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RESEARCH ARTICLE

GREEN SYNTHESIS, CHARACTERIZATION AND ELECTROCATALYTIC APPLICATION OF CURCUMIN CONJUGATED RUTHENIUM NANOPARTICLES.

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Abstract

Noble metal nanoparticles are emerging as important materials among the rapidly expanding domains with potential applications in many fields. In this work Ruthenium nanoparticles (RuNP) have been synthesized by a green synthetic pathway using citric acid as the reducing agent and curcumin as the stabilizing agent. The synthesized nanoparticles have been characterised by SEM, XRD and UV-vis spectroscopy. The nanoparticles have been used as an electrocatalyst for the determination of Hydrogen peroxide (H_2O_2). The RuNP modified electrode response under hydrodynamic conditions has been studied using various voltammetric techniques. The electrode shows a good response towards electrocatalytic reduction of H_2O_2 with a linear range from 1.66 µM to 54.70 µM. The utility of the sensor for real sample analysis has been evaluated by carrying out analysis of different milk samples and the results obtained were found to be satisfactory. The work demonstrates that the new RuNP modified electrode is a promising tool for detection of important analytes.

Introduction:-

Nanomaterials have become a topic of great interest and investment in the field of research and industries as these kinds of materials have potential applications in microelectronics (Cen et al. 2009), photocatalysis (Huang et al. 2014), chemisorption (Perenboom et al. 1981), aerosols and powder metallurgy (Schmid et al. 1995). Noble metal NP's have gained intensive commercial applications due to their exceptional optical, electronic, magnetic and catalytic properties (Mody et al. 2010; Conroy et al. 2008; Ito et al. 2005; Heilmann et al. 1999; Lopes et al. 2001; Sardar et al. 2009; Kumar et al. 2015; Mathpal et al. 2015; Heilmann et al. 2003). However, there is a serious concern regarding the hazards these engineered nanoparticles impose on the environment as a consequence of the increasing industrial and research activities (Dwivedi et al. 2015; Thomas et al. 2011; Brar et al. 2010; Bystrzejewska-Piotrowska et al. 2009; Ju-Nam et al. 2008). Hence, environmentally benign methodology for the synthesis and utilisation of these nanoparticles with aim to reduce their toxic effects is a promising field of research. In recent year's ruthenium nanoparticles have been widely used in electrochemical applications, however most of the work is for energy storage devices. (H.K Hassan et. al 2017)

Hydrogen Peroxide(H_2O_2) is widely used in pharmaceuticals, clinic, environmental, mining, textile, paper, food manufacturing and chemical industries with its major application as a bleaching agent in textile and paper industries (Campos-Martin et al. 2006; Hage et al. 2006). It is also a co-product of various oxidases and the enzyme activity

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can be measured by detecting the amount of H_2O_2 produced. It also acts as eukaryotic signal transducer (Youdim et al. 1987). Thus, the monitoring of H_2O_2 concentration is of great industrial and biological importance (Romantsova et al. 2015). There are various methods for H_2O_2 detection (Veal et al. 2007) among which electrochemical sensing methods are most preferred as it is highly selective and the response is very fast and reliable(Garcia et al. 2014; Kurowska et al. 2013; Huang et al. 2014). Herein, we have incorporated green synthesized RuNP for electrode modification to devise a sensor for the determination of $H_2O_{2.}$

Experimental:-

Apparatus:-

All electrochemical experiments were carried out with a CHI 660B electrochemical analyzer with a standard three electrode system controlled by a personnel computer. An electrochemical cell containing 0.1M phosphate buffer with a RuNP modified electrode as the working electrode, a platinum wire as the counter electrode and standard calomel electrode as the reference electrode was used for the experiments. All potentials were referred to the latter. The modified electrode was prepared according to the procedure described below.

UV-Visible absorption spectra (UV-vis) were recorded using a Perkin Elmer Lambda spectrophotometer operating in the range 200-800nm. X-ray diffraction (XRD) analysis was recorded by the X-ray generator (model 3000) from Rich Seifert, Germany. Scanning electron microscopy(SEM) studies were carried out using Hitachi-S3400N Scanning Electron Microscope equipped with Electron Dispersive Spectroscopy.

