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CHEMICAL SENSOR USING GNP-CYS-ZNHCF (II) GRAPHITE WAX COMPOSITE ELECTRODE

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ABSTRACT

A novel modified electrode was fabricated by electrochemical derivatization of ZnHCF at a GNP adsorbed graphite wax composite electrode. The electrode developed was used for the determination of catechol. The voltammetric characteristics of the ZnHCF modified electrode in the presence of different alkali metal cations were investigated by cyclic voltammetry (CV). The modified electrode was also characterized by electrochemical impedance method (EIS). The electrode surface was characterized by Transmission electron microscopy (TEM) which indicated that the ZnHCF particles were 20-30 nm in size and were dispersed uniformly on electrode surface. The modified electrode was also characterized by UV, XPS and FTIR. The modified electrodes presents good electro catalytic activity towards the oxidation of catechol and this electrode can be used for determination of catechol. A linear calibration curve is obtained in the range from 2.6×10^{-6} to 7.2×10^{-3} M of catechol with a detection limit of 1×10^{-7} M. Chronoamperometry and differential pulse voltammetry (DPV) were used for the determination of catechol from industrial waste water samples. The proposed modified electrode is simple to prepare and it shows fast response, good stability and reproducible results.

KEYWORDS

GNP, Zinc hexacyanoferrate, Electro catalysis and Catechol.

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INTRODUCTON

Use of nanomaterials for analytical applications has increased enormously in the recent years. In particular nanomaterials play a vital role in the field of chemically modified electrodes (CMEs) for the enhanced behaviour of these electrodes both with respect to sensitivity and selectivity (Abbaspour, 2005)¹. Gold nanoparticles display four unique advantages over macro electrodes when used for electro analysis: they are enhancement of mass

transport, catalysis, high surface area and control over electrode microenvironment. (Pong *et al.* 2007² Sivasankari *et.al* 2018)³ with these advantages one can use gold nanoparticles as a chemical platform to anchor redox mediators to improve the electron transport behaviour as well as sensitivity of electrode.

Catechol (1, 2- dihydroxybenzene) is one of the most important phenolic compounds which occurs naturally in fruits and vegetables and can be released to the environment during its manufacture and use. It is also detected at low levels in, groundwater, drinking-water, soil samples and in wastewaters from coal conversion. Catechol has gained importance in both biological and environmental analysis and this due to its excellent electrochemical activity. Different analytical methods have been proposed for the determination of catechol such as spectrophotometry, (Figueiredo *et al.*, 2007⁴ and Lourenço *et al.*, 2006)⁵ high-performance liquid chromatography (Lee, 1993)⁶. The electrochemical determination of catechol was also using enzymatic (Tembe, 2007⁷, Schöning, 2005⁸, Solna, 2005)⁹ or non enzymatic (Portaccio, 2006¹⁰, Rogers, 2001¹¹, Tsai, 2007)¹² electrodes. The enzymatic method for the determination of catechol suffers from some disadvantages such as high cost due to the enzyme used, low stability and limited binding of the enzyme to solid surfaces. The non enzymatic electrodes used for studying the direct electrochemistry of catechol was also examined using different types of electrodes such as mesoporous platinum and gold electrode (Capannesi, 2000)¹³. Different kinds of electrodes were used for the electrochemical determination of catechol based on its oxidation at the electrode surface to *o*-quinone.

We have developed a chemically modified electrode by a new approach using gold nanoparticles and nickel hexacyanoferrates for the determination of catechol. GNP- ZnHCF modified electrode was developed by anchoring ZnHCF onto the surface of gold nanoparticles using 3-Mercapto-2-aminopropionic acid (L-cysteine) as cross linker, to the metal ion Zn^{2+} which was attached with $-NH_2$ group of L-cysteine, this even though COOH group

is also present. The metal ion is attached effectively with NH_2 group which was confirmed by FTIR. The gold nano particles synthesized using sodium citrate method was characterized using UV-Vis and cyclic voltammetry. High surface area and size dependent behaviour of gold nanoparticles showed an enhanced electron transport behaviour and high sensitivity for the determination of catechol. The ZnHCF film was effectively used for the amperometric determination of catechol as it was found to have excellent catalytic activity over the oxidation of catechol. Differential pulse voltammetry (DPV) and flow injection techniques were effectively used for the determination of the analyte from environmental water samples.

EXPERIMENTAL

Reagents and chemicals

All reagents were of analytical grade; Graphite powder was from Aldrich (1-2 μ m), (Aldrich, Steinheim, Germany). Catechol from Alfa Aesar (Alfa Aesar chemicals, Kolkata, India). $ZnCl_2$, Potassium ferrocyanide were obtained from Merck (Mumbai, India). Double distilled water was used for all electrochemical experiments. Studies on effect of pH were carried out using 0.1M HCl and 0.1M NaOH solutions. pH 7.0 was maintained using 0.1M $NANO_3$, 0.1 M PBS), L-cysteine solution (20mM) was prepared using double distilled water and Zinc solution (0.01M) was prepared by dissolving the salt in ethanol. Potassium ferrocyanide (0.02 M) in $NANO_3$ (0.1M) solution was used to derivatize the coordinated nickel ion. All measurements were done after carefully degassing the solutions with pure nitrogen for 10-15 mins.

