Catechol sensor using GNP-CYS-CeHCF Graphite Wax Composite Electrode

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***Abstract* - A novel modified electrode was fabricated by electrochemical derivatization of CeHCF at a GNP adsorbed graphite wax composite electrode. The electrode developed was used for the determination of catechol. The voltammetric characteristics of the CeHCF 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 scanning electron microscopy (SEM) which indicated that the CeHCF particles were 50-70 nm in size and were dispersed uniformly on electrode surface. The CeHCF modified electrodes presents good electrocatalytic 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 2.6X10^{-6} to 7.2X10^{-3}M of catechol with a detection limit of 1X10^{-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; Cerium hexacyanoferrate; Electro catalysis; catechol Introduction:

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 [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 [2]. 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 [3, 4] high-performance liquid chromatography [5]. The electrochemical determination of catechol was also using enzymatic [6-7,12] or non enzymatic electrodes [8-16,13-21]. 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 [8,13]. The non enzymatic electrodes used for studying the direct electrochemistry of catechol was also examined using different types of electrodes such as mesoporous platinum [9-10,14-15] and gold electrode [11]. 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-CeHCF modified electrode was developed by anchoring CeHCF onto the surface of gold nanoparticles using 3-Mercapto-2-aminopropionic acid (L-cysteine) as cross linker, to the metal ion Ni^{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 conformed 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 CeHCF 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.

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). $CdCl_2$, 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 KNo_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 CeHCF 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. Sample preparation

Four different water samples were prepared by adding approximate $6X10^{-5}M$ of catechol into the real samples of distilled ,tap, river and drinking water. This 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.

2.4 Fabrication of GNP-CeHCF 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 $CdCl_2$ for 2 minutes. The amino group of cysteine functionalized with gold nanoparticles has a greater affinity towards transition metal ion like Cd^{2+}. The Cd^{2+} ions coordinated to amine group was then derivatized using 0.02 M potassium ferrocyanide solution dissolved in 0.1 M KNO_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)

3. RESULTS AND DISCUSSION

3.1 SEM characterization of the surface :

The SEM images of electrodes are performed in Fig. 1. The bare electrode is shown in Fig. 1(A) where a smooth surface of the wax electrode is seen. Fig. 1(B). shows the surface of the electrode prepared from GNP – graphite mixture and the presence of GNP is conformed which is 25-45 nm in size. Fig. 1(C). shows the CeHCF particle on the electrode surface which has a size of 200-250 nm.

3.3. Effect of supporting electrolytes and scan rate

The CeHCF 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 concen tration) K^+ gave a well-resolved and sharp peak. So 0.1M $KNO_3$was chosen as the background electrolyte that is shown in fig.2.

The effect of scan rate on the modified electrode was also studied at different scan rates in the range of 10-150mV/s. in fig.3. The ratio of i_{pa}/i_{pc} was found to be almost close to unity in the range studied. The CeHCF modified electrode showed a ΔE_p of 0.54 V for a potential scan rate of 20mV/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 (> $200mVs^{-1}$) 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 ($\nu^{1/2}$) with a correlation coefficient of 0.999, which is expected for a diffusion-controlled process (Fig. 3b). The electron transfer coefficient (α) was calculated from the slope of the plot of Ep Vs log ν and was found to be 0.42 and the heterogeneous electron transfer rate constant (K_s) of the CeHCF modified graphite electrode was estimated to be 0.766 s^{-1}.[23].

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 (Fig 4). 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 [24]. The hydroxylated moiety formed is electrochemically inactive and gets dissolved into the background electrolyte which results in a decrease in current response. Hence a neutral pH was chosen for subsequent experiments.

3.5 Electrocatalytic oxidation of catechol at the modified electrode

The electrocatalytic property exhibited by the CeHCF-GNP graphite wax composite electrode for the oxidation of catechol in 0.1M KNO_3 is also shown in Fig.5. 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 CeHCF-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 $2.6X10^{-6}$ to $7.2X10^{-3}M$ with a correlation coefficient of 0.999.(Fig.5a) and the detection limit was $1X10^{-7}M$.

Hydrodynamic voltammetric studies on the bare and the CeHCF –GNP graphite wax composite electrode were carried out in the potential range between 0 to 1.0V in 0.1M KNO_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 (Fig.6). Hence 0.55V was chosen as the operating potential for amperometric studies.

