Amperometric determination of hydrazine at manganese hexacyanoferrate modified graphite–wax composite electrode

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Abstract

Fabrication, characterization and application of a manganese hexacyanoferrate (MnHCF) modified graphite–wax composite electrode are described. The MnHCF mixed with graphite powder was dispersed into molten paraffin wax to yield a conductive composite, which was used as electrode material to construct a renewable three-dimensional MnHCF modified electrode. The characterization of the modified electrode has been studied by electrochemical techniques. The cyclic voltammogram of the MnHCF modified graphite–wax composite electrode prepared under optimum composition, showed a well-defined redox couple due to $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ system. The electrocatalytic oxidation of hydrazine by MnHCF modified graphite–wax composite electrode has been investigated in an attempt to develop a new sensor for its determination. It was found that the mediator catalyzed the oxidation of hydrazine. The electrocatalytic oxidation of hydrazine was also studied under hydrodynamic and chronoamperometric conditions. The anodic current increases linearly with increase in the concentration of hydrazine in the range of 3.33×10^{-5} M to 8.18×10^{-3} M. The detection limit was found to be 6.65×10^{-6} M (S/N = 3). The modified electrode can also be used for on-line detection of hydrazine. The proposed method has also been applied for the determination of hydrazine in photographic developer solution.
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Keywords: Manganese hexacyanoferrate; Modified electrode; Amperometric determination; 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 is very important in pharmacology because it has been recognized as a carcinogenic and hepatotoxic substance, which affects liver and brain [2]. The detection and determination of N_2H_4 becomes essential in view of its importance in diverse context and 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, 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 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

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electrocatalytic purpose is the transition metal hexacyanoferrates. Scharf and Grabner [17] used a Prussian blue (PB) modified glassy carbon 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 MnHCF modified graphite–wax composite electrode for hydrazine determination. The composite electrode was prepared using graphite powder, MnHCF and paraffin wax, which act as conductor, mediator and binder, respectively.

2. Experimental

2.1. Instrumentation

A Fourier-transform infrared (FT-IR) spectrum for the MnHCF complex was obtained using Perkin-Elmer Spectrum (I Model) and elemental analysis of MnHCF complex was conducted with a Perkin-Elmer Optima Emission Spectrometer (ICP-OES). Electrochemical investigations were carried out with the EG&G PAR Electrochemical System (Model 263A) equipped with GPIP (IEEE-488) interface port and IBM personal computer. A MnHCF modified graphite–wax composite electrode and a platinum wire were used as working and counter electrode, respectively. The reference electrode was a saturated calomel electrode (SCE). All experiments were carried out at room temperature (25 °C) under nitrogen atmosphere.

2.2. Materials and reagents

Graphite powder (1–2 μm, synthetic) was obtained from Aldrich. Hydrazinium chloride was purchased from Sigma. Manganese sulphate and potassium ferrocyanide were from Merck. Other chemicals employed were of analytical grade and used without further purification. All solutions were prepared using bidistilled water. pH variation was carried out by adjusting the pH of the electrolyte solution using HCl and NaOH and 0.05 M phosphate buffer was used when the pH was maintained at 7. The commercial samples analyzed were photographic developer solution obtained from a local photographic studio.

2.3. Preparation of MnHCF complex

The MnHCF complex was prepared by precipitation via the drop-wise addition of 0.1 M $MnSO_4$ to a well-stirred solution of 0.1 M $K_4[Fe(CN)_6]$ in a beaker [1]. After the addition, the mixture was stirred well for 15 min and kept undisturbed for an hour, the precipitate was then centrifuged with repeated washing using 0.1 M NaCl, followed by distilled water. The dried precipitate was then ground to a fine powder. We also confirmed that the composition of the complex is $Na_2Mn[Fe(CN)_6]$ by elemental analysis and from the typical infrared absorption at 2066 and 485/594 cm^{-1} for CN and FeCN/FeC, respectively. These results indicate that the complex obtained is MnHCF species, which is in agreement with previous studies [18].

