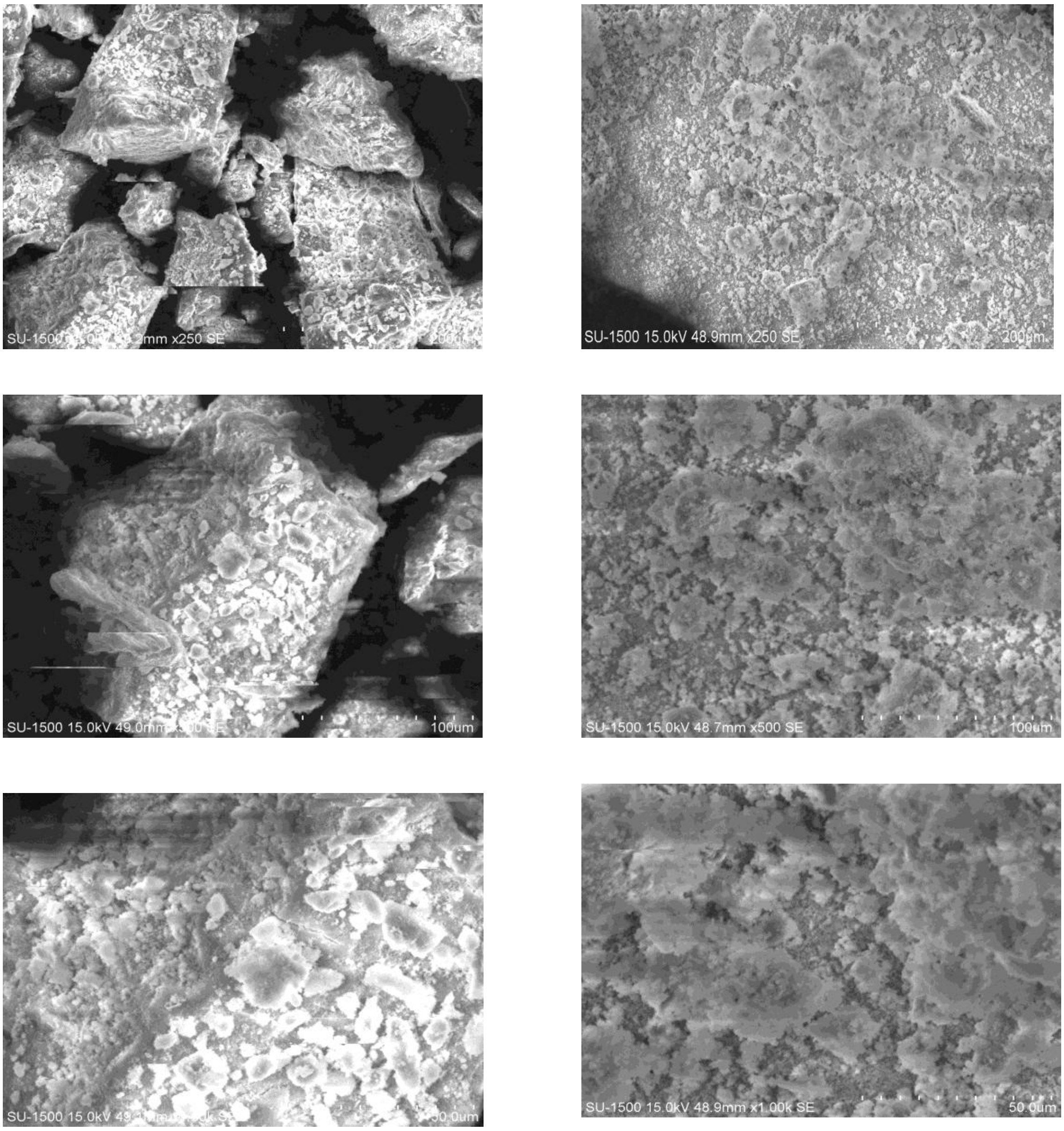
Figure 1. FTIR spectrum of nickel nitroprusside

The transmission spectrum of the Nickel nitroprusside complexes prepared using both methods revealed that the presence of peaks due to Nitrosyl (NO), Cyanide (CN) and Hydroxy (OH) groups on the modifier molecule. The band at 1618 cm^{-1} indicates the presence of nitrosyl group.

But the strong peak at 2191cm^{-1} signifies the stretching frequency of cyanide group of the nitroprusside complex. Presence of broad peak at 3394 cm^{-1} due to OH group stretching vibration and the sharp peak at 1941 cm^{-1} might be due to bending vibration of the crystal water present in the NiNP compound, from this it's evident that the compound is hydrated. Peaks assigned for the functional groups were well coordinated with the reported literature values [10, 11, 33]

3.2. SEM characterization

Surface morphology, shape and size of n-NiNP and b-NiNP particles were analyzed using SEM images (Fig. 2). Evident difference in the size of the NiNP particles synthesized from two different approaches was observed. Considerably bigger lumps were observed in case of b-NiNP, where as in case of n-NiNP clearly dispersed smaller particles can be seen.