Reagents:-

Ruthenium trichloride was purchased from SRL Pvt. Ltd., India. Hydrogen peroxide was obtained from Merck, India. Curcumin was extracted from fresh rhizomes using the method reported in literature (A.M Anderson et. al 2000). Graphite rods (3mm dia) has been purchased from sigma and Paraffin wax impregnated graphite electrodes were used for the modification. All other reagents were of analytical grade and used without further purification. All the solutions were prepared using double distilled water. The electrolyte solutions were purged with pure nitrogen to remove free oxygen before the experiment. The pH of the electrolyte solutions used was maintained at 7 using phosphate buffer.

Synthesis of Ruthenium nanoparticles(RuNP):-

10 mL of 1mM freshly prepared aqueous solution of ruthenium trichloride was added to 10mL of stored pure lemon extract with constant stirring for the reduction of ruthenium ions. The reaction mixture was kept in the magnetic hot stirrer at 50-60^{0}C until the colour changes from dark black to brown colour which denotes the complete reduction of metal ions. Freshly prepared curcumin extract was added to the above solution to stabilize the nanoparticles and stirring was continued for about an hour. There was a slow colour change from brown to yellow and finally a permanent yellowish black colour indicates complete stabilisation of RuNP. The solution was centrifuged several times to obtain the pure RuNP, The supernatant was decanted and kept in oven for drying.

Electrode Fabrication:-

Drop casting method was adopted for electrode fabrication. The paraffin impregnated graphite electrode (PIGE) was prepared by the previously reported procedure (Scholz et al. 1994; Scholz et al. 1994). The graphite rods were immersed into molten wax under vacuum until air bubbles cease to evolve from the rods. After re-establishment of the atmospheric pressure the graphite rods were removed from the solution prior to solidification of paraffin. The PIGE were then polished to a mirror like finish by rubbing over a finest quality emery paper. The polished electrode was then rinsed with methanol and washed thoroughly with double distilled water. The ethanolic solution of the synthesized RuNP was then drop cast onto the surface of the PIGE. The electrode was allowed to dry at room temperature for 24 hours. The resulting RuNP modified electrode was used for further studies. All voltammograms of the modified electrodes were recorded after the electrode had reached equilibrium with the background electrolyte.

Results and Discussion:-

Surface morphology study by using SEM:-

The synthesised curcumin conjugated RuNP has been studied using SEM. **Fig-1(a)** and **(b)** are the images obtained for the nanoparticles under various magnification. The SEM shows the particles were predominantly spherical in shape and **Fig-1(c)** shown the EDX spectrum of RuNP.

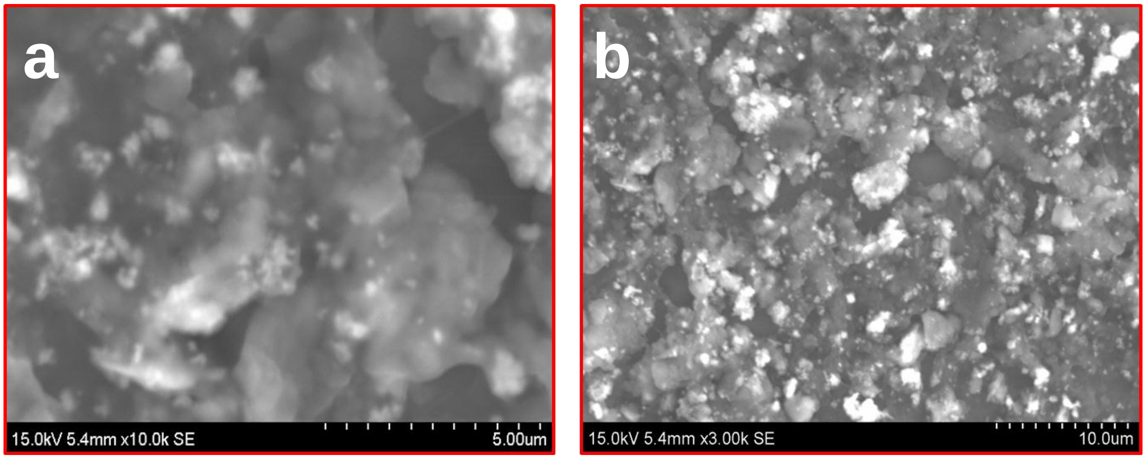

Fig.1:- (a) and (b)SEM images for the Curcumin conjugated RuNP under different magnifications.

