A GNP-Cys-ZnHCF Graphite Compostie Electrode for the Determination of Hydrazine

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***Abstract* - Hydrazines are compounds of interest in both the chemical and pharmaceutical industry. Hydrazine is used in agriculture as pesticides, blowing agents, pharmaceutical intermediates, photographic chemical, water treatment for corrosion protection, textile dyes, jet and rocket fuel. Individuals may be occupationally exposed to hydrazine in the workplace and accidental discharges into water, air, and soil may occur during storage, handling, transport, and improper waste disposal. In the development of chemically modified electrodes (CMEs) there as been considerable interest in recent years, as they offer a lot of advantages over other electrochemical methods. CMEs improve the sensitivity and selectivity of electrochemical analysis by improving the kinetics of the reaction via an electrocatalytic process at the CME surface. A Nickel hexacyanoferrate(II)-L-cysteine-gold nano particle (ZnHCF-L-Cys-GNP) graphite wax composite electrode was prepared for determination of hydrazine. This electrode has favorable properties with respect low cost, simple preparation and easy renewal of the electrode surface. GNP present in the electrode display four unique advantages over macro electrodes when used for electro analysis: enhancement of mass transport, catalysis, high surface area and control over electrode microenvironment. The modified electrode was characterized by SEM, FTIR, different electrolytes, scan rates and pH. The modified electrode showed good electrocatalytic activity towards the oxidation of hydrazine under the optimal conditions and showed a linear response over the range from 4.9x10^{-7} to 1.03x10^{-3}M of hydrazine with a correlation coefficient of 0.999. The limit of detection was found to be 1.2x10^{-8}M. The analytical utility of the electrode for determination of hydrazine in flow system was evaluated by hydrodynamic and chronoamperometric studies.**

***Keywords: GNP; Zinc hexacyanoferrate; Hydrazine*.**

1. INTRODUCTION

The development of novel electrode materials for use in the determination of clinically, industrially and environmentally important compounds is currently an area of very active investigation. Hydrazine (N_2H_4) and its derivatives have been found to have wide applications in industry, agriculture, as explosives, antioxidants, photographic developer, oxygen scavengers and propellants. Hydrazine is a base product in fuel cell [1] and also it is very important in pharmacology because it has been recognized as a carcinogenic and hepatotoxic substance, which affects liver and brain glutathione [2]. As N_2H_4 is also a toxic material it must be treated with precaution. So, the detection and determination of N_2H_4 becomes essential in view of its importance in diverse context. Thus there is a growing need for the development of simple, economical and accurate on-line monitoring devices for determination of trace amounts of hydrazine in different samples such as water, industrial and environmental materials.

Several techniques such as spectrophotometry [3], coulometry [4], amperometry [5], potentiometry [6], titrimetry [7] and chemiluminescence [8] have been reported for the determination of hydrazine. The direct oxidation of hydrazine has been studied at several electrodes including mercury [9,10], silver and gold [10], platinum [11] and nickel [12]. Although metals such as Pt, Au, and Ag are very active in the anodic oxidation of hydrazine, but they are too expensive for practical applications and require a large overpotential for hydrazine determination.

A major attention has been focused on the development of chemically modified electrodes during the last two decades. They exploit the ability of certain surface–bound redox mediators to enhance electron-transfer kinetics and thus lower the operating potential. Hence relatively large amounts of electrochemical research have been devoted to the development and application of different types of chemically modified electrodes. Wang et al [13] described a modified electrode based on 3,4-dihydroxy benzaldehyde for the remote monitoring of hydrazine. A few kinds of transition metal complexes are efficient electrocatalyst for the anodic oxidation of hydrazine [14-16]. One important group of inorganic compounds utilized for electrode modification and electrocatalytic purpose is the transition metal hexacyanoferrates. Scharf et al [17] used a PB modified GCE electrode for the electrocatalytic oxidation of hydrazine. Electrocatalytic efficiency of various transition metal hexacyanoferrate modified graphite electrodes for the oxidation of hydrazine has been reported [1]. The objective of the present study is to fabricate and characterize a new amperometric sensor utilizing ZnHCF-L-Cys-GNP modified graphite-wax composite electrode for hydrazine determination.

