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ELECTROCHEMICAL STUDIES OF PARACETAMOL ON POLYANILINE-SILVER NANOSTRUCTURAL THIN FILMS MODIFIED GLASSY CARBON ELECTRODE

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Abstract:

Analysis of biomolecule of paracetamol through stripping voltammetric determination procedure on polyaniline-silver thin films modified glassy carbon electrode. The effect of pH was studied at different pH media such as 1.0 to pH 13.0. The voltammetric investigation of paracetamol was carried out from −0.2 V to 1.2 V *versus* Ag/AgCl using modified glassy carbon (GC) as working electrode. The electroanalytical determination parameters are highly dependent on their configuration and on the dimensions of the working carbon electrode. The cyclic voltammogram exhibited one oxidation and one reduction peak. Peak current dependence on the scan rate is studied by varying the scan rate from 25 to 500 mV/s at concentration 300 ppm. The best limit of detection obtained for paracetamol was 10 ppb and the linear range from 100 to 600 ppb on GCE configuration. The biosensors were successfully applied for the detection of paracetamol in several drug formulations.

Key Words: Paracetamol, Cyclic Voltammetry, Differential Pulse Voltammetry & Polyaniline-Silver

Introduction:

Recent progress of nanotechnology has created huge potential to build highly sensitive, low cost, portable sensors with low power consumption. Carbon nanotubes (CNTs) represent very interesting nanomaterial, due to the various novel properties that make them useful in the field of nanotechnology and pharmaceuticals [1]. CNTs are the best conductor of electricity on a nanoscale level, similar to copper, but with the ability to carry much higher currents [2]. Analytical chemistry seems to be one of the sciences interested in several advantages which are brought by CNTs for various potential applications, e.g., chromatography [3], battery electrode materials, sensors and biosensors [4, 5]. In the last decades, modern computer-based voltammetric techniques have been used to realize the determination of organic chemicals in various types of samples, especially pharmaceutical field [6]. The advance in experimental electrochemical techniques in the field of drug analysis is due to their simplicity, low cost, and relatively short analysis times, no need for derivatizations or time-consuming extraction steps. Moreover, the electrochemical methods possess the dual character in relation with both pollutants detection and destruction. Several electrochemical methods for the destruction of pharmaceuticals have been reported [7]. These methods use the electron as the main reagent, but also require the presence of supporting electrolytes. In general, the supporting electrolytes exist in the wastewaters to be treated, but not always in sufficient concentrations. These processes can operate at ambient temperature without a need of temperature control [8]. The applications of electrochemical technologies for wastewater treatment are benefiting taking into account their advantages, e.g., versatility, environmental compatibility and potential cost effectiveness among others [9]. However, the electrode material is the most important parameter in the electrochemical process and represents the key of process performance. Recently, metal oxides can offer promising electro active materials due to enhancement of the electrochemical reversible redox reaction, wide potential window and large surface-volume ratio. Mixing of two or more dissimilar nanomaterials coated on the electrode surface called nanocomposite. It has unique physical, electrical, optical and chemical properties. The major advantages of the composite electrode materials are to enhance the electro active surface and good electrical contact between components and transducers [10]. Electroanalytical methods are simple, economical, rapid and sensitive to reach the lower limit of detection. Among the electro-analytical techniques, voltammetry coupled with pulse waveform (e.g., SWV) is considered a highly sensitive technique with very low detection profiles attributed to zero background current.The aim of this paper is to explore the determination of paracetamol on polyaniline-silver nanostructural thin films modified glassy carbon electrode.

2. Experimental:

2.1. Chemicals and Apparatus: All reagents were of AR grade purchased commercially. Solutions were prepared using deionized double distilled water. Stock standard solution of paracetamol (1000 ppm) was prepared in 50% ethanol. The voltammetric studies were carried out in exploratory and determination mode on a software connected CH Instruments Electrochemical Workstation (model CH 650C). The voltammetric cell

consisted of a three electrode assembly with polymer modified glassy carbon electrode as a working electrode, a platinum wire as auxiliary electrode and Ag/AgCl electrode as reference electrode. Nitrogen gas was purged through the solution for 5 min. A Hanna instrument pH/ORP meter was used for pH measurements.

Preparation of PANI/Ag Nanocomposites: The PANI/Ag nanocomposites were synthesized by *in situ* chemical oxidation polymerization of aniline monomer in the presence of Ag nanoparticle colloidal solution. In a typical synthesis process, aniline–hydrochloride was added to the prepared Ag nanoparticles colloidal solution (200 ml). The obtained mixture was stirred for 30 min. By addition of the aqueous solution of KPS, the mixture was allowed to react for 12 h under constant stirring at −3 °C [11].