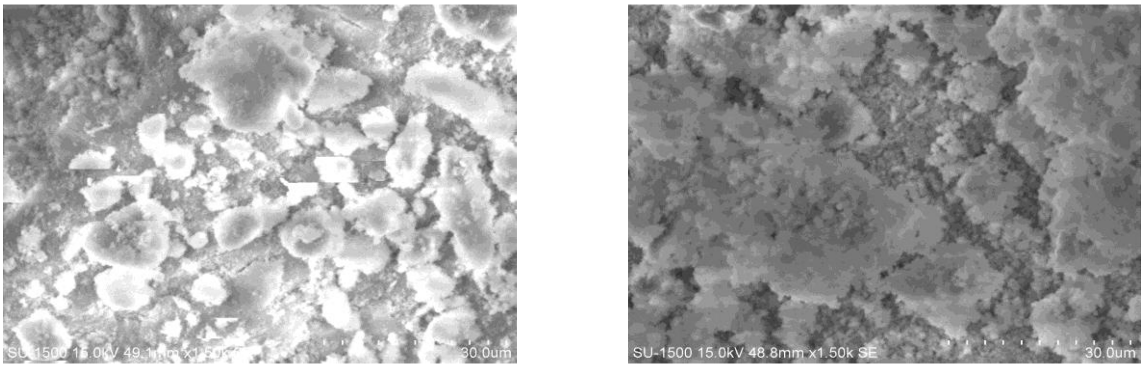
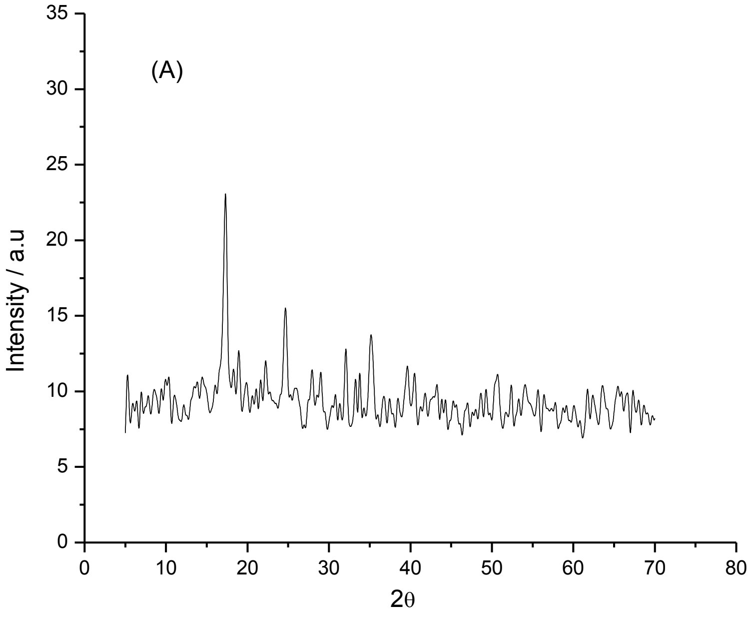


Figure 2. SEM images of nickel nitroprusside particles prepared by drop by drop (left column, n-NiNP), and bulk mixing (right column, b-NiNP) methods.

From the SEM images it is clear that agglomeration of NiNP particles found to be significantly less and that avoided the formation of lumps in case of DbD method [34, 35]. Patch like structures are present on the surface of the lumps in case of b-NiNP, but very minute grain like structures are resulted from the DbD method.

3.3. XRD characterization

XRD spectroscopy has been used to check the phase purity of the synthesized complexes. The XRD pattern of both i.e. n-NiNP and b-NiNP were recorded (Fig. 3). Sharp reflections were observed at d-spacing corresponding to b-NiNP. Though Bragg's reflections were observed at same 2ϴ value in both cases, peaks are observably broad in n-NiNP pattern compared to its bulk counterpart [36-39]. Average crystallite size of n-NiNP and b-NiNP synthesized from two approaches were calculated using Scherrer formula, it has been found to be 2.77 and 27.19 nm respectively. This XRD data therefore, provides strong evidence for particle size reduction during the DbD process and it is well matches with the XRD pattern of n-NiNP crystallographica pdf No 23-462.



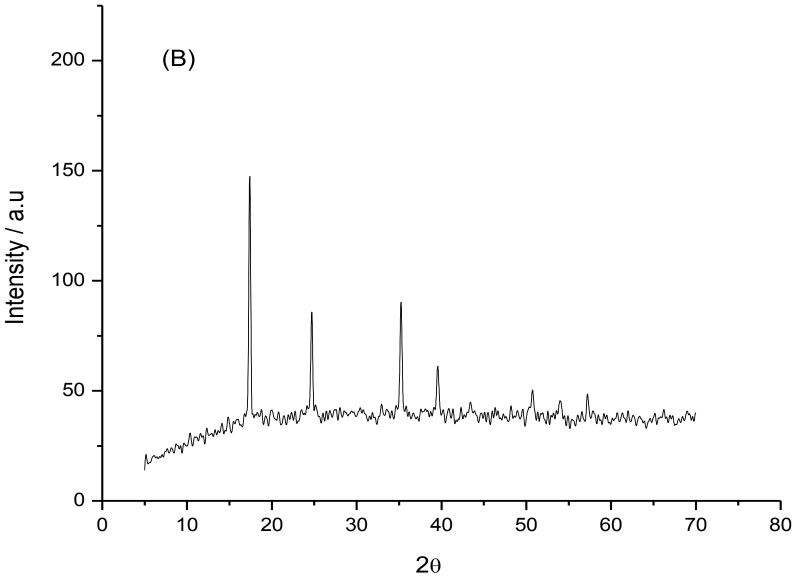


Figure 3. XRD patterns of NiNP particles prepared from (A) DbD and (B) bulk mixing methods.