Apparatus and material

Electrochemical measurements were carried out using Electrochemical workstation CH Instruments 660B, Tx, USA controlled by an IBM personal computer with standard three-electrode configuration. The surface modified ZnHCF graphite paraffin wax composite electrode was used as the working electrode, a platinum wire as the counter electrode and a standard calomel electrode as the reference.

Sample preparation

Four different water samples were prepared by adding approximate $6 \times 10^{-5} \text{M}$ of catechol into the real samples of distilled, tap, river and drinking water. These samples, at their natural pH (pH 6.8–7) were filtered through a Whatmann 41 filter paper. 20.0 mL of this solution was subsequently introduced into a separating funnel. Diethyl ether (10 mL) was added to the separating funnel. The funnel was shaken vigorously for 10 min during the extraction. After extraction, the organic phase was removed, dried in a stream of nitrogen, and the residue was dissolved using the background electrolyte.

Fabrication of GNP-ZnHCF paraffin wax composite electrode

Graphite powder (1 g) was extra to one hundred twenty five cubic centimeter of synthesized gold nanoparticles answer (0.6mM) and therefore the mixture was stirred for 2 hours at three hundred rate in temperature. The stirred mixture was centrifuged at 1450 rate for half-hour and therefore the residue was unbroken nightlong for drying. A GNP graphite paraffin wax composite electrode was prepared as reported by mixing 900mg of gold nanoparticles adsorbed graphite powder with paraffin wax in the ratio of 4:1. Gold nanoparticles plumbago wax mixture was tightly packed in a very little glass tube of 3mm diameter. The conductor was removed gently from the tube once it turns laborious.

The conductor ready during this magnitude relation showed a superb hardness and conduction. This composite electrode was first dipped in 20 mM L-cysteine solution for 2 hours. Then, this L-cysteine modified GNP composite electrode was dipped in 0.01 M ethanolic solution of ZnCl_2 for 2 minutes. The amino group of cysteine functionalized with gold nanoparticles has a greater affinity towards transition metal ion like Zn^{2+} . The Zn^{2+} ions coordinated to amine group was then derivatized using 0.02 M potassium ferrocyanide solution dissolved in 0.1 M NaNO_3 by cycling the potential in the range -0.2 V to 1.0 V at the scan rate of 50 mV s^{-1} (Richard Prabagar and Sriman Narayanan, 2006).

RESULTS AND DISCUSSION

UV Absorption Study

In the present study the spectrum characteristic of the absorption due to surface plasmon resonance of Au NPs could be observed at 520nm (Figure No.1). It is well-known that the colloidal gold nanoparticles in an aqueous solution exhibit a broad absorption band in the visible region at wavelength from 517 nm to 575 nm due to the Mie theory (Lu *et al.*, 2004)¹⁴ Also, the surface plasmon band was symmetric indicating that the colloidal solutions had no aggregation of particles. The formation of gold nanoparticles was further evidenced by the photograph shown in Figure No.1 (B).

XPS Study

XPS is a powerful tool to examine the elemental distribution on the electrode surface. To prove that GNP – L-Cys and ZnHCF have been modified onto the surface of electrode, XPS experiments were performed. Two XPS bands of Zn appear at 932.3 and 952.1 eV, corresponding to the Zn (2p_{3/2}) and Zn (2p_{1/2}) signals respectively (Figure No.2), which demonstrates the immobilization of ZnHCF on the modified electrode surface. Another two peaks are observed due to existence of O impurity in the sample, which originates from the surface contamination of the ZnHCF. The S (2p_{3/2}) signal appeared at 162.5 eV indicates the formation of S–Zn bond on the modified electrode. The above results demonstrated that ZnHCF were chemically bound to the surface of the GNP – L-Cys modified electrode to form the ZnHCF deposited on the electrode surface. The above results were consistent with the previous reports.

TEM characterization of the surface

Figure No.3 shows the TEM images of (a) bare graphite wax composite electrode (b) GNP adsorbed graphite wax composite electrode in the range from 6-9nm and (c) ZnHCF –GNP- graphite wax composite electrode. The figure clearly suggests the formation of ZnHCF particles on the electrode surface and that the particle size ranges from 25-30nm.