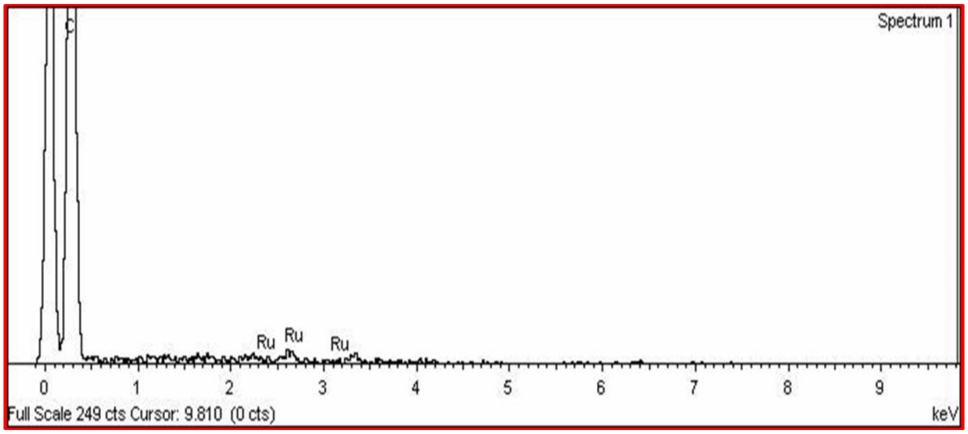

Fig.1:-(c) Curcumin conjugated RuNP EDX spectram

Absorption spectral studies:-

The formation of curcumin conjugated RuNP has been confirmed by UV-Vis and emission spectral studies. **Fig-2(a)** shows the yellowish pure curcumin absorption at 253 nm and 435 nm arising due to the aromatic ring structure of the molecule, **Fig-2(b)** is the spectrum of curcumin conjugated RuNP exhibiting absorption at 320 nm 440 nm corresponding to curcumin and RuNP respectively. The shift in absorptions indicates the curcumin conjugation to RuNP (Kunduet al. 2013).

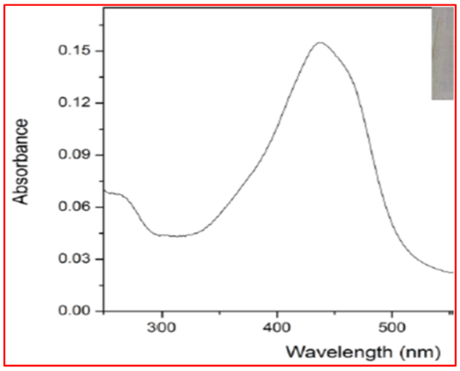

Fig.2:- (a) UV-vis absorption spectrum of synthesized curcumin in alcoholic solution.

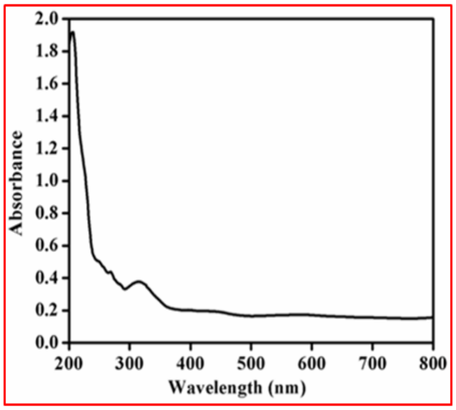

Fig.2:- (b) UV-Vis absorption spectrum of synthesized curcumin conjugated RuNP.