3.4. Cyclic voltammetric studies

Cyclic voltammogram of n-NiNP and b-NiNP modified CPE's were recorded in 0.5 M KNO_3 in a potential range between 0 - 1 V vs. Ag/AgCl electrode at a scan rate of 0.05 Vs^{-1} (Fig. 4). Each voltammogram contains a pair of peaks with a formal potential $E^o = (E_{Pa} + E_{Pc})/ 2$ of 0.45 and 0.48 V respectively for n-NiNP, b-NiNP complexes. These peaks are well resolved and the ratio of the anodic and cathodic peak currents were found to be almost unity which indicates that the process is reversible and these peaks are due to $[Fe (II) (CN)_5NO]/ [Fe (III) (CN)_5NO]$ redox couple. The redox potentials of both NiNP particles prepared by the two approaches were in good agreement with the literature [14, 15, 17, 40].

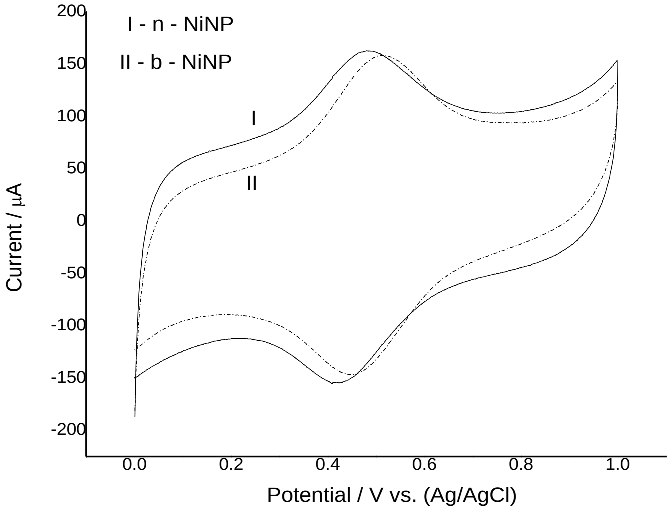


Figure 4. Cyclic voltammograms of NiNP - modified carbon paste electrodes in 0.5 M KNO_3.

3.5. Electrocatalytic behavior of nickel nitroprusside modified carbon paste electrodes.

Above procedure has been repeated in presence of sulfide. Fig. 5 shows the cyclic voltammograms of the n-NiNP and b-NiNP modified CPE's in the absence and presence of 1.2 mM sulfide. Addition of 1.2 mM sulfide resulted in a considerable increase of the anodic peak current and cathodic peak current tended to decrease. This phenomenon is consistent with the mediated oxidation or strong electrocatalytic effect [41, 42]. The electrochemical response i.e. increase in the anodic peak current due to electrocatalytic oxidation of sulfide was appreciably greater in case of n-NiNP CPE compared to b-NiNP CPE. Improved response in case of n-NiNP CPE can be explained on the basis of increased surface to volume ratio of coordination nano particles [3].

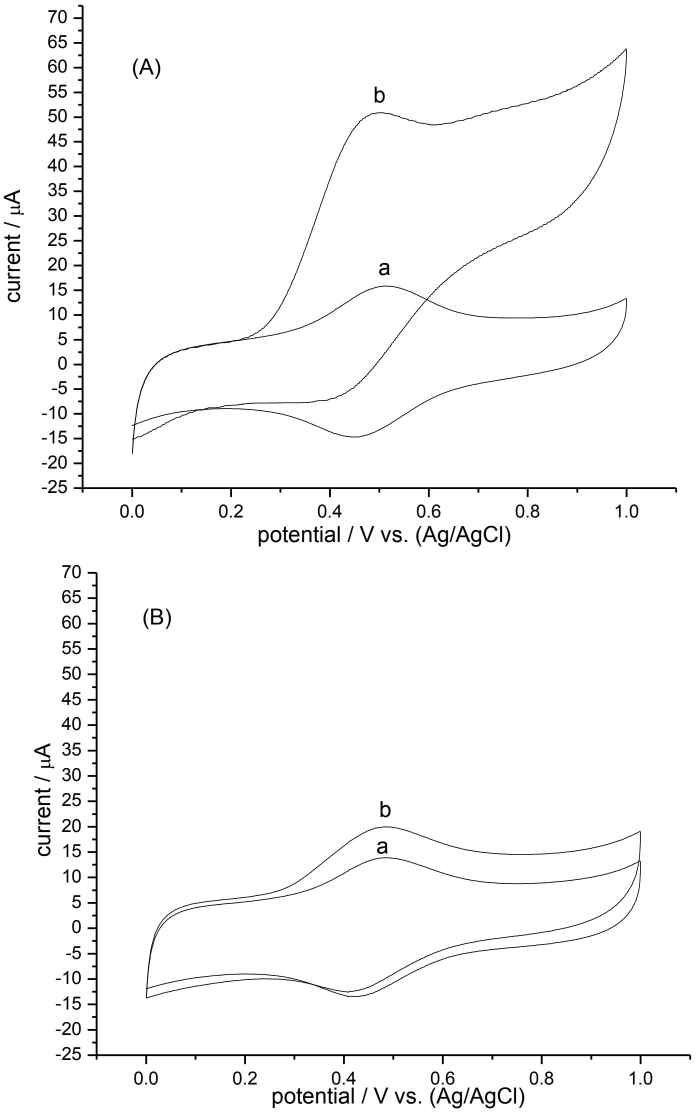


Figure 5. Overlaid **c**yclic voltammograms of n-NiNP (A)**,** b-NiNP (B) modified CPEs (a) in absence (b) in presence of 1.2 mM sulfide.