FTIR characterization of the surface

Figure No.4 shows the FTIR spectra of (a) pure cysteine, (b) cysteine adsorbed GNP graphite
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powder and (c) GNP-Cys-ZnHCF. The absorbance peaks at 1139 cm^{-1} , 1572 cm^{-1} and 2552 cm^{-1} , in Fig 2a which can respectively be ascribed to NH_3^+ rocking, $-\text{COO}-$ asymmetric stretching, and SH stretching vibrations 21.

The peak of $-\text{SH}$ was changed between the cysteine and cysteine bound GNP, indicating that the $-\text{SH}$ group on cysteine is involved in binding to GNP. (Figure No.2b). The peak of $-\text{COO}-$ asymmetric stretch on cysteine did not change significantly compared with that on Au-cysteine, indicating that the $-\text{COO}-$ was not effectively involved in Zn binding. Fig.2c shows that the peak of NH_3^+ rocking shifted from 1139 cm^{-1} of the original cysteine spectrum to 1241 cm^{-1} for the cysteine-bound GNP-Zn complex. The absence of the characteristic absorption peak of $\text{S}-\text{H}$ group around 2550 cm^{-1} demonstrates the formation of GNP-cysteine-Zn complex by the reaction between GNP-cysteine and Zn.

Effect of supporting electrolytes and scan rate

The ZnHCF modified electrode was characterized by cyclic voltammetry and the effect of supporting electrolyte was studied. It was found that among the cations studied, (Na^+ , K^+ , Ba^{2+} , Ca^{2+} , NH_4^+ at 0.1M concentration) Na^+ gave a well-resolved and sharp peak. So 0.1M NaNO_3 was chosen as the background electrolyte.

The effect of scan rate on the modified electrode was also studied at different scan rates in the range of 10-150 mV/s . in Figure No.5. The ratio of i_{pa}/i_{pc} was found to be almost close to unity in the range studied. The ZnHCF modified electrode showed a ΔE_p of 0.54 V for a potential scan rate of 20 mV/s . This slight deviation from ideal behavior arising even at low scan could be attributed to the limitations associated with charge transfer in the film. Wider splitting was observed at higher scan rates ($> 200 \text{mVs}^{-1}$) indicating the limitations arising from the charge transfer kinetics. The anodic and cathodic peak currents were linearly proportional to the square root of the scan rate ($v^{1/2}$) with a correlation coefficient of 0.999, which is expected for a diffusion-controlled process (Figure No.5b).

The lepton transfer constant (α) was calculated from the slope of the plot of E_p Vs $\log v$ and was found to be zero.42 and therefore the heterogeneous lepton transfer rate constant (K_s) of the ZnHCF modified graphite electrode was estimated to be 0.766 s^{-1} . (Pournaghi- Azhar. 1998)¹⁵.

The performance of the modified electrode was studied under different pH conditions in the range of 2-9. The pH of the background electrolytes was varied using HCl and NaOH. It was found that the peak current did not vary much in the pH range 2-6 but a maximum response in current was obtained at pH 7 (Figure No.6). The current response again decreases at pH 8 and above. The poor response at very basic pH could be due to the hydroxylation of the mediator. (Ravishankar, 2001)¹⁶. Hence a neutral pH was chosen for subsequent experiments.

Electro catalytic oxidation of catechol at the modified electrode

The electro catalytic property exhibited by the ZnHCF-GNP graphite wax composite electrode for the oxidation of catechol in 0.1M NaNO_3 is also shown in Figure No.7. It is seen that on bare graphite wax composite electrode, the oxidation of catechol occurs at a higher potential around 0.74V (curve c) whereas on the ZnHCF-GNP graphite wax composite electrode, the oxidation of catechol occurs at 0.55 V (curve d). Also the catalytic current at the modified electrode was nearly 14 times higher than that obtained at the bare electrode for catechol oxidation. The modified electrode showed linear response for the catalytic oxidation of catechol. The linear range for the determination of catechol is from 2.6×10^{-6} to $7.2 \times 10^{-3} \text{M}$ with a correlation coefficient of 0.999. (Figure No.7a) and the detection limit was $1 \times 10^{-7} \text{M}$.

Hydrodynamic voltammetric studies on the bare and the ZnHCF-GNP graphite wax composite electrode were carried out in the potential range between 0 to 1.0V in 0.1M NaNO_3 in order to check the applicability of the modified electrode in flow system. The bare electrode showed a poor response to catechol whereas there was a considerable increase in response with the modified electrode around 0.54V (Figure No.8). Hence 0.55V was

chosen as the operating potential for amperometric studies.