2. EXPERIMENTAL

2.1 Reagents and chemicals

All reagents were of analytical grade; Graphite powder was from Aldrich (1-2µm), (Aldrich, Steinheim, Germany).Catechol from Alfa Aesar (Alfa Aesar chemicals, Kolkata, India). $NiCl_2$, 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 cadmium solution (0.01M) was prepared by dissolving the salt in ethanol. Potassium ferrocyanide (0.02 M) in KNO_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 min.

2.2 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.

2.3 Fabrication of GNP-ZnHCF paraffin wax composite electrode

Graphite powder (1 g) was added to 125 ml of synthesized gold nanoparticles solution (0.6mM) and the mixture was stirred for two hours at 300 rpm in room temperature. The stirred mixture was centrifuged at 1450 rpm for 30 minutes and the residue was kept overnight 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 graphite wax mixture was tightly packed in a small glass tube of 3mm diameter. The electrode was removed gently from the tube after it turns hard. The electrode prepared in this ratio showed an excellent hardness and conductivity. 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 $NiCl_2$ for 2 minutes. The amino group of cysteine functionalized with gold nanoparticles has a greater affinity towards transition metal ion like Ni^{2+}. The Ni^{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} .

3. RESULTS AND DISCUSSION

3.1 SEM characterization of the surface

Fig.1 shows the SEM images of (a) bare graphite wax composite electrode (b) GNP absorbed 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 150-200nm .

3.2 FTIR characterization of the surface:

Fig.2 shows the FTIR spectra of (a) pure cysteine, (b) cysteine adsorbed GNP graphite 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, $-COO^-$ asymmetric stretching, and SH stretching vibrations[18].

The peak of -SH was changed between the cysteine and cysteine bound GNP, indicating that the -SH group on cysteine is involved in binding to GNP. (Fig.2b). The peak of $–COO^-$ asymmetric stretch on cysteine did not change significantly compared with that on Au-cysteine, indicating that the $–COO^-$ was not effectively involved in Ni binding. Fig.2c shows that the peak of NH_3^+ rocking shifted from 1139 cm^{-1} of the original cysteine spectrum to 1241cm^{-1} for the cysteine-bound GNP-Ni complex. The absence of the characteristic absorption peak of S–H group around 2550 cm^{-1} demonstrates the formation of GNP-cysteine-Ni complex by the reaction between GNP-cysteine and Ni.

3.3. Electrochemical behavior of the modified electrode

Cyclic voltammetry was used to study the electrochemical behaviour of ZnHCF modified electrode. The result have been obtained with the ZnHCF modified electrode in 0.1 M $NaNO_3$ at a scan rate of 20mVs^{-1}. Redox peaks were observed at 0.366V and 0.29V corresponding to the anodic and cathodic reactions respectively, and the formal potential was found to be 0.328 V. Different electrolytes were used to test the performance of the modified electrode. In the redox reaction of the metal hexacyanoferrates, the transfer of an electron is always accompanied by the simultaneous motion of a counter cation in and out of the cage structure in order to maintain the charge balance. In the reduction a counter cation insertion into the film and its exclusion upon oxidation have been verified by Kulesza et al [19]. Thus the size of the counter cation along with its mobility plays a key role in determining the voltammetric response of the ZnHCF modified electrode. The cyclic voltammetric responses of the ZnHCF modified electrode in solution of 0.1 M LiCl, $NaNO_3$, KNO_3, NH_4Cl, KCl and NaCl has been studied.(Fig not shown) It was clear that the higher peak currents along with lower formal potential for ZnHCF modified electrode could be achieved in presence of Na^+ ions. Anions were found not to alter the electrochemical behavior of ZnHCF, and hence 0.1 M $NaNO_3$ was chosen as the suitable supporting electrolyte for further experiments.