3.6. Electrocatalytic oxidation of sulfide at nickel nitroprusside modified and bare carbon paste electrodes

The electrocatalytic activity of n-NiNP modified CPE to oxidize the sulfide was compared with that of the bare CPE. Overlaid cyclic voltammograms of n-NiNP and bare CPE in the absence and presence of 1.5 mM sulfide in 0.5 M KNO_3 at a scan rate of 0.05 Vs^{-1} shown in Fig. 6. From the voltammograms it is clear that presence of n-NiNP as a modifier molecule considerably enhanced the anodic peak current of modified electrode in the presence of sulfide. From these studies it is evident that n-NiNP particles shows considerably improved electrocatalytic activity compared to bare CPE. Electrocatalytic oxidation of sulfide at the n-NiNP modified CPE carried out according to the EC' mechanism [9, 43]

$$\mathrm{KNi}\,[\mathrm{Fe}^{\mathrm{II}}\,(\mathrm{CN})_5\mathrm{NO}] \rightarrow \mathrm{Ni}\,[\mathrm{Fe}^{\mathrm{III}}\,(\mathrm{CN})_5\mathrm{NO}] + \mathrm{K}^+ + \mathrm{e}^- \qquad \text{(E)}$$

↑______________________________

k ↓

$$\mathrm{Ni}\,[\mathrm{Fe}^{\mathrm{III}}\,(\mathrm{CN})_5\mathrm{NO}] + 2\mathrm{K}^+ + \mathrm{HS}^- \rightarrow \mathrm{KNi}\,[\mathrm{Fe}^{\mathrm{II}}\,(\mathrm{CN})_5\mathrm{NO}] + \mathrm{S}^0 + \mathrm{H}^+ \qquad \text{(C)}$$

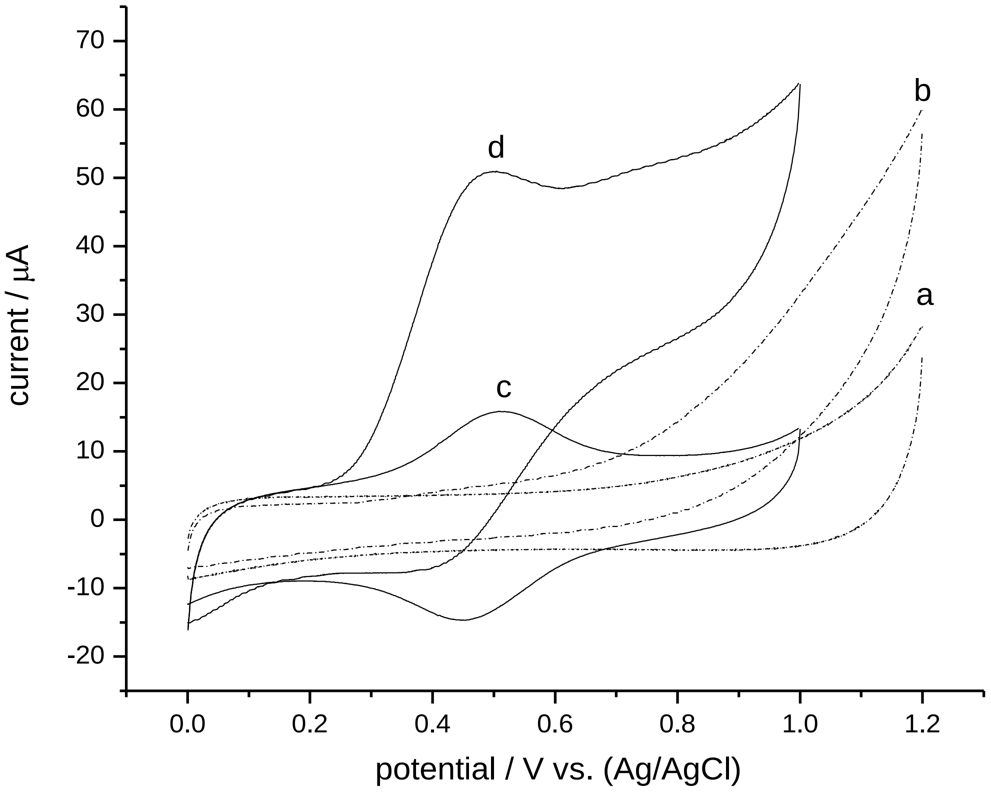


Figure 6. Cyclic voltammograms of bare CPE in absence (a) and in presence (b) of 1.5 mM sulfide, n-NiNP modified CPE in absence (c) and in presence (d) of 1.5 mM sulfide.