Flow injection analysis

The flow- rate dependence of the current response at a constant concentration of catechol was examined by recording the peak currents at different flow rates. The current response was found to be decrease with increasing flow rate. At a flow rate of 0.5 min^{-1} , the determination of catechol can be performed in 2 min including the sampling and washing. Figure No.9 displayed the flow injection response of the ZnHCF-GNP- graphite wax composite electrode for catechol solution of increasing concentration from 8.9, 19.2 23.3 μM . Well-defined and sharp peaks were observed at a detection potential of 0.54V (versus Ag/AgCl). The flow injection peak currents were proportional to the catechol concentration. The resulting calibration plot had a slope of $18.9 \mu\text{A mM}^{-1}$ for ZnHCF modified electrode, and the correlation coefficient of 0.999. A detection limit of $1 \times 10^{-7} \text{ M}$, can be estimated on the signal-to-noise ratio ($S/N=3$). Figure No.9a shows the modified electrode response to same concentration of catechol (spiked) in environmental water sample.

Both the results appear almost in agreement with each other in sensitivity. The results indicated that the detection limits are appreciably low and are more sensitive. In all cases the response was rapid and reproducible. After an initial loss activity, the electrodes exhibited a very stable response during hours of continuous flow injection.

Interferences

The effect of some possible interferences in environmental water such as metal ions, anions and organic compounds was tested. A large number of ions, such as K^+ , Zn^{2+} , NO_3^- , Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} (with the concentration of $4 \times 10^{-4} \text{ M}$) and ethanol, toluene and benzene (with the concentration of $2 \times 10^{-3} \text{ M}$) had no influence on the signals of catechol.

Determination of catechol from water samples

In order to check the validity of the proposed method for the determination of catechol. Four different water samples were spiked with $6 \times 10^{-5} \text{ M}$ of catechol and were analyzed under optimized condition using above method, this results are summarized in Table No.1.

Table No.1: Real Sample analysis of catechol

S.No	Samples	Concentration of Catechol (μM)		Recovery (%)
		Added	Found ^a	
1	Sample I	30	29.20 ± 0.70	98.4
		40	39.81 ± 0.49	99.5
2	Sample II	30	29.9 ± 0.50	99.6
		40	39.68 ± 0.48	99.2
3	Sample III	30	29.76 ± 0.48	99.2
		40	39.16 ± 0.47	97.9
4	Sample IV	30	29.82 ± 0.49	96.06
		40	38.99 ± 0.45	97.47

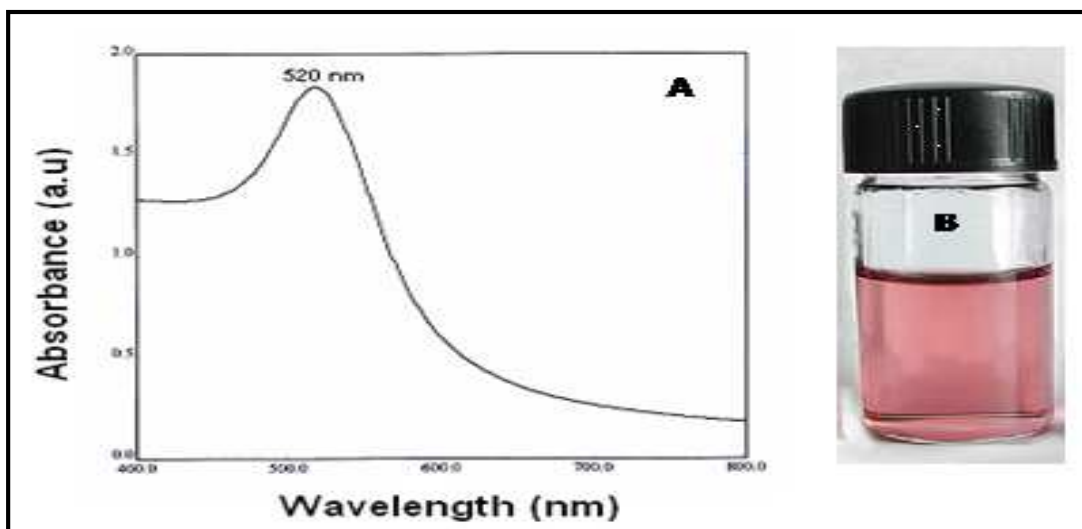


Figure No.1: (A) UV-vis spectrum of the Au nanoparticles (B) photograph of the Au colloid