2.2. Modification of the Electrodes: A GCE (3-mm diameter) was polished using 1.0 and 0.05 mm alumina slurry and rinsed thoroughly with Milli- Q water. Ultrasonic agitation for 30 min of 2.0 mg of chemically prepared polyaniline-silver nanostructured in 2 mL of water gave a homogeneous green solution. 20 □ L of this solution was placed on the GCE surface. The electrode was then dried at room temperature to obtain a polymer-silver modified GCE.

2.3. Pharmaceutical Sample Preparation: One tablets of containing paracetamol were weighed, powdered and then placed into a 250 ml of conical flask; warm water was added into the flask. The sample was swirled to dissolve for 30 minutes in sonicator and left cool. The sample solution was filtered through a filter paper (Whatman No.42) into 100 ml volumetric flask. An aliquot of the solution was then analyzed according to the proposed voltammetric procedure.

2.4. AFM Topographic Analysis: The structural characterization of polyaniline nanofiber modified GCE and the modified surface adsorbed with ibuprofen was performed by atomic force microscopy (AFM). NanoSurf Easyscan 2 AFM microscope operated in tapping mode under ambient conditions was employed. TopAl208 probes with a spring constant of 20–80 N/m were used.

3. Results and Discussion:

Effect of pH: Cyclic voltammograms of drug were recorded using nano PANI/Ag modified glassy carbon electrode in acid, neutral and alkaline conditions at a scan rate of 100 mVs^{-1}. Cyclic voltammograms exhibited one oxidation peak. At acidic pH the peak current and peak shape were good, but at neutral medium peak response was low. In basic medium the peak was broad and little variation of peak current compared with acid medium. The background current was recorded for all pHs and subtracted properly in calculating the peak currents. The peak potential and current of the well-defined anodic peaks noticed in the cyclic voltammogram were considered for the study of effect of pH. Figure 1 shows the variation of peak potential with pH. Protonation followed by oxidation led to the dependence of peak potential with pH for drug. The peak current decreased with increasing of pHs. The drug exhibited maximum peak current response (Fig.2) at pH 1.0. The electroanalytical determination procedure for the drugs on nano modified glassy carbon electrode was developed owing to higher peak current responses.

Electrochemical Studies: Cyclic voltammograms at various sweep rates ranging between 25 and 500 mVs^{-1} in acid pH were recorded and the results were collected. A typical representation of the cyclic voltammogram is presented in figure 3. The oxidation peak in the first cycle appeared around 720 mV. The anodic peak was shifted to lower positive potential favouring the oxidation in the PANI/Ag/GCE. The peak current was correlated with the sweep rate (Figure 4). A linear correlation between peak current and the square root of sweep rate was observed. A straight line resulted from this correlation is presented in figure 5. The log i_p vs. log plot (Figure 6) also exhibits straight line with a slope value of 0.3648. These facts suggested a diffusion-controlled reaction. No corresponding cathodic peak was observed in the reverse scan. The E_p vs. log plot yields a straight line and ***n*** value (0.8855) is calculated from the slope. It is having fractional value. The electron transfer was calculated from the slop. The electron transfer is thus considered to be irreversible here. The concentration was correlated with peak current leads straight line.

Stripping Analysis: The accumulation of the drug on the modified electrode surface under the optimum accumulation conditions was understood from the changes in the electrode surface before and after accumulation. AFM was employed to study the surface morphology of the paracetamol on nano PANI/Ag coated glassy carbon electrode. Figure 7 shows the bigger uniform granular like structure.

DPSV of Drugs: Under optimum experimental conditions, (Table 1) the influence of concentration on the stripping signal was studied. The experimental results showed that the peak current increased with the increase in the concentration of metal ions. A representative differential stripping voltammogram is given in figures 8. A calibration was made, which indicated the linear dependence of peak current with concentration (Figure 9). The reproducibility of the stripping signal was understood from the relative standard derivation calculated for five identical measurements at a concentration level of 50 ppb. The LOD was found to be 20 ppb. The pharmaceutical samples were collected from medical shops and determined through DPV under optimum experimental conditions. Various tablets having ibuprofen were analysis to detection of content of drug. Stripping voltammograms of the drugs at pH 1.0 were recorded under optimized conditions. The concentration of the drug in commercial formulations determined by the proposed method was in good agreement with the reported value of the company (Table 2).

4. Conclusion:

The AFM of drugs polymer-silver nanostructures thin films topography shows uniformly adsorbed on the electrode surface and forms a nanospherical morphology. The anodic peak was observed at 0.73 V, assigned for the oxidation of paracetamol, which is not accompanied by corresponding cathodic reduction. These behavior suggested that the irreversibility of the electrode process. The electrochemical response of paracetamol at the modified surface reveals the irreversible and diffusion electrochemical process. The range of determination was found between 100 ppb and 600 ppb, the lower limit of detection is 10 ppb.