3.7. Electrochemical behavior

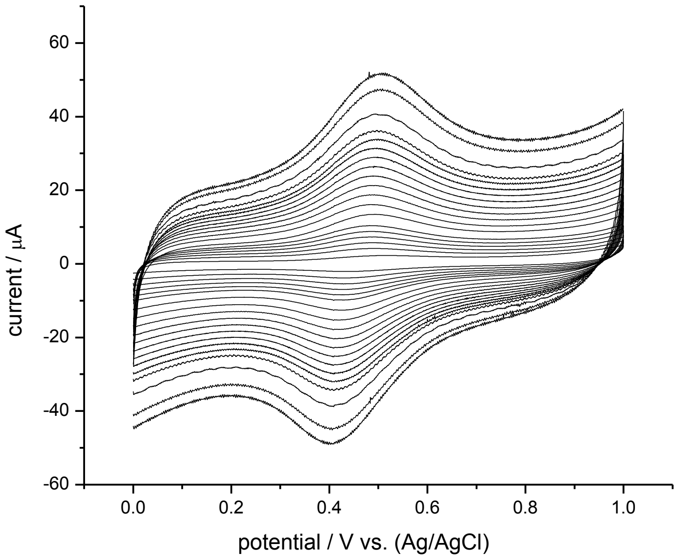


Figure 7. (A) Overlaid cyclic voltammograms of n-NiNP CPE in 0.5 M KNO_3 at varied scan rates: 5 – 200 mV s^{-1}.

The n-NiNP modified CPE has been characterized by cyclic voltammetric studies. To understand type of the process occurring at the electrode cyclic voltammograms have been recorded at the various scan rates in 0.5 M KNO_3 as a supporting electrolyte in the absence of analyte. Fig. 7(A) shows the cyclic voltammograms of n-NiNP in 0.5 M KNO_3. The ratio of cathodic to anodic peak current was found to be almost unity. Fig. 7 (B) shows anodic and cathodic peak currents were directly proportional to scan rate between 5 – 200 mV s^{-1} but not to square root of scan rate as shown in Fig. 7(C). This confirms the redox process occurring at the electrode is surface confined [12]. The E_p ranges about 30 – 53 mV for a scan rate from 5 – 200 mVs^1, this suggests the facile charge transfer in the above mentioned scan rate range [9].

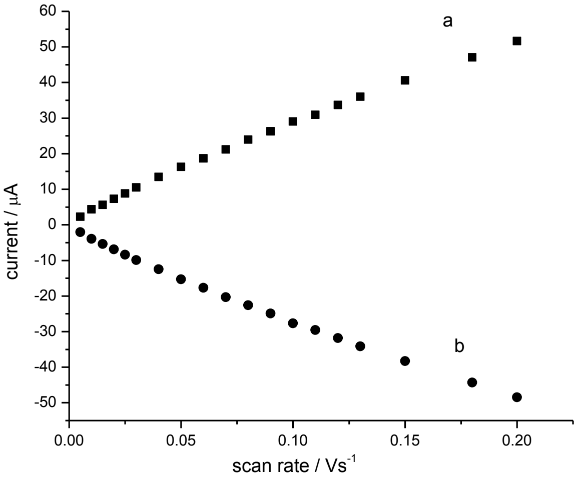


Figure 7. (B) Plot of scan rate vs. anodic (a) and cathodic (b) currents.

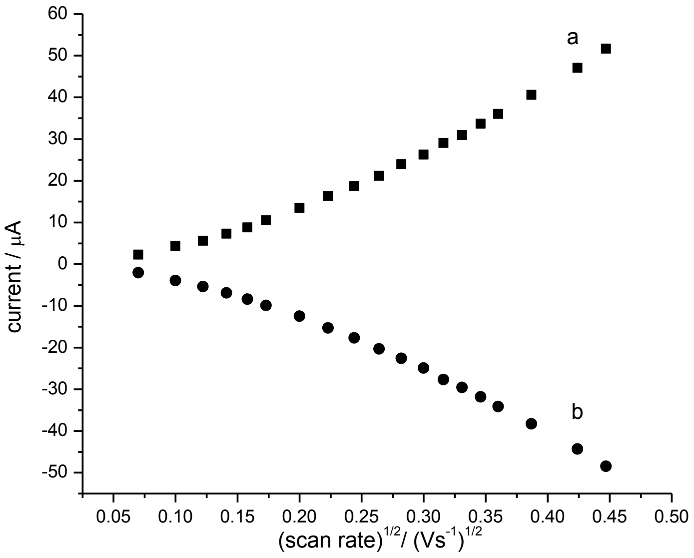


Figure 7. (C) Plot of square root of scan rate vs. anodic (a) and cathodic (b) currents.

The cyclic voltammograms of n-NiNP modified CPE were recorded in presence of 0.04 mM sulfide in 0.5 M KNO_3 at varied scan rates (Fig. 8(A)). From this study it was confirmed that anodic peak currents were linearly proportional (r = 0.996) to square root of the scan rate (Fig. 8(B)). This indicates that the electrode reaction is diffusion controlled process, which is suitable behavior for quantitative application [44].