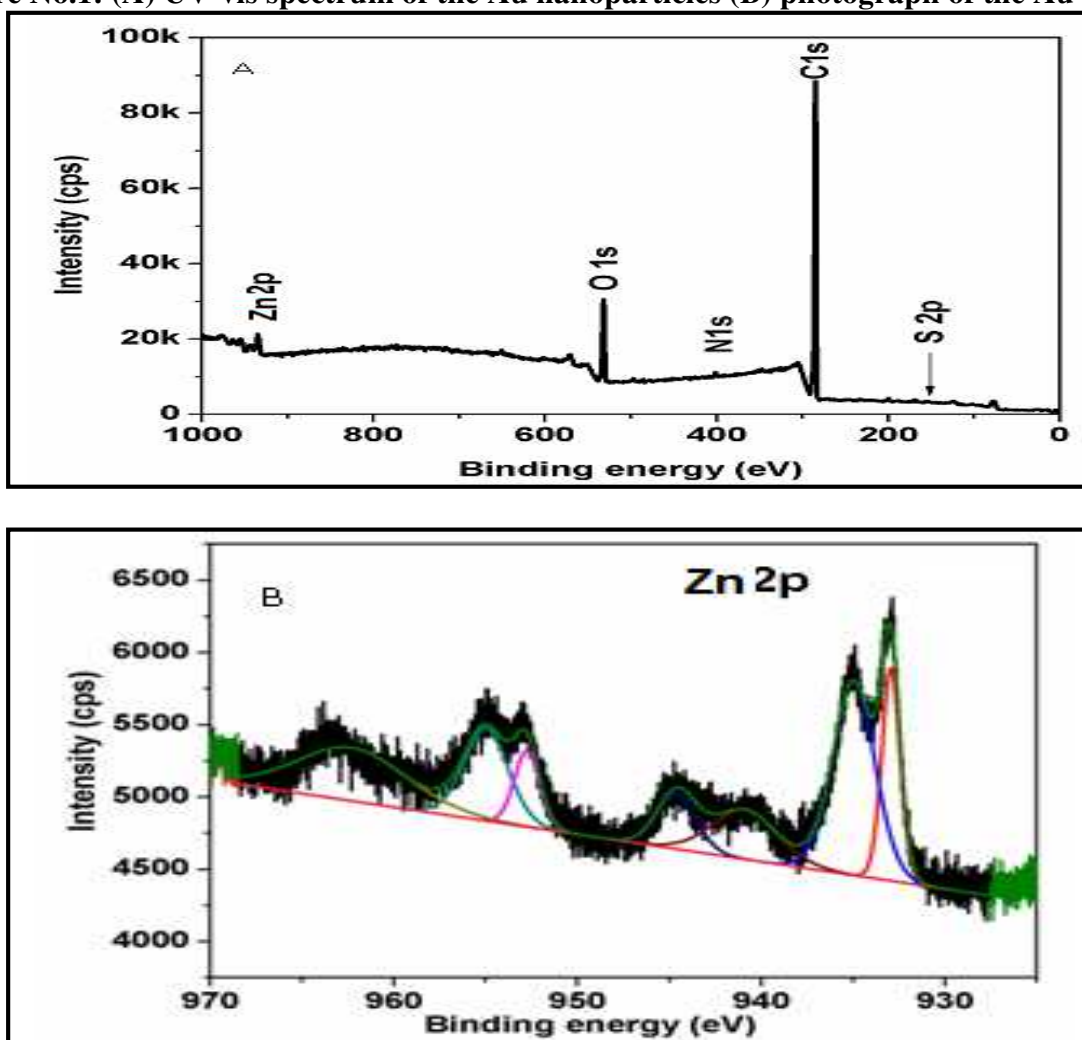


Figure No.2: XPS spectra of (A) Survey spectra (B) 2P_{3/2} and 2P_{1/2} peaks of ZnHCF modified electrode