2.4. Fabrication of MnHCF modified graphite–wax composite electrode

The MnHCF modified graphite–wax composite electrode was prepared by thoroughly mixing 0.650 g of graphite powder and 0.050 g MnHCF particles in an agate mortar for atleast 10 min. The above mixture was then added to 0.300 g of melted paraffin wax. The liquid paste was mixed thoroughly, transferred into a glass tube with 4 mm inner diameter and 4 cm length, and then packed tightly in the tube. After solidification and removal from the tube, the electrode was obtained in the form of a rod and it was coated with molten paraffin. The paraffin was removed at both ends, at the top for making electrical connection and at the bottom to provide the sensor surface. The modified electrode consists 5% (w/w) of mediator and it produced the best current response. Hence, MnHCF modified graphite–wax composite electrode with 5% mediator was used for all experiments. Similarly an electrode with same composition of graphite powder and paraffin wax without the mediator was also prepared and used as the bare electrode.

3. Results and discussion

3.1. Electrochemical behavior of MnHCF modified electrode

The electrochemical behavior of the bare and MnHCF modified graphite–wax composite electrode as working electrodes was studied by recording cyclic voltammograms in 0.1 M NaCl in the potential range of −0.4 to 0.8 V at a scan rate of 20 mV/s. The results obtained are shown in Fig. 1. The curve a represent the electrochemical response of the bare electrode, which was found to be insignificant. The curve c corresponds to the voltammogram for MnHCF modified graphite–wax electrode, which shows a pair of redox peaks with anodic peak at 0.44 V
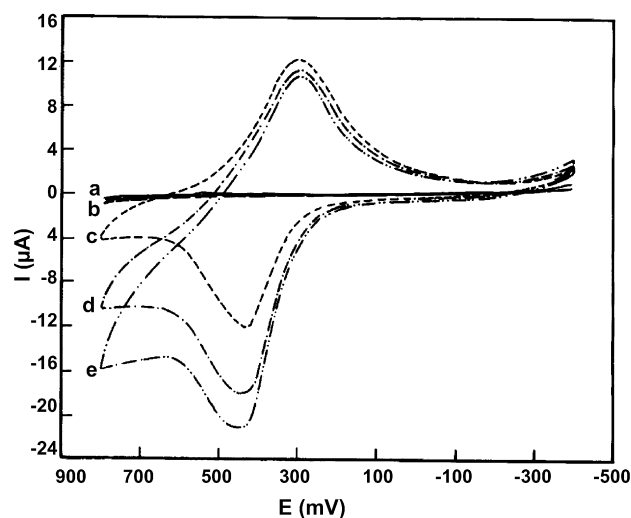

Fig. 1. Cyclic voltammogram in 0.1 M NaCl for (a) bare electrode, (b) 1.27×10^{-4} M N_2H_4 at bare electrode, (c) MnHCF modified, graphite–wax composite electrode, (d) 1.27×10^{-4} M and (e) 1.87×10^{-4} M N_2H_4 at MnHCF graphite–wax modified electrode. Scan rate: 20 mV/s.
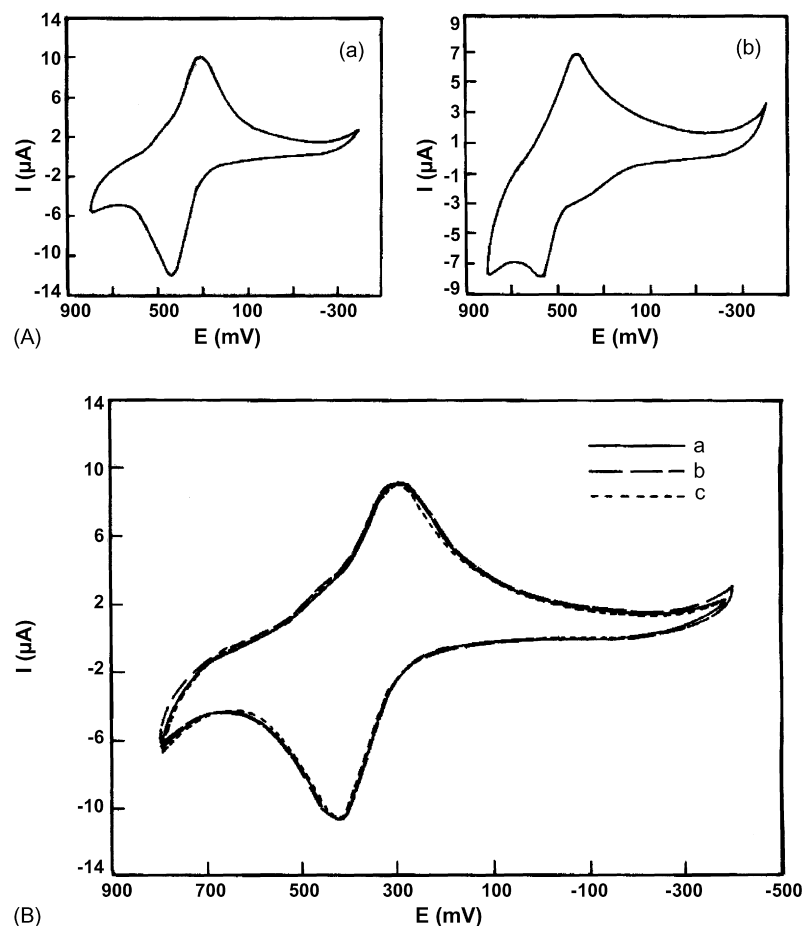
Fig. 2. Cyclic voltammograms of the MnHCF modified graphite–wax composite electrode in 0.1 M solution of (A) different cations (a) KCl and (b) NaCl and, (B) different anions (a) NaNO$_3$, (b) Na$_2$SO$_4$ and (c) NaCl. Scan rate: 20 mV/s.