The effect of scan rate on the electrochemical behaviour of the modified electrode was studied in 0.1M $NaNO_3$. Fig.3 shows the cyclic voltammogram of the ZnHCF modified electrode at various scan rate such as 10, 20, 30 upto 150 mV. On varying the scan rate from 10mV-150mV/s, the peak-to-peak separation varied from 0.047 to 0.18V. Peak-to-peak separation must be zero for the ideal behaviour of the modified electrode. All the modified electrodes have shown higher peak separation and larger peak width, and the non-ideal behaviour of the electrodes which are attributed the following reasons: (a) distribution of species with different E^0 values [20] (b) repulsive interactions between ions in the lattice and (c) difference in spatial distribution of redox centers. Moreover, it can be seen from the inset of Fig.3A that the peak currents (Ip_a and Ip_c) have a linear relation with the square root of the scan rate corresponding to a diffusion- controlled reversible reaction and display the nature of a surface wave. Owing to the various reasons associated for increase in ΔE_p at higher scan rates, Laviron derived a general expression where the limitation is attributed to charge transfer kinetics. Based on this Laviron equation the electron transfer rate constant (K_s) was calculated to be 0.766 s^{-1}.(Fig.3B)

The performance of the modified electrode was also studied under different pH conditions in the range 2-9. The pH of the background electrolyte 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 (Fig 3C). At pH greater 7 there is a decrease in current response. The possible reason could be the hydroxylation of ZnHCF [21]. the hydroxylated moiety formed is electrochemically inactive and gets dissolved into the background electrolyte which results in a decrease in current response at pH greater than 7. Hence a neutral pH was chosen for further experiments.

3.4. Electrocatalytic oxidation of Hydrazine

In order to assess the electrocatalytic activity of the ZnHCF modified composite electrode towards the oxidation of hydrazine, cyclic voltammograms were recorded in the presence and absence of hydrazine in 0.1 M $NaNO_3$. As shown in Fig.4 upon the addition of $7.6x10^{-5}$M hydrazine, there was a dramatic enhancement in the anodic peak current at the modified electrode whereas a slight increase in the anodic current was observed at the bare electrode. Also, the anodic potential for oxidation of hydrazine at the ZnHCF modified electrode is at 0.38 V, whereas at the bare electrode hydrazine undergoes oxidation about 0.65 V. The decrease in overpotential and enhancement of anodic peak current for hydrazine oxidation indicates the strong electrocatalytic effect of the ZnHCF modified electrode.

The ZnHCF present at the electrode surface gets oxidised at its oxidation potential. This oxidised form of the mediator in turn oxidizes hydrazine to t- butyl quinone (TBQ) and gets reduced. The reduced form of ZnHCF again gets oxidised at the electrode surface producing the oxidation current at the same time. Thus an enhanced anodic current was observed for every addition of hydrazine. The quantification of hydrazine was carried out by measuring the catalytic current as a function of hydrazine concentration. The catalytic current was found to increase linearly with the concentration of hydrazine in the range from $4.9x10^{-7}$ M to $1.03x10^{-3}$M with a correlation coefficient of 0. 999.(Fig 4a) Thus the sensor could be used to determine the concentration of hydrazine in the above range. The detection limit was found to be$1.2x10^{-8}$M.

3.5 Amperometric determination of hydrazine

Hydrodynamic voltammetry was performed to study the electrocatalytic response of ZnHCF modified composite electrodes under dynamic conditions and to optimize the operating potential for amperometric measurements. In hydrodynamic voltammetric studies, the potential of the working electrode was increased gradually in stirred solution, and the resulting steady state current was measured and plotted against the applied potential. The plot of current versus applied potential in the presence of $4.76x10^{-5}$M hydrazine at the bare and modified electrodes is shown in fig.5. Almost negligible response is observed with the bare electrode while a significant increase in current was observed with the modified electrode. The current increases from 0.2V and approaches to a maximum value at of 0.4V. Hence a potential greater than or equal to 0.4V can be applied for electrocatalytic oxidation of hydrazine in flow systems.

The amperometric response of the ZnHCF- modified electrode for the electrocatalytic oxidation of hydrazine was studied. The current-time response obtained for the ZnHCF modified electrode in a stirred solution (300rpm) for successive increments of $4.14x10^{-5}$M hydrazine is shown in fig.6. The current response increases with increasing concentration of hydrazine. The plot of catalytic current versus hydrazine concentration is shown in fig 6a. A good linear response was obtained in the range $4.9x10^{-7}$ - $1.03x10^{-3}$M hydrazine with the correlation coefficient of 0.999. The response of the modified electrode on continual usage was checked by repeating the experiments for 6 times using the same amount of hydrazine which showed 1.9% variation.