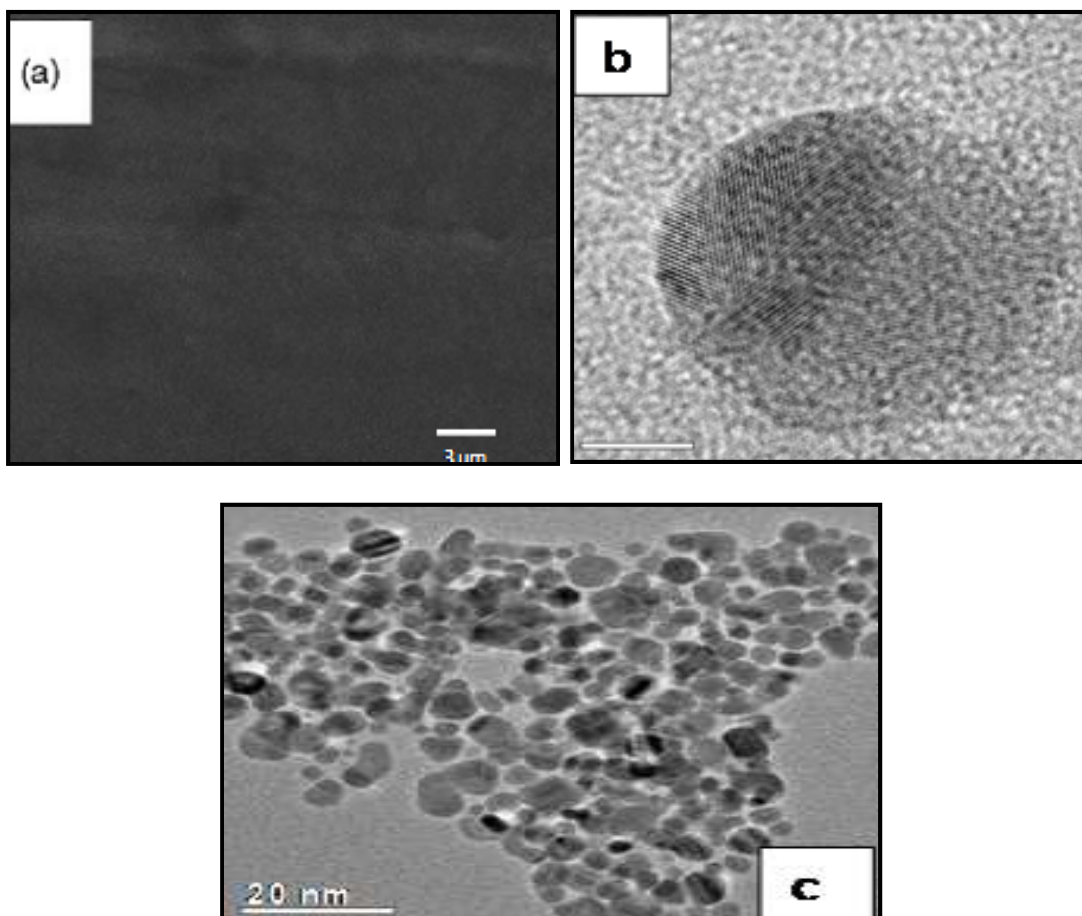


Figure No.3: The TEM images (A) represent as a bare electrode, (B) presence of GNP on graphite matrix (C) ZnHCF particles on the modified electrode

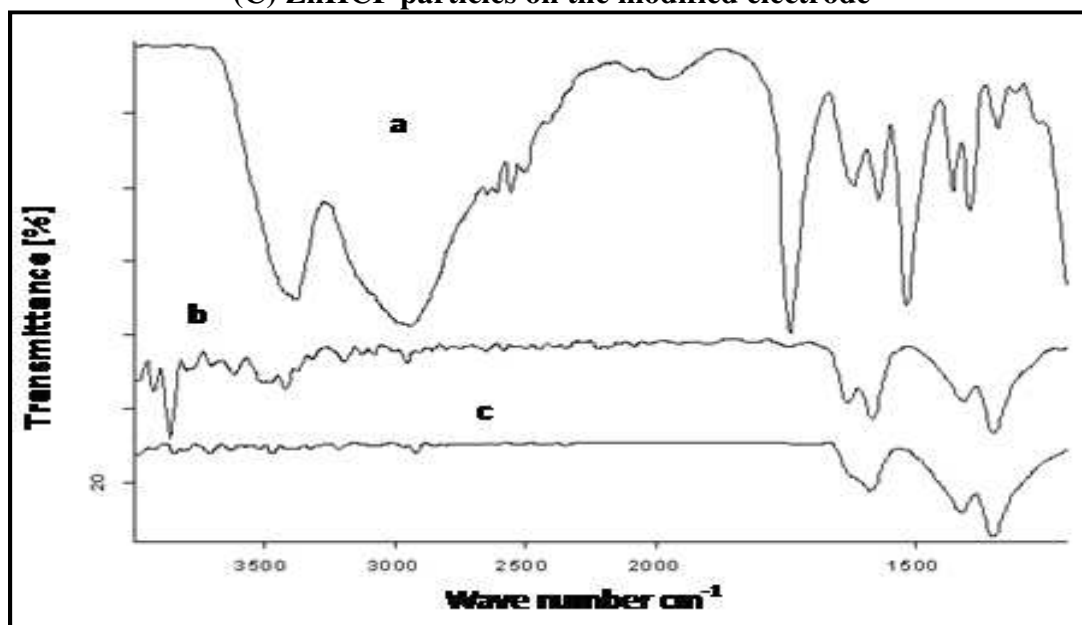


Figure No.4: FTIR spectra of (a) pure cysteine (b) cysteine adsorbed GNP graphite powder and (c) GNP-Cys- ZnHCF modified electrode