and cathodic peak at 0.30 V with a midpoint potential of 0.37 V. These peaks can be attributed to the reversible redox reaction of Fe^{II} to Fe^{III} in MnHCF.

In order to maintain the electroneutrality during electrochemical transformation, ions from the supporting electrolyte diffuse in and out of the lattice of the mediator [19]. Hence to study the influence of the supporting electrolytes on the voltammetric properties of the MnHCF modified electrode, cyclic voltammograms of the electrode was examined in 0.1 M solutions of various background electrolytes with different cations such as K$^+$, Na$^+$, NH$_4^+$ and Li$^+$. Well-defined voltammogram was obtained in the electrolytes containing Na$^+$ ion indicating that Na$^+$ can easily penetrate into the cavities of the MnHCF lattice. In presence of K$^+$, voltammogram was well defined but the redox peaks shifted towards more positive potential (Fig. 2A-b). With other cations, the peak shapes were not well defined. It should be pointed out that this behavior of the MnHCF is contradictory from that of PB and its analogues, which is not highly permeable to Na$^+$ ion and showed poor response. To summarize, the selective ion transportation in the MnHCF is very complex, and cannot be explained simply in terms of hydrated ionic radii and the system's cavity size as reported for PB [20]. Hence the exact reason for such abnormal behavior (Na$^+$ > K$^+$) is not clear at present. Further, the performance of the MnHCF modified

electrode was also examined in supporting electrolytes with different anions such as NaCl, NaNO$_3$ and Na$_2$SO$_4$. From the cyclic voltammograms (Fig. 2B), the electrochemical behavior of the modified electrode was found to be independent of the nature of anions. As well defined redox peaks and higher currents were obtained in NaCl medium, further experiments were carried out using 0.1 M NaCl as the supporting electrolyte.