3.6. Interference Study

To evaluate the selectivity of the proposed method interference studies were carried out. The common foreign substances present in the water samples are different cations and anions. The effect of various cations and anions were tested by cyclic voltammetry in order to check the interference for hydrazine oxidation. Various interferent-to-analyte ratios (tolerance limit molar ratio) causing less than ± 4% relative error for a hydrazine concentration of 3.2×10^{-5} M is listed in Table 1 which indicates that most of the cations and anions do not interfere with this electrocatalytic method for hydrazine determination. Thus, the ZnHCF modified graphite-wax composite electrode allows amperometric detection of hydrazine at a significantly lower operating potential and hence yields an improved selectivity.

3.7. Analysis of hydrazine in water samples:

In order to demonstrate the electrocatalytic oxidation of hydrazine and determination in real samples, the modified electrode was used to determine the amount of hydrazine in water samples and spiked with hydrazine and the results were compared with standard method based on p-dimethylamino benzaldehye reaction [22]. The results of the above study are summarized in table 2. Each value is an average of five measurements and the statistical treatment of the data indicates that the results obtained by the proposed method are precise and accurate. The good recoveries close to 100% for the water samples analysis indicates no serious interference due to matrix effect.

3.8. Study of reproducibility and stability

To characterize the reproducibility of the ZnHCF modified graphite-wax electrode, repetitive measurement were carried out in 9.6×10^{-5} M hydrazine. Ten replicate measurements of hydrazine detection by the modified electrode showed a reproducibility of 2.0 %, which suggests a good reproducibility of the present method. In addition, stability of the ZnHCF modified electrode for the determination of hydrazine on storage was investigated by keeping the electrode in a desiccator at room temperature when not in use and recording a cyclic voltammogram each day. In the first week the current response decreased marginally retaining about 97% of its original response at the end of the week. After that the current remained constant and about 96% of the original response remained at the end of 30days (Fig not shown). These results indicate that the modified electrode has a good reproducibility and better stability.

4. CONCLUSION

A GNP-L-CYS-ZnHCF modified amperometric sensor based on carbon composite method has been constructed and characterized. The redox activity of the mediator is attributed to the $Fe(CN)_6^{3-/2-}$ group of ZnHCF. Electrochemical characterization of the modified electrode reveals the sole participation of the cation (Na^+) in the electrochemical process. The modified electrode performed better in pH 7 whereas pH of the medium showed a negligible influence on the peak potentials of the modified electrode in both acidic and neutral range studied. The modified electrode electrocatalyzes the oxidation of hydrazine at a reduced potential (400 mV) compared to the unmodified electrode. The use of above electrode as an amperometric sensor for the determination of hydrazine in water sample has been demonstrated. The modified electrode possesses several advantages. It is robust, stable, and reproducible and exhibits the merits such as simple fabrication, cost effective and surface renewability. These features suggest that the ZnHCF modified graphite-wax composite electrode could be used as a useful amperometric sensor for monitoring hydrazine in environmental sample

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Table 1
A partial list of literature reporting amperometric determination of N_2H_4 at different potentials at various CMEs

Electrode	Mediator	Applied potential (mV)	References
GC	PCoPP	620	[15]
GC	PB	700	[14]
GC	CGA	300	[2]
GWC	CuHCF	700	[23]
CPE	ST-NiTsPc	480	[17]
Graphite rod	CoHCF	700	[24]
GNP-L-CYSGWC	ZnHCF	380	This work

GC- Glassy Carbon
GWC- Graphite-Wax Composite
CPE- Carbon Paste Electrode
PCoPP- Polymer films of Cobalt protoporphyrin dimethylester
PB- Prussian Blue
CGA- Chlorogenic acid
ZnHCF- Zinc Hexacyanoferrate
CuHCF- Copper Hexacyanoferrate
ST-NiTsPc- Silica modified Nickel Tetrasulfonated Phthalocyanine
CoHCF- Cobalt Hexacyanoferrate
CoPCNF- Cobalt pentacyanonitrosylferrate
MnHCF-Manganese Hexacyanoferrate

Table 3
Results for determination of hydrazine in water sample

Sample	Hydrazine (mg/L)			% Recovery
	Added	Found*		
		Proposed method	Standard method	
Drinking Water	37.61 72.33 93.74	36.01 ± 2.3 71.94 ± 2.0 92.97 ± 2.5	34.32 ± 2.6 70.25 ± 2.3 94.75 ± 3.0	98.3 99.4 99.2

* Average of five measurements ± R.S.D.