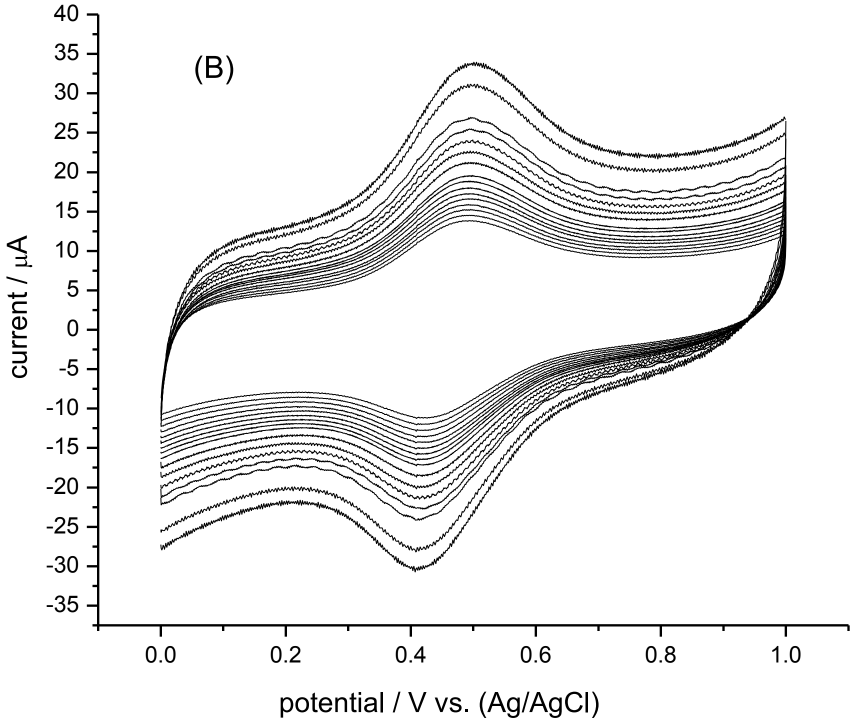


Figure 8. (A) Overlaid cyclic voltammograms of n-NiNP CPE in 0.5 M KNO_3 at varied scan rates in presence of 0.3 mM sulfide.

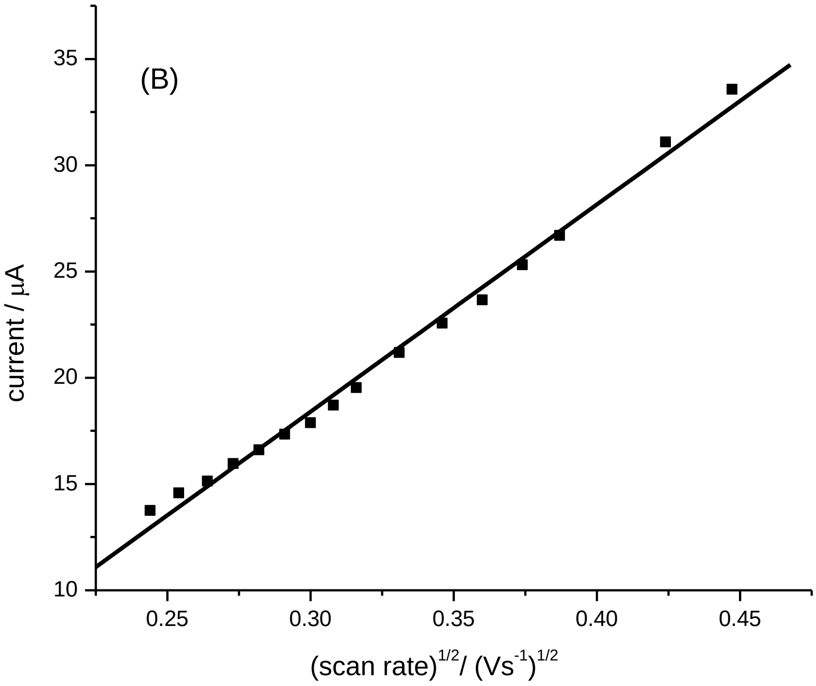


Figure 8. (B) Plot of square root of scan rate vs. anodic peak currents

3.7. Interference study

Electroactive active cations and anions such as $Ca^{+2,}$ Mg^{+2}, Cl^-, F^-, PO_4^-, CO_3^{-2}, HCHO, NO_3^-, SO_3^{-2}, NO_2^- generally present along with the dissolved sulfide in water have been tested for there interference. Negligible current response was exhibited from all the tested species except SO_3^{-2}, NO_2^-, these two ions interfered seriously even at 10, 5 ppm respectively. Interference from sulfite was over come up to 200 ppm by treating the sample with 1 ml of 1000 ppm of formaldehyde which forms stable hydroxy methane sulphonic acid adduct. By adding 5 ml of 1 % sulfamic acid nitrite was converted in to nitrogen gas there by its interference can be overcome up to 30 ppm [45, 46].

3.8. Calibration plot

Certain volume of 0.5 M potassium nitrate solution was taken in a three electrode 10 ml electrochemical cell. 0 and 1.0 V vs. Ag/AgCl were adjusted as initial and final potentials respectively and the cyclic voltammograms were recorded at a scan rate of 0.05 V s^{-1}. At varied concentrations of sulfide, the experiments were repeated and the proportionality between the increased peak current values with varied sulfide concentration was observed (Fig. 9, 10). A calibration graph was constructed by plotting the peak currents vs. the sulfide concentrations. A linear response was obtained in the concentration range 2 – 14 $x10^{-5}$ M and 0.2 – 1.4 mM of sulfide. The standard deviation (SD) and regression coefficient (r^2) values were found to be 0.084, 0.719and 0.999, 0.999, for lower and higher end calibration graphs respectively. Linear regression equations Y = 13.246 + 3.548 * X and Y= 13.28 + 32.825 * X are obtained for the lower and higher end calibration graph respectively. The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.1 x 10^{-5} M and 0.43 x10^{-4} M respectively for the lower end calibration graph.