3.6. 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.Fig.7 displayed the flow injection response of the CeHCF-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 μA mM^{-1} for CeHCF modified electrode, and the correlation coefficient of 0.999. A detection limit of 1X10^{-7}M, can be estimated on the signal-to-noise ratio (S/N=3). Fig.7a 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.

3.7. Interferences

The effect of some possible interferents 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 4X 10^{-4}M) and ethanol, toluene and benzene (with the concentration of 2X10^{-3} M) had no influence on the signals of catechol.

3.8 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 6X10^{-5}M of catechol and were analyzed under optimized condition using above method, this results are summarized in table1.

4. CONCLUSION

A GNP graphite paraffin wax composite electrode was prepared by the oxidative electroderivatization of CeHCF in 0.1 M KNO_3, and the resulting modified electrode exhibited a good electrocatalytic activity and good stability for catechol. In a flow injection analysis, the detection limit of catechol was estimated to be of the order of 1X10^{-7}M.

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Table 1 Real Sample analysis of catechol

Samples	Concentration of Catechol (μM)		Recovery (%)
	Added	Found[a]	
Sample I	30 40	29.20± 0.70 39.81± 0.49	98.4 99.5
Sample II	30 40	29.9 ± 0.50 39.68 ± 0.48	99.6 99.2
Sample III	30 40	29.76 ± 0.48 39.16 ± 0.47	99.2 97.9
Sample IV	30 40	29.82 ± 0.49 38.99 ± 0.45	96.06 97.47

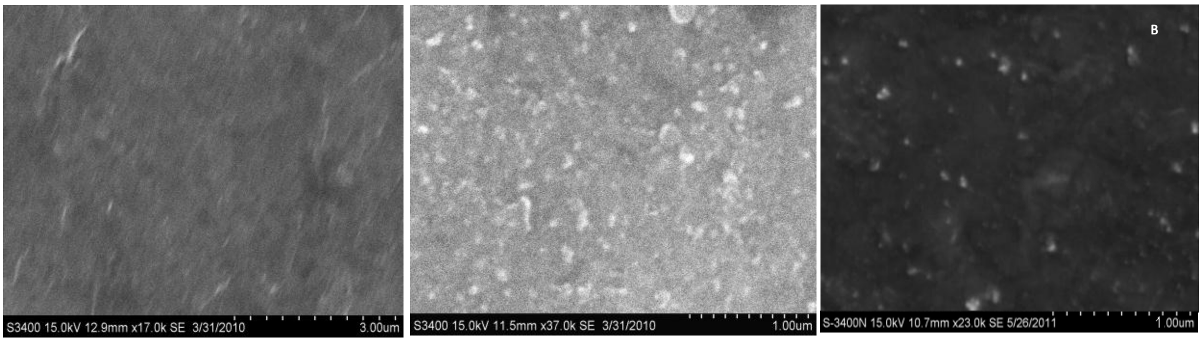

Fig. 1. The SEM images (A) represent as a bare electrode, (B) presence of GNP on graphite matrix (C) CeHCF particles on the modified electrode.