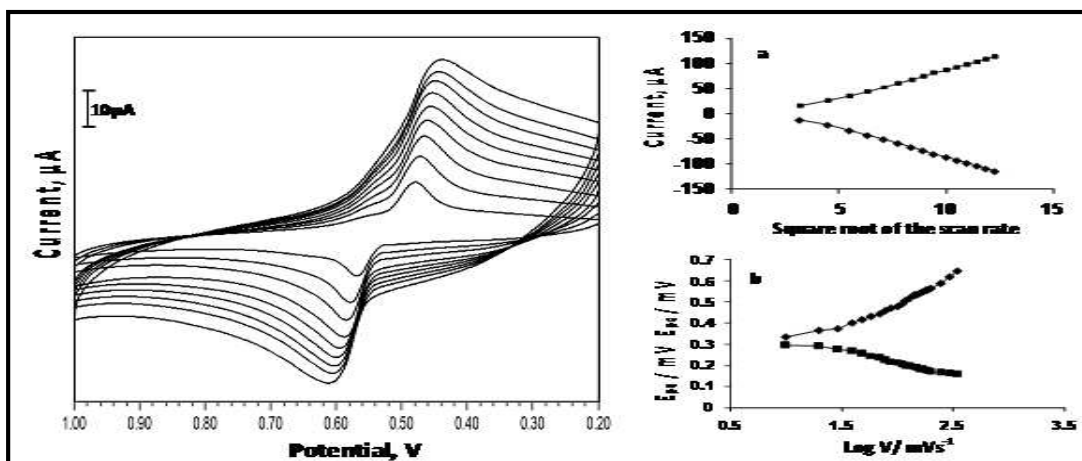


Figure No.5: Cyclic voltammogram of the ZnHCF modified electrode at different scan rates in 0.1M NANO₃ (pH 7.0). The scan rates from inside to outer are 10-100 mVs⁻¹ with increments of 10 from 10 mV⁻¹, (3.5a) dependence of peak current I_{pa} and I_{pc} on square root of scan rate(v), (3.5b) variation of peak potential vs. logarithm of scan rates (logv)

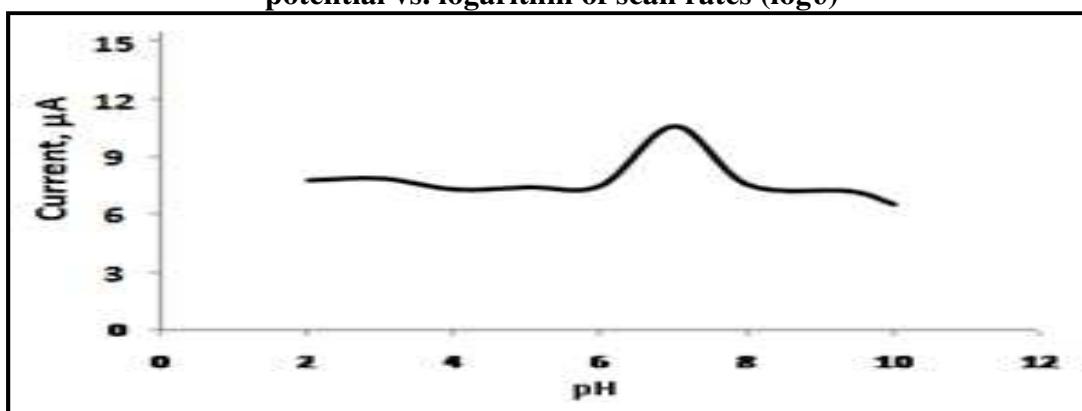


Figure No.6: Plot of pH Vs Current for modified electrode. It was found that the peak current did not vary much in the pH range 2-6 but a maximum response in current was obtained at pH 7

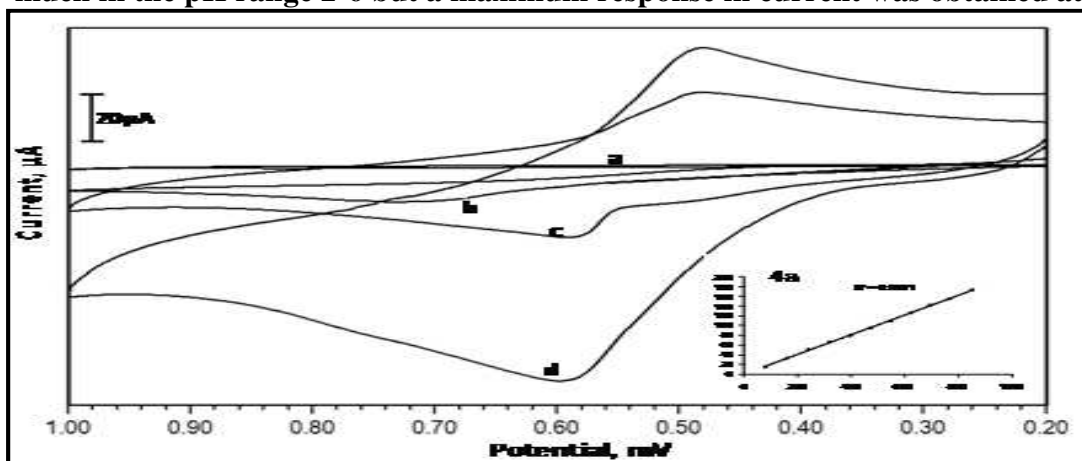


Figure No.7: Cyclic voltammograms in 0.1 M NANO₃ (pH 7.0) at a scan rate of 20 mVs⁻¹ (a) bare electrode in the absence of catechol (b) bare electrode in the presence of Catechol (c) modified electrode in the absence of catechol (d) ZnHCF modified electrode in the presence of 7.6x10⁻⁵M catechol.