In order to determine the dependence of formal potentials of MnHCF modified electrode on the electrolyte concentrations, nernstian plot analysis of voltammetric data was carried out. The cyclic voltammetric response of MnHCF modified electrode recorded in NaCl solution with concentrations ranging from 0.01 to 1.0 M was studied and the resulting cyclic voltammograms are shown in Fig. 3 (for clarity of presentation, only three cyclic voltammograms are shown). The voltammetric formal potentials of the redox peaks were displaced in a negative direction with decreasing electrolyte concentration. This result is in agreement with involvement of K$^+$ ions in the redox reactions as reported for nickel hexacyanoferrate [21]. When the formal potentials were plotted versus logarithms of concentrations (NaCl), straight line with slope of 0.060 V per decade change in Na$^+$ concentration was obtained (inset Fig. 3). The same slope value was obtained from experiments performed with different concentrations of NaNO$_3$ and Na$_2$SO$_4$ also. This result observed for the modified
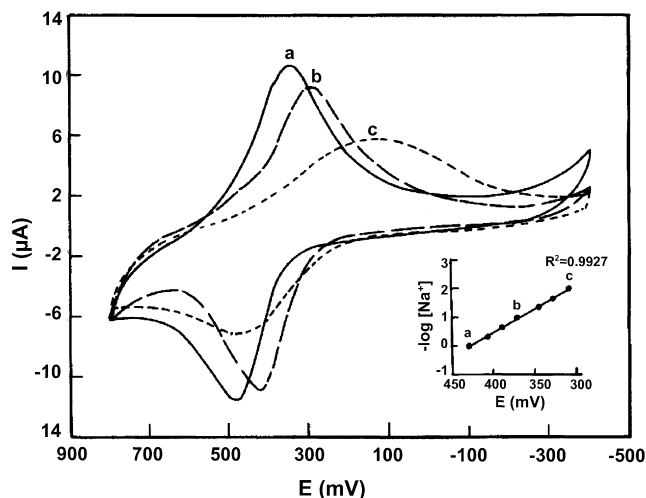
Fig. 3. Cyclic voltammograms of the MnHCF modified graphite–wax composite electrode in (a) 1.0 M, (b) 0.1 M and (c) 0.01 M NaCl solution. The inset, is the plot of formal potential vs. −log[Na$^+$].

electrode indicates the involvement of Na$^+$ in the reaction mechanism.

$$Na_2Mn[Fe(CN)_6] \leftrightarrow NaMn[Fe(CN)_6] + Na^+ + e^- \qquad (1)$$

The effects of scan rate on the peak current of MnHCF modified electrode was examined. With increasing scan rates both redox peak currents increased linearly in the range from 5 to 200 mV/s. A plot of anodic peak current versus square root of scan rate yielded a straight line with slope = 3.45 μA/mV and correlation coefficient = 0.9982. These data suggests that the redox reaction involve one electron diffusion-controlled process. The electrochemical rugosity (Γ) for the modified electrode was calculated using the equation
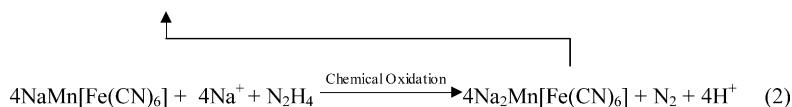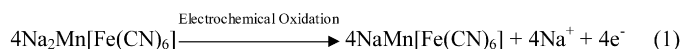
$$\Gamma = \frac{Q}{nFA}$$

where Q is the charge obtained by integrating the area under anodic wave of the cyclic voltammogram and other symbols have their usual meanings. The electrochemical rugosity of the modified electrode was found to be 1.39×10^{-8} mol/cm^2 at a scan rate of 20 mV/s.

To arrive at the optimum pH, for better performance of the modified electrode, the effect of pH on the voltammetric behavior of the electrode was studied. The dependence of the peak current and peak potential of the electrode was examined by varying the pH of the electrolyte (0.1 M NaCl) using NaOH and HCl. The pH of the medium in the range 2–8 did not affect the peak current and potentials of the MnHCF modified graphite–wax composite electrode. But at extreme pHs (>9) a decrease in current response is observed as higher pH may lead

to hydrolysis of the redox active moiety ([Fe(CN)$_6$]$^{4-}$), which results in a decrease in the electrochemical response. Hence, potential scanning with modified electrode was not performed in highly alkaline medium. This effect is similar to the observation made for other transition metal hexacyanoferrate modified electrodes [22,23].

3.2. Electrocatalytic oxidation of hydrazine

The electrocatalytic oxidation of hydrazine by the MnHCF modified graphite–wax composite electrode at pH 7 (0.05 M phosphate buffer) is also shown in Fig. 1 and for comparison the oxidation of hydrazine with the bare electrode is also shown in the figure. As can be seen from curve b in Fig. 1, no significant response was observed at the bare electrode for the oxidation of hydrazine. Thus, the bare electrode cannot be used for analytical determination of hydrazine because it does not show any measurable current. But with the MnHCF modified electrode, an increase in the anodic peak current was observed upon addition of hydrazine (curve d) and the cathodic current tends to decrease. The anodic peak current increases with increasing hydrazine concentration (d, e). The enhancement in the anodic peak current reveals the effective electrocatalytic function of the mediator. The anodic current enhancement in the presence of the analyte can be attributed to the oxidation of hydrazine by ferricyanide formed on the electrode surface during anodic scanning. When modified electrode is used, there is a reduction of overvoltage (about 550 mV) for the oxidation of hydrazine compared to bare composite electrode where the oxidation takes place above 1.0 V. This demonstrates that MnHCF is a good catalyst for electrooxidation of hydrazine. The possible mechanism of the electrocatalytic oxidation of hydrazine at the MnHCF modified graphite–wax composite electrode is described as follows:

$$4Na_2Mn[Fe(CN)_6] \xrightarrow{\text{Electrochemical Oxidation}} 4NaMn[Fe(CN)_6] + 4Na^+ + 4e^- \qquad (1)$$

$$4NaMn[Fe(CN)_6] + 4Na^+ + N_2H_4 \xrightarrow{\text{Chemical Oxidation}} 4Na_2Mn[Fe(CN)_6] + N_2 + 4H^+ \qquad (2)$$

The linear plot of catalytic current (i_{pa}) versus square root of scan rate ($\gamma^{1/2}$) for the oxidation of hydrazine indicates a diffusion-controlled behavior of the hydrazine oxidation reaction on the MnHCF modified graphite–wax composite electrode. Table 1 summarizes a partial list of literature reporting the electrocatalytic oxidation of hydrazine based on chemically modified electrodes. The overpotential for hydrazine oxidation with MnHCF modified electrode is considerably reduced when compared with other transition metal hexacyanoferrates modified electrodes [14,25–27].

The effect of pH on the peak current and peak potential for the electrocatalytic oxidation of 6.66×10^{-5} M hydrazine at the modified electrode was investigated by recording cyclic voltammograms in 0.1 M NaCl with different pHs. The pH variation is done as mentioned before. From pH 2 to 5 the peak current increased gradually with increase in pH of the medium and reached a maximum at pH 7, then decreased. From pH 8 to 10

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	CFA	330	[24]
GC	CGA	300	[2]
Graphite rod	NiHCF	470	[25]
GWC	CuHCF	700	[26]
CPE	ST-NiTsPc	480	[17]
Graphite rod	CoHCF	700	[27]
GC	CoPCNF	800	[28]
GWC	MnHCF	450	This work

GC, glassy carbon; GWC, graphite–wax composite; CPE, carbon paste electrode; PCoPP, polymer films of cobalt protoporphyrin dimethylester; PB, Prussian blue; CFA, caffeic acid; CGA, chlorogenic acid; NiHCF, nickel hexacyanoferrate; CuHCF, copper hexacyanoferrate; ST-NiTsPc, silica-modified nickel tetrasulfonated phthalocyanine; CoHCF, cobalt hexacyanoferrate; CoPCNF, cobalt pentacyanonitrosylferrate; MnHCF, manganese hexacyanoferrate.

there was sharp fall in peak current. The decrease in current in the alkaline range may be due to the slow dissolution of MnHCF at the electrode surface. On the other hand, the pH of the supporting electrolyte has no significant effect on the peak potential. But, according to thermodynamics the formal potential is dependent on pH as given by the following equation

$$E = E^0 - 0.059\,pH \qquad (3)$$

In the present case, $E^0 = -0.23V_{SHE} + RT/4F \ln(a_{N_2H_4}/pN_2)$. However, experimental observation indicates that the oxidation potential of hydrazine was not influenced by the change in pH implies that the processes occurring at the electrode surface is kinetically controlled rather than thermodynamically controlled one. To have a maximum catalytic current response, the background electrolyte pH was maintained at 7 using 0.05 M phosphate buffer solution.