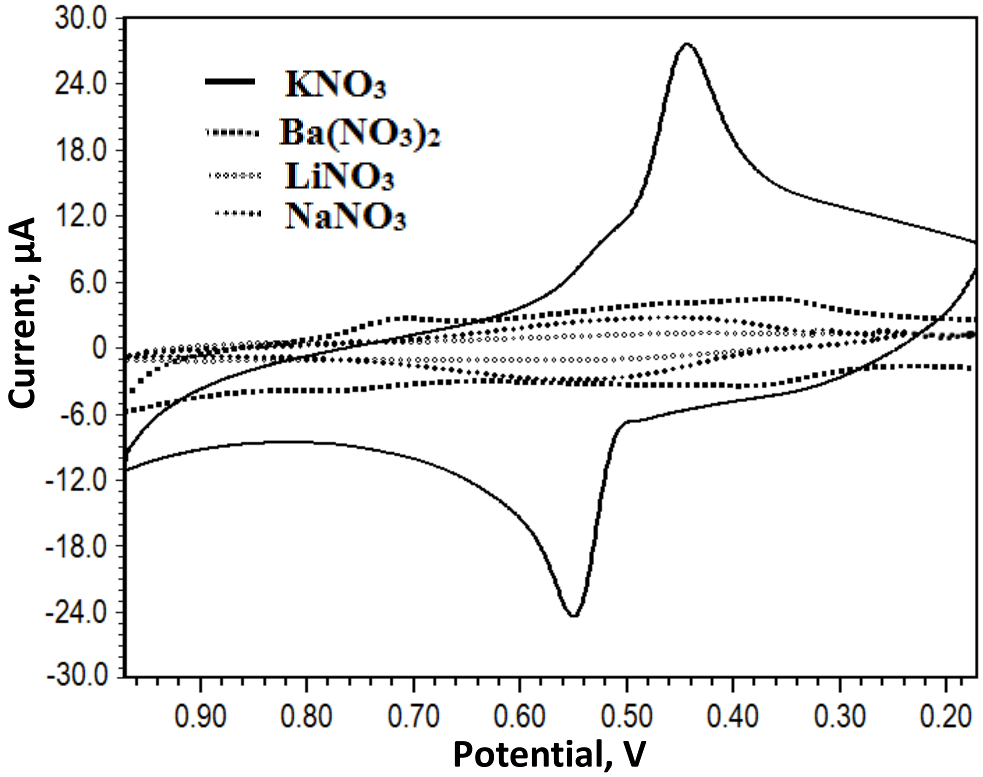

Fig. 2 Cyclic voltammograms of the GNP-CeHCF modified composite electrode in the presence of different supporting electrolytes 0.1 M (a) KNO_3, (b) $BaNO_3$ (d) $LiNO_3$ (g)$NaNO_3$; scan rate: 20 mVs^{-1}.

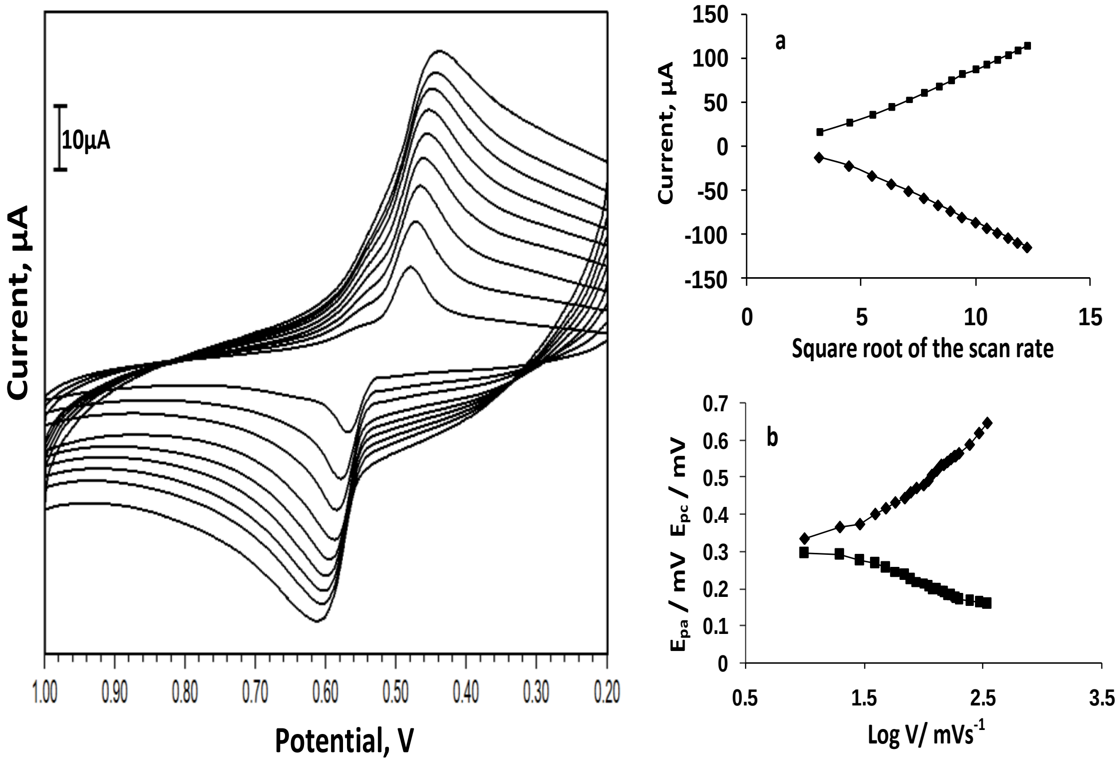

Fig. 3.cyclic voltammogram of the CeHCF modified electrode at different scan rates in 0.1M KNO_3 (pH 7.0). The scan rates from inside to outer are 10-100 mVs^{-1} with increments of 10 from 10 mV^{-1} , (3a) dependence of peak current I_{pa} and I_{pc} on square root of scan rate(υ), (3b) variation of peak potential vs. logarithm of scan rates (logυ).