Fourier-transform infrared (FT-IR) analysis:-

In order to study the formation of curcumin conjugated RuNP, FT-IR technique was used and the resultsare shown in the **Fig-3**. A detailed study of FT-IR spectra of curcumin has been reported by Kolovet al.2005. The FT-IR spectral data for curcumin (A) shows pronounced peaks at 1381 cm^{-1}, 1463 cm^{-1} and 1543 cm^{-1} corresponding to the curcuminenol form C-O stretching. In the curcumin conjugated RuNP spectra the two peaks seem shifted to 1635 cm^{-1} and 1651 cm^{-1} corresponding to the formation of curcumin conjugated ruthenium nanoparticles. The conjugation of RuNP may be via C=O group of curcumin.

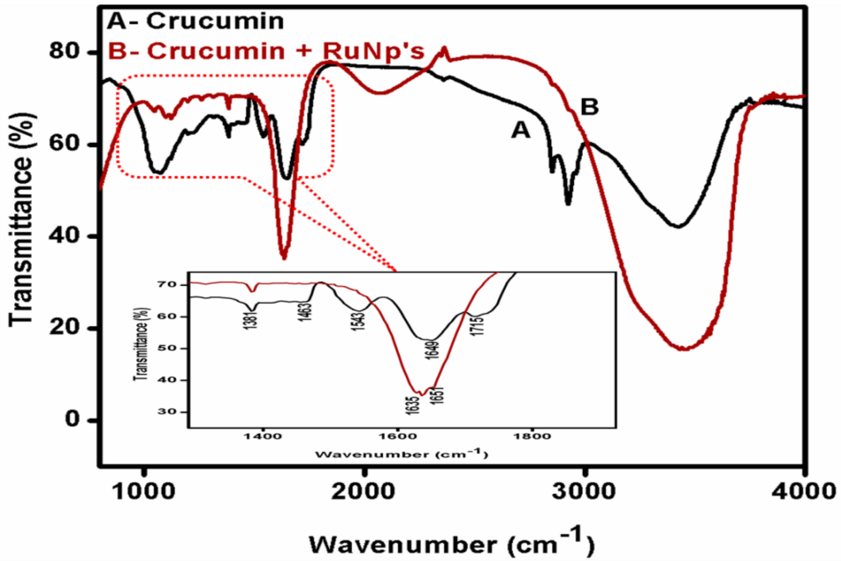

Fig.3:- FT-IR spectra of curcumin and curcumin conjugated RuNP

X- ray diffraction study:-

The **fig-4** shows XRD pattern of the synthesized RuNP. The three distinct diffraction peaks at 40.8, 47.4, 69.3 indexed with the planes (1 0 1), (0 0 2) and (1 1 0) for the hexagonal structure of Ru (JCPDS card no. 88-2333). The well resolved and intense XRD pattern clearly showed that the RuNP were amorphous in nature. In addition, the unassigned peaks suggest that the crystallisation of bio-organic phase occurs on the surface of the nanoparticles (Kundu et al. 2013).