3.3. Hydrodynamic study for the oxidation of hydrazine

To evaluate the optimum condition for amperometric determination of hydrazine in flow systems, hydrodynamic voltammograms were recorded. Fig. 4 compares hydrodynamic voltammograms for 6.45×10^{-4} M hydrazine at the (a) bare and (b) MnHCF modified electrode over the potential range from -0.4 to $+0.8$ V. The curve a illustrates that at the bare electrode no oxidation of hydrazine occurs when the potential is lower than 0.8 V. In contrast, with the MnHCF modified electrode hydrazine oxidation occurs favorably at about 0.3 V and the current reaches a limiting value in the potential range of 0.45–1.0 V. These results are also in agreement with the cyclic voltammetric investigation. Hence a potential of +0.45 V was selected as the working potential for the amperometric determination of hydrazine using MnHCF modified electrode under dynamic condition.
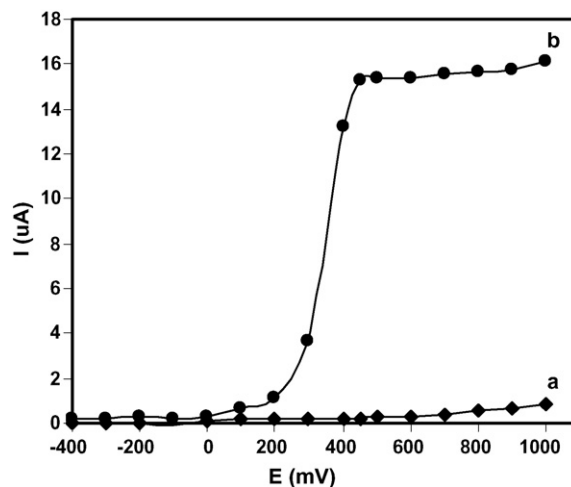

Fig. 4. Hydrodynamic voltammograms obtained with (a) bare and (b) MnHCF modified graphite–wax composite electrodes in presence of 3.2×10^{-4} M, N_2H_4. Electrolyte: 0.1 M NaCl; pH: 7.0 (0.05 M phosphate); stirring rate: 300 rpm.

3.4. Chronoamperometric study for hydrazine determination

The amperometric response of the MnHCF modified graphite–wax composite electrode obtained for successive addition of 0.3 mM hydrazine to a continuously stirred 0.1 M NaCl solution (pH 7, phosphate buffer) at an applied potential of 0.45 V is shown in Fig. 5. The electrode response time was less than 4 s and the inset of Fig. 5 shows the calibration graph for hydrazine determination using the MnHCF modified graphite–wax composite electrode. The response of the electrode is linear over the concentration range of 3.33×10^{-5} M to 8.18×10^{-3} M with a sensitivity of 47.53 μA/mM and correlation coefficient $(r) = 0.9991$. Beyond this concentration range, the calibration curve deviates from linearity. The detection limit was found to be 6.65×10^{-6} M (S/N = 3). Thus the
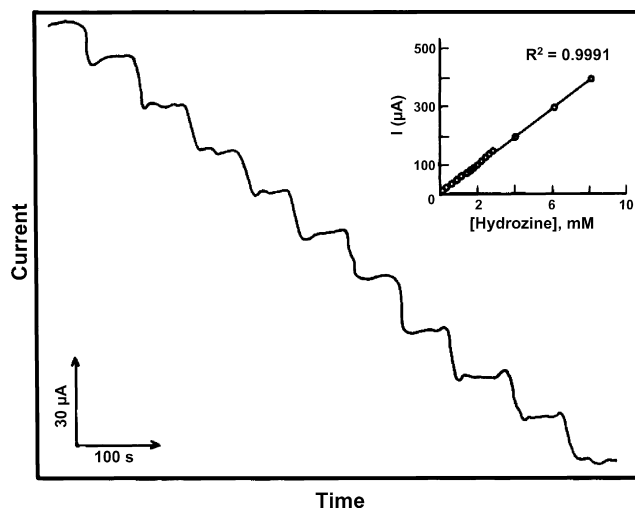

Fig. 5. Amperometric response of the MnHCF modified graphite–wax composite electrode for the successive addition of a 0.3 mM N_2H_4. Applied potential: 0.45 V; other conditions as in Fig. 4. The inset is the calibration graph.

Table 2
Effect of foreign ions on the determination of 3.2×10^{-5} M hydrazine

Ion	Tolerance limit (molar ratio)
K^+, Na^+, Cs^+, Li^+, Rb^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}	100
NO_3^-, Cl^-, PO_4^{3-}, Br^-, I^-, CN^-	100
Pb^{2+}, Cu^{2+}, Ag^+, Zn^{2+}	50
Fe^{2+}, Ni^{2+}	10
NO_2^-, SO_3^{2-}	10

Table 3
Results for determination of hydrazine in photographic developer solution

Sample	Amount of hydrazine found (mg/L)[a]		Error (%)
	Proposed method	Standard method	
I	140.01 ± 2.3	138.76 ± 3.3	0.9
II	144.34 ± 2.6	142.44 ± 2.0	1.3
III	142.97 ± 2.1	144.11 ± 2.5	0.8

[a] Average of five measurements $\pm$ R.S.D.

determination of hydrazine in real samples can be performed based on the electrocatalytic oxidation of hydrazine by MnHCF modified electrode.