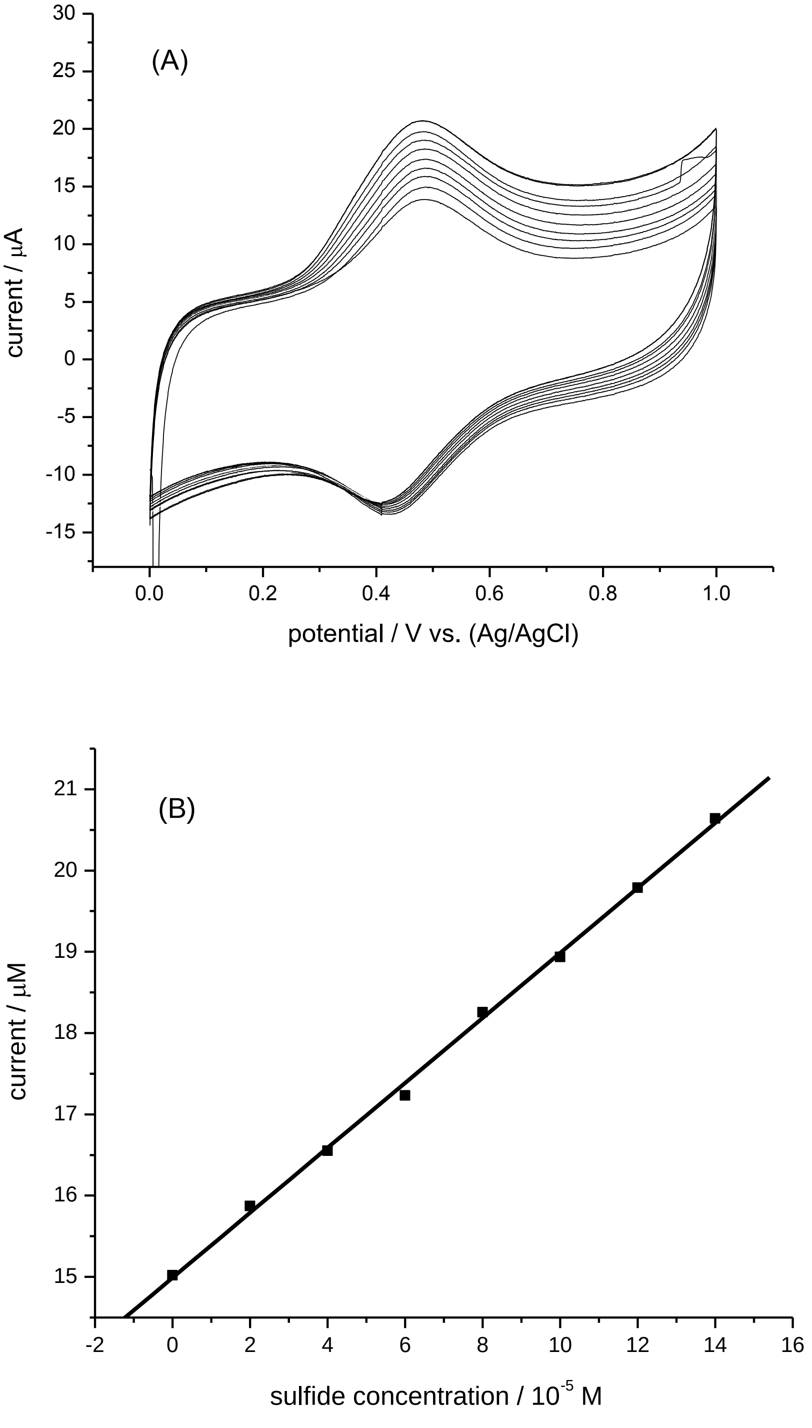


Figure 9. (A) Overlaid cyclic voltammograms of n-NiNP modified CPE in presence of 2, 4, 6, 8, 10, 12, 14, 16 x 10^{-5} M sulfide. (B) Plot of sulfide concentrations vs. respective anodic currents.

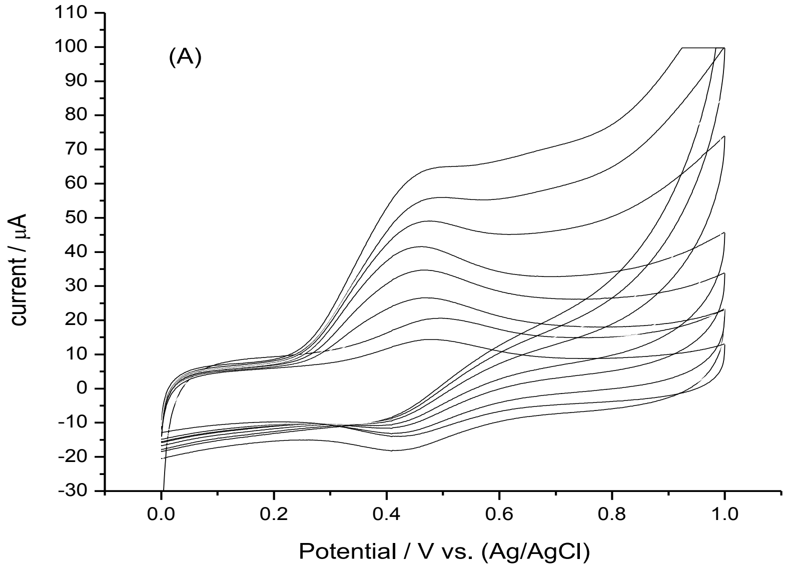


Figure 10. (A) Overlaid cyclic voltammograms of n-NiNP modified CPE in presence of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 mM sulfide in 0.5 M KNO_3 at 0.05 Vs^{-1} scan rate.