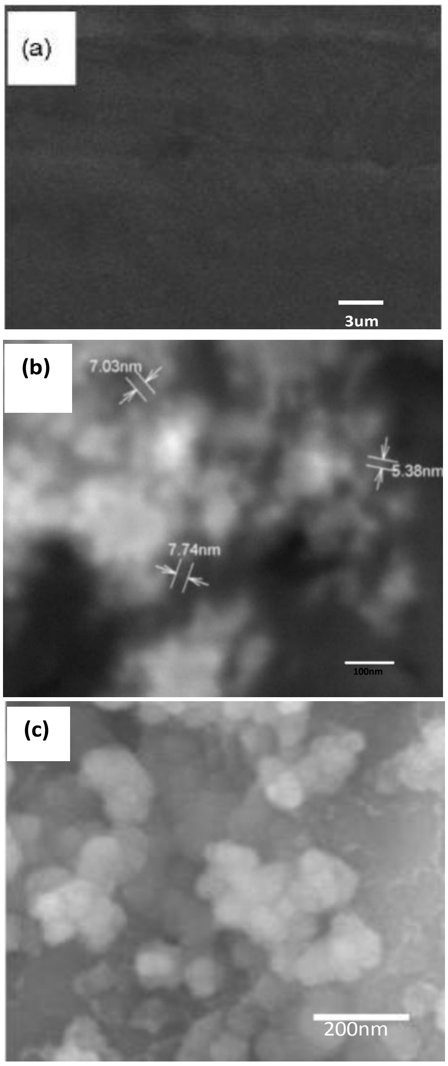

Fig. 1. The SEM images (A) represent as a bare electrode, (B) presence of GNP on graphite matrix (C) ZnHCF particles on the modified electrode.

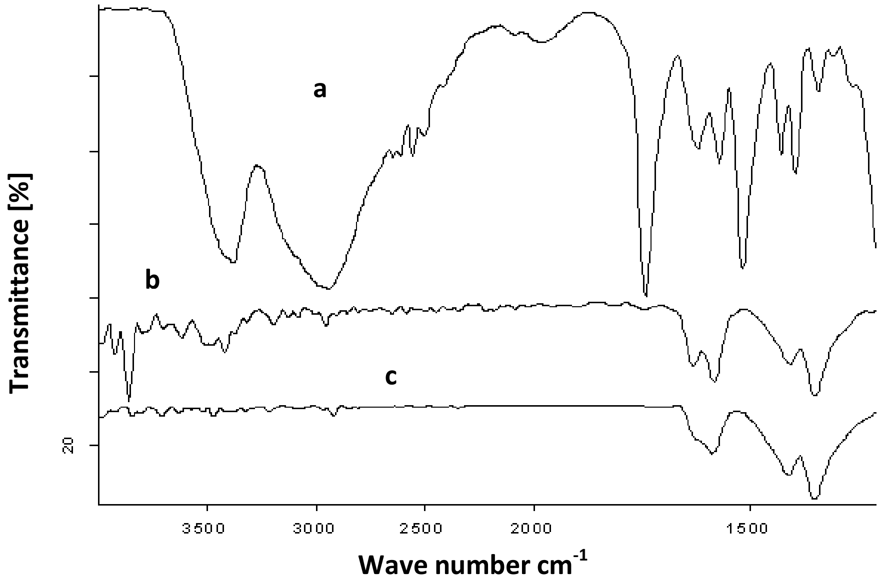

Fig. 2 FTIR spectra of (a) pure cysteine (b) cysteine adsorbed GNP graphite powder and (c) GNP-Cys- ZnHCF modified electrode.