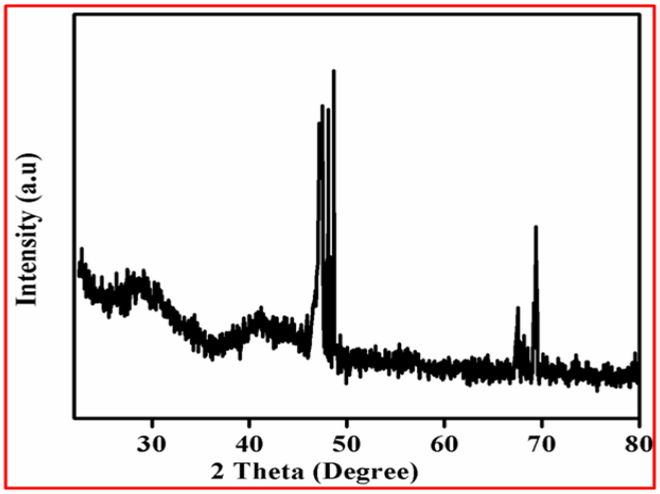

Fig.4:- XRD pattern of synthesized curcumin conjugated RuNP

Electrochemical behaviour of RuNP modified Electrode:-

Cyclic voltammetric behaviour of the Curcumin conjugated RuNP:-

The electrochemical behaviour of the curcumin conjugated RuNP has been studied by cyclic voltammetry method. The voltammogram for the RuNP modified electrode in 5mM $K_4[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl as background electrolyte solution is shown in **Fig-5**. From the voltammogram the oxidation (E_{pa}) and reduction (E_{pc}) peak potential for the bare PIGelectrode was found at 0.28 V and 0.09 V respectively. Whereas for the RuNP modified electrode, the voltammetric peaks were observed at 0.25 V (E_{pa}) and 0.09 V (E_{pc}). The peak to peak separation value (ΔE_p) has been 0.09V and 0.08 V for the bare PIG electrode and curcumin conjugated RuNP modified electrode respectively. Thus, a decrease in the ΔE_p value in the case of the modified electrode suggests the curcumin conjugated RuNP modified electrodes exhibit good electrochemical properties and fast electron transfer kinetics in comparison with the bare electrode (Manikandan et al. 2017).

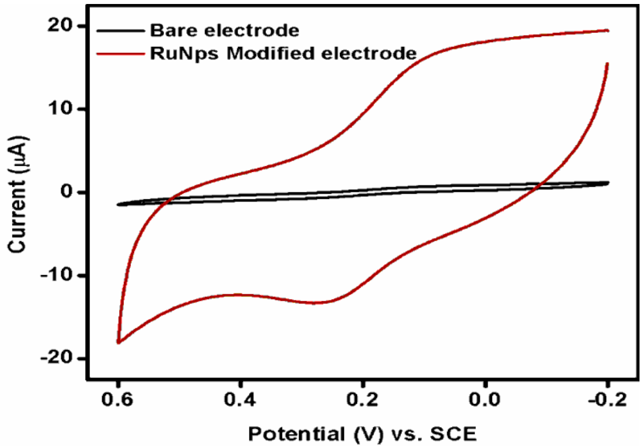

Fig. 5:- Cyclic voltammogram of bare and modified electrode in 5mM $K_4[Fe(CN)_6]^{3-/4-}$containing 0.1 M KCl as supporting electrolyte at scan rate of 50 mV s^{-1}

Application of RuNP modified electrode towards electrocatalytic reduction of H_2O_2 by cyclic voltammetry method:-

The electrocatalytic activity of RuNP modified electrode towards H_2O_2 was studied using cyclic voltammetry. **Fig-6** shows the cyclic voltammetric response of bare and modified electrode in 0.1 M phosphate buffer (pH-7). RuNP modified electrode shows oxidation potential at 0.26 V and reduction at - 0.02 V. The modified electrode in the presence of 6.6 µM of H_2O_2 showed higher catalytic current with lower reduction potential when compared to bare electrode and thus exhibiting excellent electrocatalytic activity towards H_2O_2 determination. The linear response for H_2O_2 determination was in the range of 1.66 µM to 25 µM.

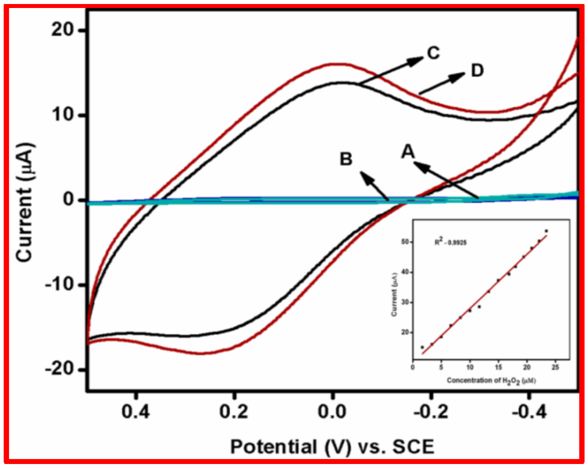

Fig.6:- Cyclic voltammetric response of bare and modified electrode in the presence of 6.6 μM of H_2O_2 in 0.1 M phosphate buffer pH-7 at scan rate of 50 mV s^{-1} inset fig. is plot of conc. of H_2O_2 vs. Current

Electrocatalysis of H_2O_2 under Hydrodynamic conditions:-

The RuNP modified electrode towards H_2O_2 was studied under hydrodynamic conditions. **Fig-7** illustrates the hydrodynamic voltammogram of bare and RuNP modified electrodes in the presence of 6.6 μM H_2O_2 in phosphate buffer (pH-7) as supporting electrolyte at a potential range of -0.4 to 0.4V under stirring conditions at a rate of 300 rpm. From the figure it is clear the electrocatalytic determination of H_2O_2 was very much higher using the RuNP modified electrode when compared to the bare electrode response. An enhanced current response using the RuNP modified electrode with - 0.1 V as the maximum was observed.