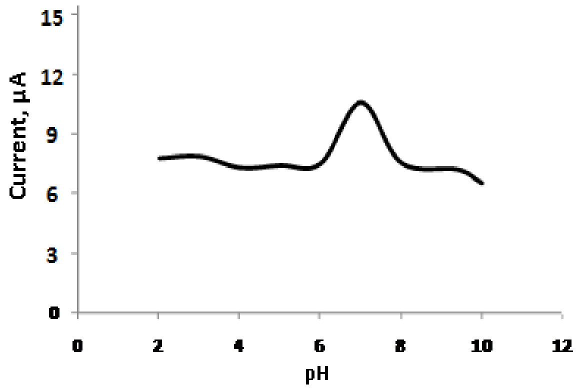

Fig.4 Plot of pH Vs Current for modified electrode. It was found that the peak current did not vary much in the pH range 2-6 but a maximum response in current was obtained at pH 7 .

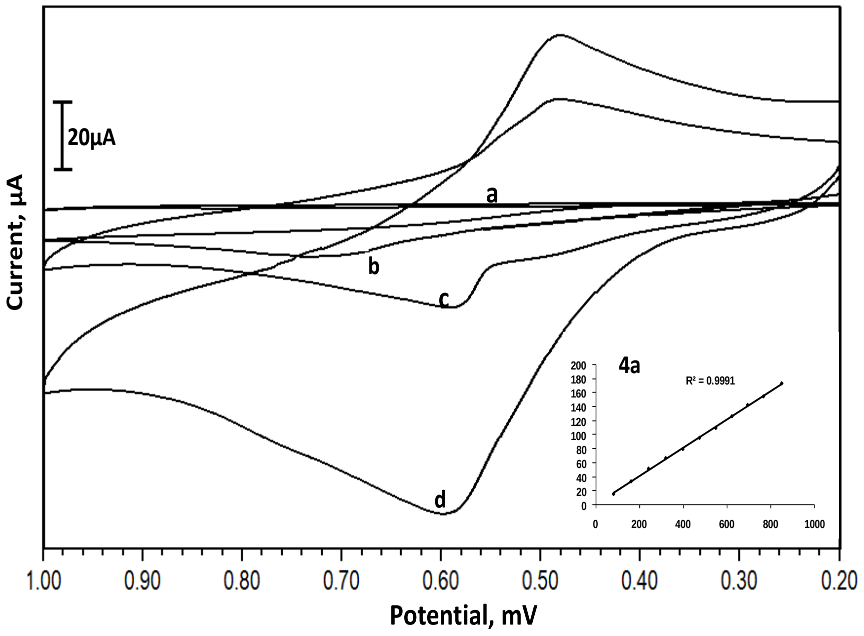

Fig.5.Cyclic voltammograms in 0.1 M KNO_3 (pH 7.0)at a scan rate of 20 mVs^{-1} (a) bare electrode in the absence of catechol (b) bare electrode in the presence of Catechol (c) modified electrode in the absence of catechol (d) CeHCF modified electrode in the presence of $7.6x10^{-5}$M catechol .Fig.5acalibration graph for catechol measurement.