5. References:

1. Uslu B, Ozkan S A, 2007. Electroanalytical application of carbon based electrodes to the pharmaceuticals. Analytical Letters, 40(5): 817-853
2. Kim J H, Nam K W, Ma S B, Kim K B, 2006. Fabrication and electrochemical properties of carbon nanotube film electrodes. Carbon, 44(10): 1963-1968
3. Cruz-Vera M, Lucena R, Cárdenas S, Valcarcel M, 2008. Combined use of carbon nanotubes and ionic liquid to improve the determination of antidepressants in urine samples by liquid chromatography. Analytical and Bioanalytical Chemistry, 391(4): 1139-1145
4. Ahammad A J S, Lee J J, Rahman M A, 2009. Electrochemical sensors based on carbon nanotubes. Sensors, 9(4): 2289-2319.
5. Hirlekar R, Yamagar M, Garse H, Vij M, Kadam V, 2009. Carbon nanotubes and its applications: a review. Asian Journal of Pharmaceutical and Clinical Research, 2(4): 17-27
6. Shahrokhiana S, Ghalkhani M, Adeli M, Amini M K, 2009. Multi-walled carbon nanotubes with immobilised cobalt nanoparticle for modification of glassy carbon electrode: Application to sensitive voltammetric determination of thioridazine. Biosensors and Bioelectronics, 24(11): 3235-3241
7. Murugananthan M, Yoshihara S, Rakumab T, Shirakashi T, 2008. Mineralization of bisphenol A (BPA) by anodic oxidation with boron-doped diamond (BDD) electrode. Journal of Hazardous Materials, 154(1-3): 213-220
8. Koparal A S, Yavuz Y, Gurel C, Oğutveren U B, 2007. Electrochemical degradation and toxicity reduction of C. I. Basic Red 29 solution and textile wastewater by using diamond anode. Journal of Hazardous Materials, 145(1-2): 100-108
9. Bensalah N, Alfaro M A Q, Martínez-Huitle C A, 2009. Electrochemical treatment of synthetic wastewaters containing Alphazurine A dye. Chemical Engineering Journal, 149(1-3): 348-352
10. Rasu Ramachandran1, Shen-Ming Chen, George peter Gnana kumar, Pandi Gajendran Natrajan Biruntha Devi, Int. J. Electrochem. Sci., 10 (2015) 8607 – 8629
11. Mansour Ghaffari-Moghaddam, Hassan Eslahi, Arabian Journal of Chemistry (2014) 7, 846–855

Table 1: Optimum parameters condition of stripping voltammetry of paracetamol on modified glassy carbon electrode at pH 1.0

Parameters	**DPSV**	
	Range Examined	**Optimized Value**
Accumulation potential (mV)	400 to 800	700
Deposit time (sec)	5 to 60	40
Initial scan potential (mV)	0 to 600	0
Pulse height (mV)	25 to 150	50
Pulse width (msec)	25 to 125	25
Pulse period	25 to 125	50
Scan rate (mV/sec)	20 to 80	60
Scan increment (mV)	2 to 20	6
Stirring rate (rpm)	50 to 250	300
Rest period (Sec)	2 to 10	5

Table 2: The amount of compounds determined on PANI-Ag/GCE in tablets

Brand Name	**Company Name**	**Tablets (mg)**	**Experimental Value (mg)**	**% of RSD**
Calpol	Glaxosmithkline	500	491	1.9
Crocin	Glaxosmithkline	500	495	2.2
Colimex tabs	Wallace	500	489	2.5
Doliprane	Nicholas piramal	500	498	2.6
Cyclopam	Indoco	500	499	1.4