The chronoamperometric response of the RuNP modified electrode towards the reduction of H_2O_2 was studied. A potential of - 0.1 V was fixed for the amperometric determination on the basis of the maximum current response obtained from the hydrodynamic studies. **Fig-8a** shows the amperogram corresponding to the successive addition of 0.03 mL of 0.01 M of H_2O_2 to 0.1M PBS under stirring at a rate of 300 rpm. A sharp increase in the current was observed for every addition of H_2O_2. The modified electrode also showed a fast response (0.2 s). **Fig-8b** shows the calibration plot wherein the linear range observed was from 1.66 μM to 54.70 μM with a detection limit of 0.53μM. The sensitivity has been determined to be 5.32μA/μM with correlation coefficient of 0.985. The rapid response of the RuNP modified electrode for the reduction of H_2O_2 could lead to its viable application as an electrochemical sensor in flow systems.

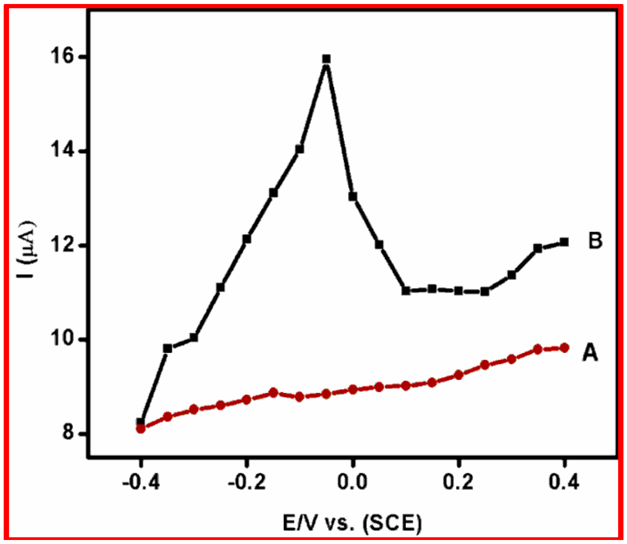

Fig.7:- The hydrodynamic voltammograms of bare (a) and modified electrode (b) in the presence of 6.6 μM of H_2O_2 under the dynamic conditions in 0.1 M phosphate buffer as supporting electrolyte

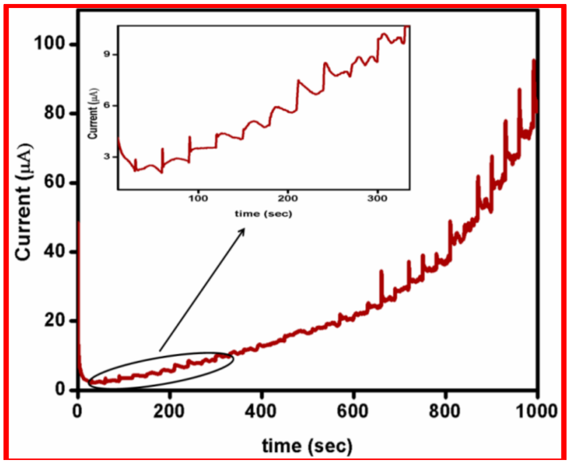

Fig.8:- (a) chronoamperometric response for the successive addition of H_2O_2 and corresponding current increase in the concentration range from 1.6 to 54.7 µM