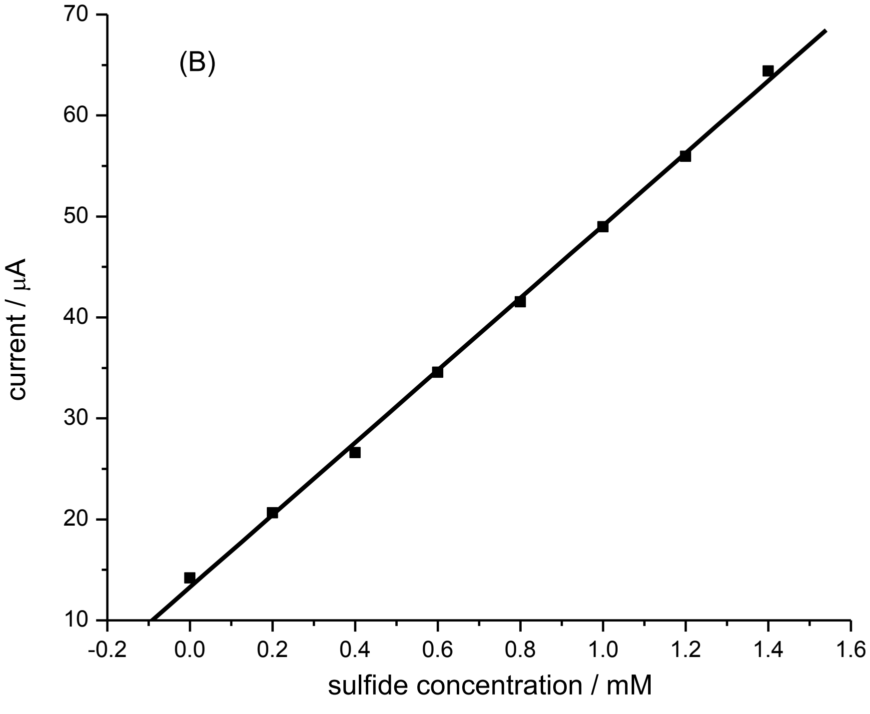


Figure 10. (B) Plot of varied sulfide concentration vs. anodic peak current response.

3.9. Application study

The applicability of the proposed electrochemical sensor has been tested by quantifying the dissolved sulfide content from a variety of environmental sample matrices such as sewage and tap water samples. Various sample solutions were prepared using following procedure and analyzed by the proposed electrochemical sensor as well as standard ethylene blue method. The validity of the proposed method has been checked by the recovery study. Known concentrations of sulfide were spiked with the samples and total sulfide content was analyzed.

3.10. Sample preparation

Measured volumes of sewage water samples were collected from two different sewage lines and alkaline zinc acetate solution was added immediately to avoid the loss of dissolved sulfide [47]. Then the samples are treated with 1 ml each of formaldehyde (1000 ppm) and sulfamic acid (5%) solutions to avoid the interference from sulfite and nitrite present if any. pH of certain volumes of sewage samples were adjusted to pH 5 using 0.5 M KNO_3 solution prepared by using sodium acetate acetic acid buffer solution of pH 5, then used for analysis using proposed sensor. Sulfide present in the samples was also analyzed by standard Methylene blue method [47]. Good agreement between the results obtained from the two methods was found (Table 1).

Table 1. Quantification of sulfide in sewage and tap water samples

Sample	Sulfide originally found (10^{-4} M)		Sulfide added (10^{-4} M)	Total sulfide(10^{-4} M)		% Recovery	
	Proposed Method	Standard Method		Proposed Method	Standard Method	Proposed Method	Standard Method
1[a]	0.50 ± 0.07	0.48 ± 0.02	1	1.44 ± 0.08	1.50 ± 0.03	96	101
2[b]	0.31 ± 0.08	0.30 ± 0.01	0.5	0.78 ± 0.07	0.80 ± 0.01	96	100
3[c]	--	--	1.5	1.48 ± 0.05	1.50 ± 0.01	96	100

All the values are average of four measurements ± RSD
[a] Water sample collected from open sewage line near nayandalli, Bangalore, Karnataka, India.
[b] Water sample collected from open sewage line near kengeri, Bangalore, Karnataka, India.
[c] Laboratory tap water sample.

4. CONCLUSION

Nickel nitroprusside complex particles have been synthesized from DbD and bulk mixing methods. Synthesized complexes were characterized using SEM, XRD, FTIR and CV. From the SEM images it was clear that complex synthesized from both the approaches have same surface morphology, but considerably bigger lumps and relatively small complex particles have been resulted from bulk mixing and DbD method respectively. XRD pattern confirms the phase purity and the particle size of NiNP is in the nano meter range. Electrochemical investigations revealed that n-NiNP incorporated the enhanced electrocatalytic activity compared to its bulk counterpart b-NiNP. To confirm the applicability of developed electrochemical sensor calibration curves have been constructed using cyclic voltammetry in the two ranges. Interference of sulfite and nitrite was overcome by using the formaldehyde and sulfamic acid. Results of sulfide estimated from the proposed electrochemical sensor were well matched with that of the standard ethylene blue method.

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