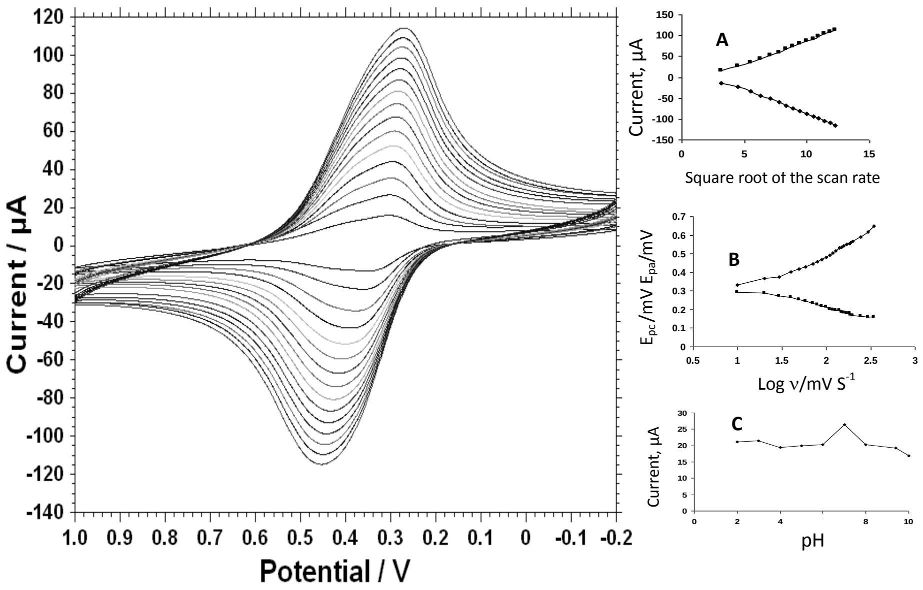

Fig. 3.cyclic voltammogram of the ZnHCF modified electrode at different scan rates in 0.1M NaNO$_3$ (pH 7.0). The scan rates from inside to outer are 10-150 mVs^{-1} with increments of 10 from 10 mV^{-1} , (A) dependence of peak current I_{pa} and I_{pc} on square root of scan rate(υ), (B) variation of peak potential vs. logarithm of scan rates (logυ). (C) effect of pH on catalytic current of the ZnHCF modified electrode with 1.6x10^{-5} M of BHA in 0.1M NaNO$_3$.

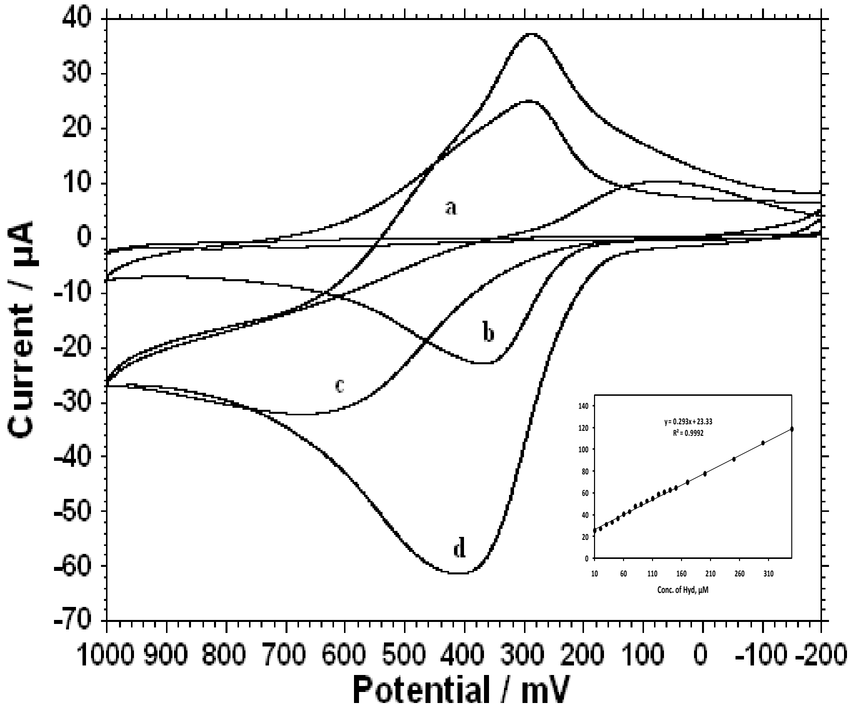

Fig.4.Cyclic voltammograms in 0.1 M NaNO$_3$ (pH 7.0)at a scan rate of 20 mVs^{-1} (a) bare electrode in the absence of Hyd (b) modified electrode in the absence of Hyd(c) bare composite electrode in the presence of 7.6x10^{-5}M Hyd (d) ZnHCF modified electrode in the presence of 7.6x10^{-5}M Hyd. Inset: calibration graph for Hyd measurement.