Figure No.7: Acalibration graph for catechol measurement

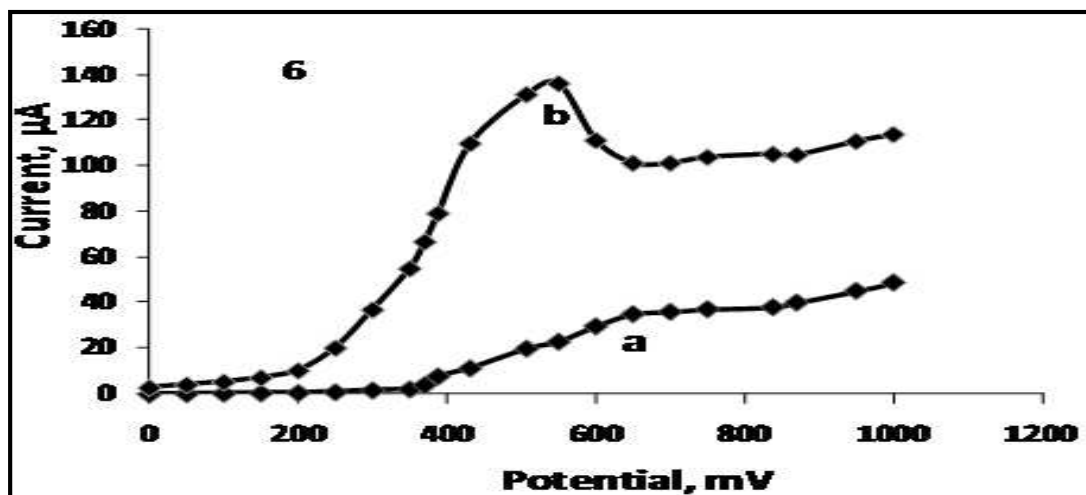


Figure No.8: Hydrodynamic voltammograms obtained with (a) bare (b) ZnHCF modified electrode in the presence of $9.6 \times 10^{-5} \text{M}$ catechol

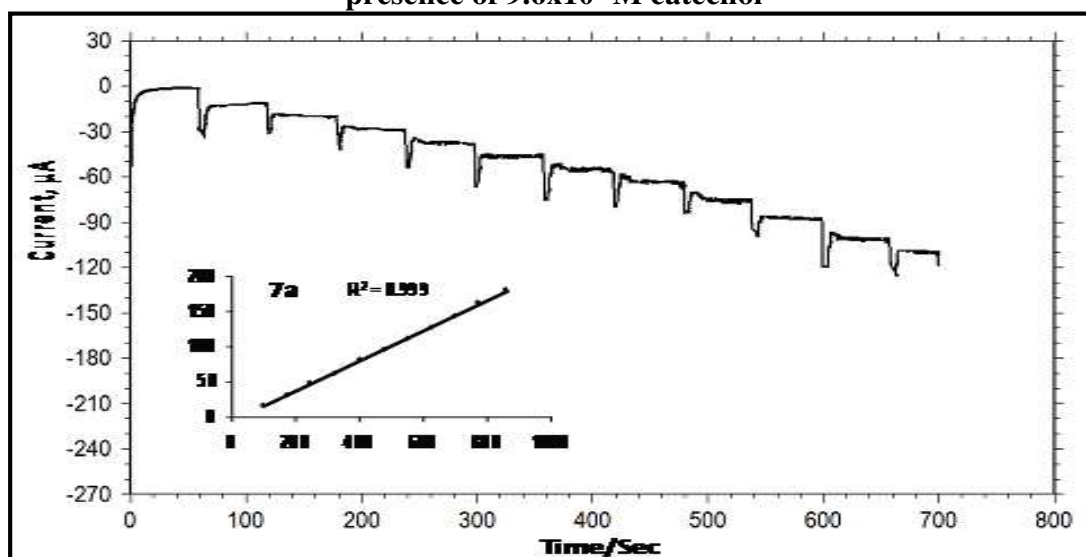


Figure No.9: Chrono-amperometric response of the ZnHCF modified electrode for three replicate additions of $8.9 \mu\text{M}$, $19.2 \mu\text{M}$ and $23.3 \mu\text{M}$ of catechol Figure No.9a extracted from environmental water sample in 0.1M NaNO_3 , operational voltage 0.55V . Flow rate 0.5 ml min^{-1}

CONCLUSION

A GNP graphite paraffin wax composite electrode was prepared by the oxidative electro derivatization of ZnHCF in 0.1 M NaNO_3 , and the resulting modified electrode exhibited a good electro catalytic activity and good stability for catechol. In a flow injection analysis, the detection limit of catechol was estimated to be of the order of $1 \times 10^{-7} \text{M}$.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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