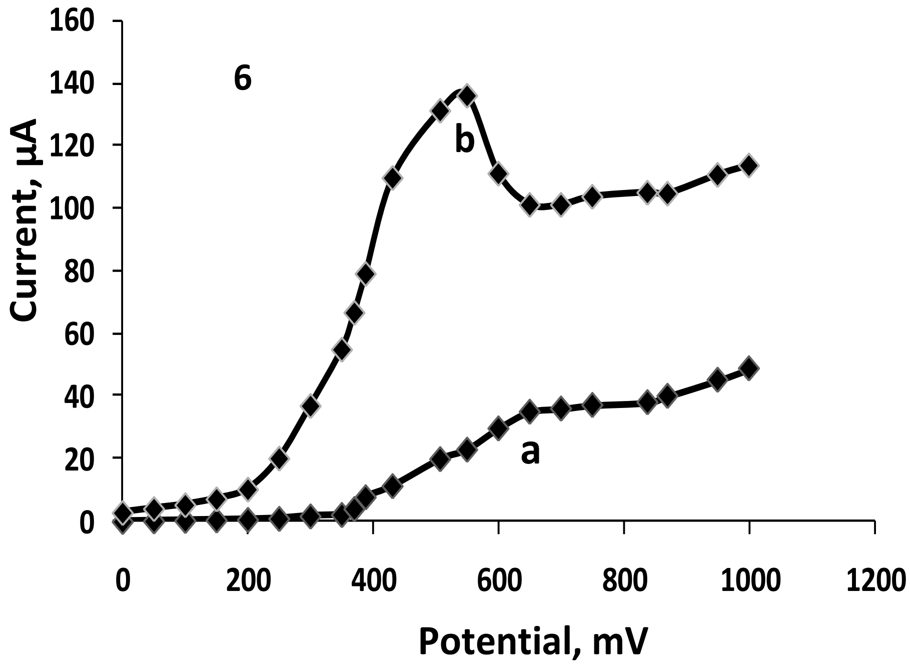

Fig.6 Hydrodynamic voltammograms obtained with (a) bare (b) CeHCF modified electrode in the presence of $9.6x10^{-5}$M catechol .

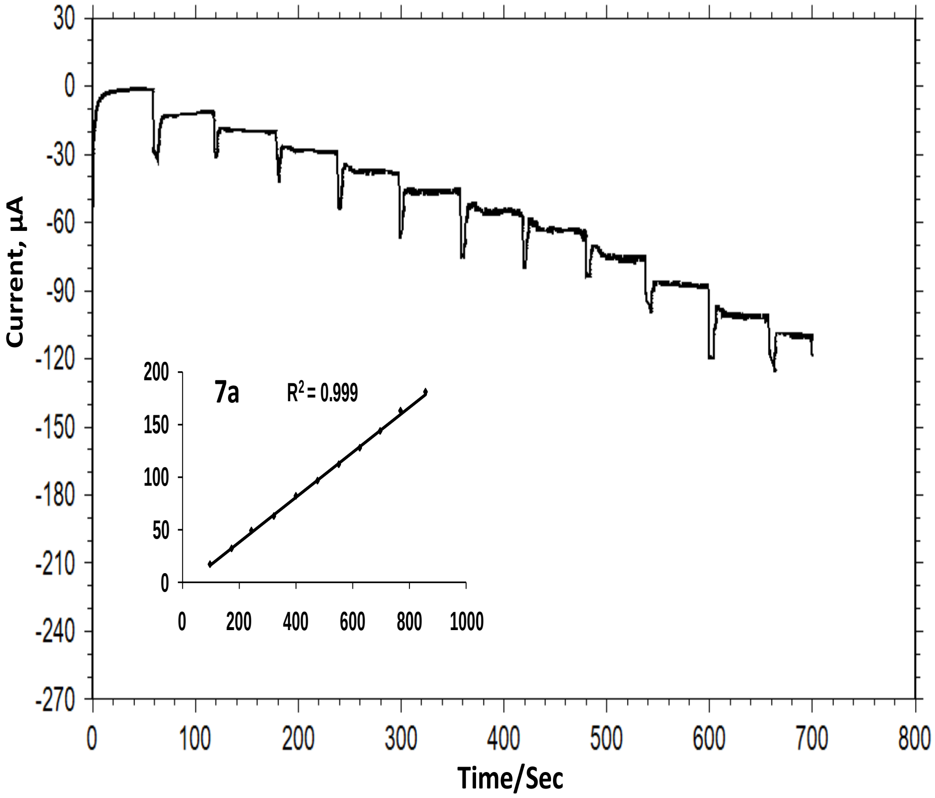

Fig. 7 . Chrono-amperometric response of the CeHCF modified electrode for three replicate additions of 8.9µM, 19.2µM and 23.3µM of catechol Fig.7a extracted from environmental water sample in 0.1M KNO_3 , operational voltage 0.55V. flow rate 0.5 ml min^{-1}.