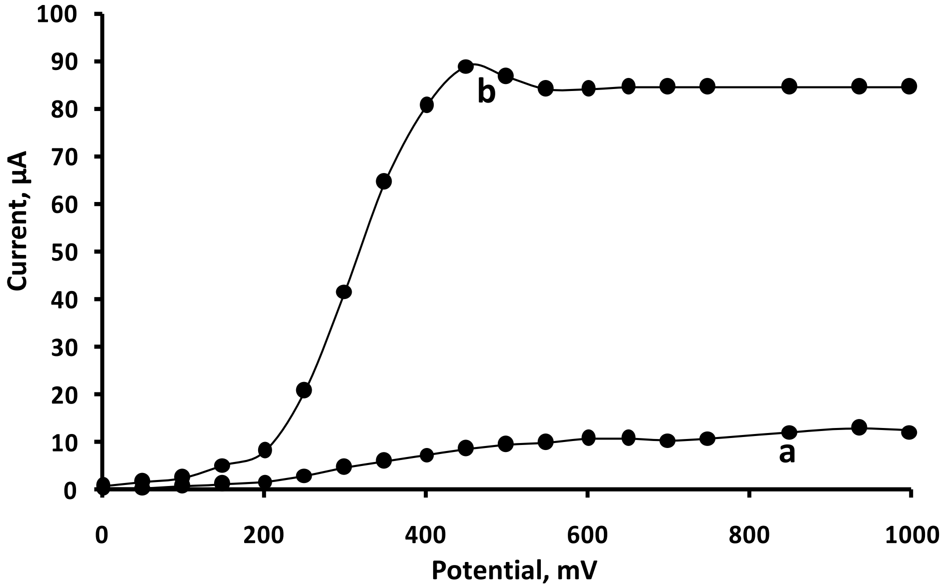

Fig. 5. (A) Hydrodynamic voltammograms obtained with (a) bare and (b) ZnHCF modified electrode in presense of hydrazine.

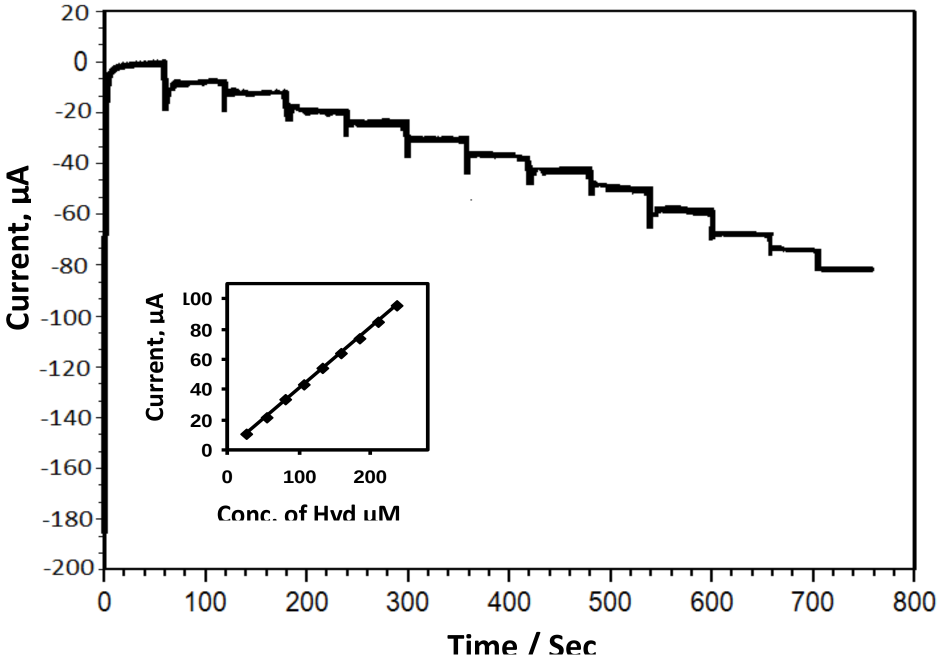

Fig 6. Chronoamperometric response at ZnHCF modified electrode for each addition of 4.14×10^{-5}M Hydrazine to 0.1 M $NaNO_3$ (pH 7.0) stirring rate: 300 rpm; potential: 0.5 V. Inset: Calibration graph for Hydrazine measurement.