3.5. Interference study

To evaluate the selectivity of the proposed method interference studies were carried out. The common foreign substances present in the photographic developer solution are different cations and anions. Another major interferent in the determination of hydrazine is ascorbic acid, which is also used as an antioxidant in photographic developer solution. The effect of various cations/anions and ascorbic acid were studied in order to check the interference in hydrazine determination. Various interferent-to-analyte ratios (tolerance limit molar ratio) causing less than $\pm 4\%$ relative error for a hydrazine concentration of 3.2×10^{-5} M is listed in Table 2 which indicates that most of the cations and anions do not interfere with this amperometric method for hydrazine determination. Under the experimental conditions, ascorbic acid interfered significantly with the hydrazine measurement at a ratio of 1:1. One way of over coming this effect is to coat the sensor surface with a film of nafion as reported elsewhere [29]. As nafion is a cation exchange polymer it repels ascorbic acid, an anionic species and can provide a transport channel only for hydrazine. Further investigation in this regard is under progress. Thus, the MnHCF modified graphite–wax composite electrode allows amperometric detection of hydrazine at a significantly lower operating potential and hence yields an improved selectivity.

3.6. Analysis of hydrazine in photographic developer

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 photographic developer samples (three different brands). A known amount of the sample solutions was added to the background electrolyte followed by addition of known volume of standard solution of hydrazine (standard addition method) and then subjected to amperometric measurement. The commercial samples were also analyzed by a standard method based on *p*-dimethylamino benzaldehyde reaction [30] for comparison and the results of the above study are summarized in Table 3. 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 as compared with standard method.
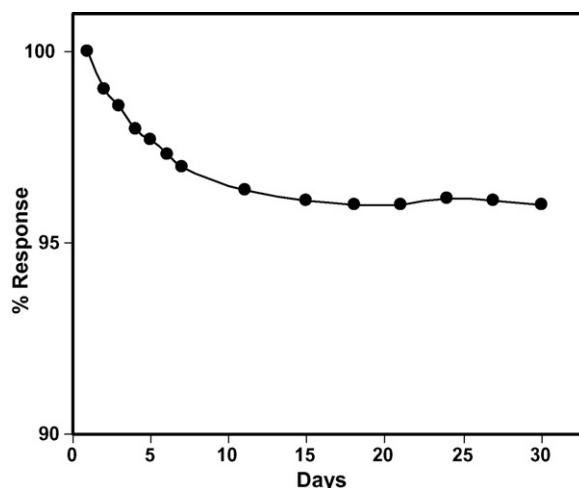

Fig. 6. The long-term stability of the MnHCF modified graphite–wax composite electrode towards the sensing of 5.67×10^{-4} M N_2H_4 in 0.1 M NaCl solution.

3.7. Study of reproducibility and stability

To characterize the reproducibility of the MnHCF modified graphite–wax electrode, repetitive measurements were carried out in 9.6×10^{-5} M hydrazine. Ten replicate measurements of hydrazine detection by the modified electrode showed a relative standard deviation (R.S.D.) of 2%, which suggests a good reproducibility of the present method. In addition, stability of the MnHCF 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 30 days (Fig. 6). These results indicate that the modified electrode has a good reproducibility and better stability.

4. Conclusion

A manganese hexacyanoferrate modified amperometric sensor based on carbon composite has been constructed and characterized. The redox activity of the mediator is attributed to the $Fe(CN)_6^{4-/3-}$ group of MnHCF. Electrochemical characterization of the modified electrode reveals the 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 (450 mV) compared to the unmodified electrode. The use of above electrode as an amperometric sensor for the determination of hydrazine in photographic developer solution 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 MnHCF modified graphite–wax composite electrode could be used as a useful amperometric sensor for monitoring hydrazine in real samples.

Acknowledgement

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