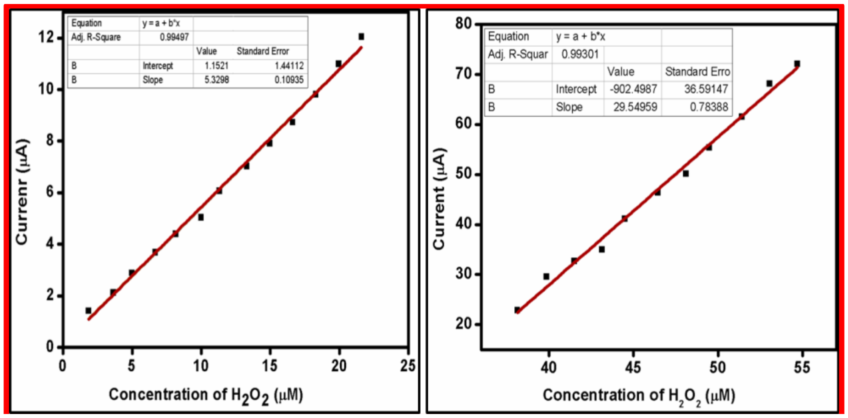

Fig.8:- (b) current vs. concentration plot for corresponding chronoamperometric response

Interference studies:-

The selective determination of H_2O_2 was investigated in the presence of different concentrations of analytes by using RuNP modified electrode. The selection of the interferents was made based on their commercial availability. Various interferents such as Ascorbic acid, Dopamine, Gallic acid, Citric acid and Uric acid were added in order to verify the selectivity of the modified electrode towards H_2O_2 **(fig-9)**. It was found that the above compounds did not show any interference with H_2O_2 reduction as they undergo oxidation reaction at the electrode. The electrode could thus be used to selectively determine H_2O_2 in the presence of these interferents.

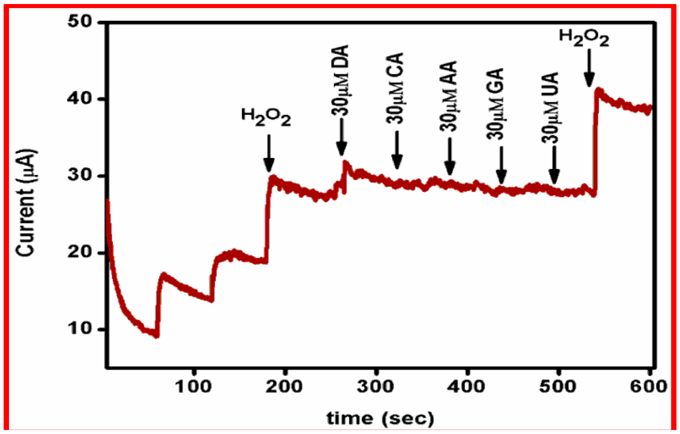

Fig.9:- Intereference study of different species in the presence of 3µM of H_2O_2.

Real sample Analysis:-

The selective electrocatalytic property of the RuNP modified electrode makes it suitable for a wide range of analytical applications. The applicability of the modified electrode in measuring the concentration of H_2O_2 in two different brands of milk purchased commercially has been tested. The **table-1** shows that analysis of H_2O_2 by standard addition methods and the recoveries obtained.

Table 1:- Determination of H_2O_2 in different milk samples.

Smple ID	Added (µM)	Found (µM)	Recovery (%)
I	10	9.87(±0.017)	98.7
	20	19.76(±0.023)	98.8
II	10	9.98(±0.018)	99.8
	25	25.2(±0.024)	100.8

Stability of RuNP modified Electrode:-

The stability of the RuNP modified electrode was studied by cycling the electrode in phosphate buffer pH-7 solution at a scan rate of $50mVs^{-1}$ for 100 cycles. No appreciable change in the current response and the peak potential was observed. The catalytic current for the reduction of H_2O_2 was also found to be reproducible. The RuNP modified electrode was found to exhibit high stability and reproducibility. The modified electrode was kept in air tight container in refrigerator (± 5^0C) when not in use.

Conclusion:-

In this study we have successfully synthesized Ruthenium nanoparticles by green synthetic pathway. The synthesized RuNP has been used for fabricating a modified electrode. The modified electrode was used for determining $H_2O_2$with a linear range of 1.66 µM to 54.70 µM and a detection limit of 0.53 µM. The method successfully demonstrates the application of RuNP for electrocatalysis. The electrode has a simpler and easier fabrication process with good selectivity and sensitivity for the detection of chosen analyte with enhanced stability and reproducibility.

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