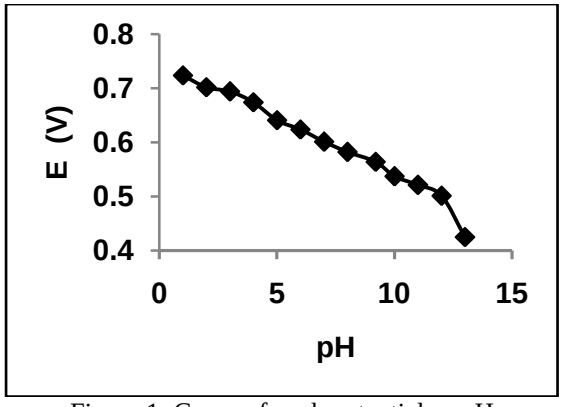

Figure 1: Curve of peak potential vs pH

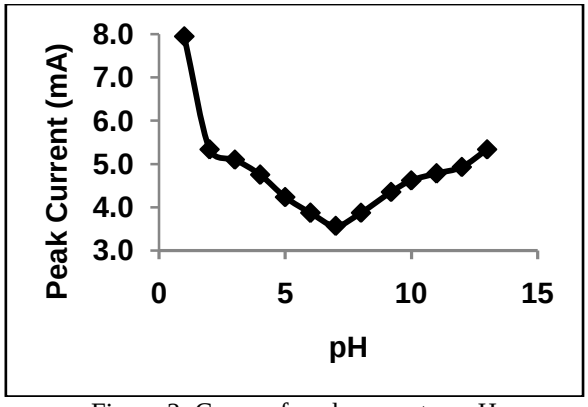

Figure 2: Curve of peak current vs pH

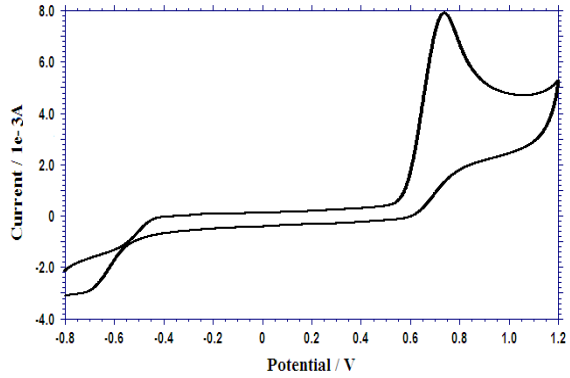

Figure 3: Cyclic voltammogram of 300 ppm paracetamol on nanostructured PANI/Ag modified electrode at 100 mV/s in pH 1.0.

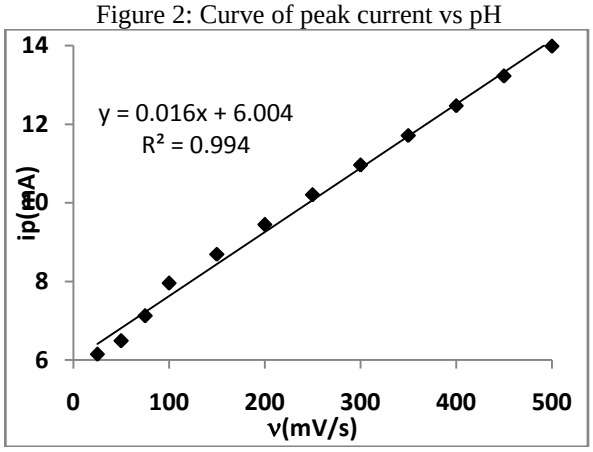

Figure 4: Plot of peak current vs scan rate

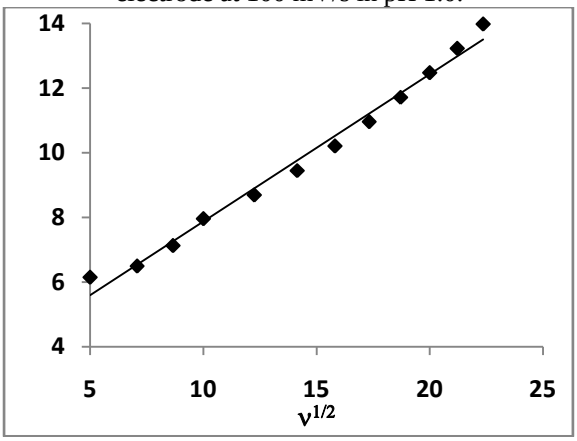

Figure 5: Plot of peak current vs square root of scan rate

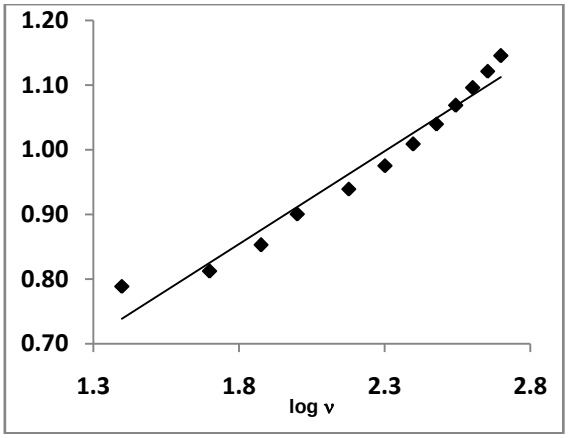

Figure 6: Plot of log peak current vs log scan rate

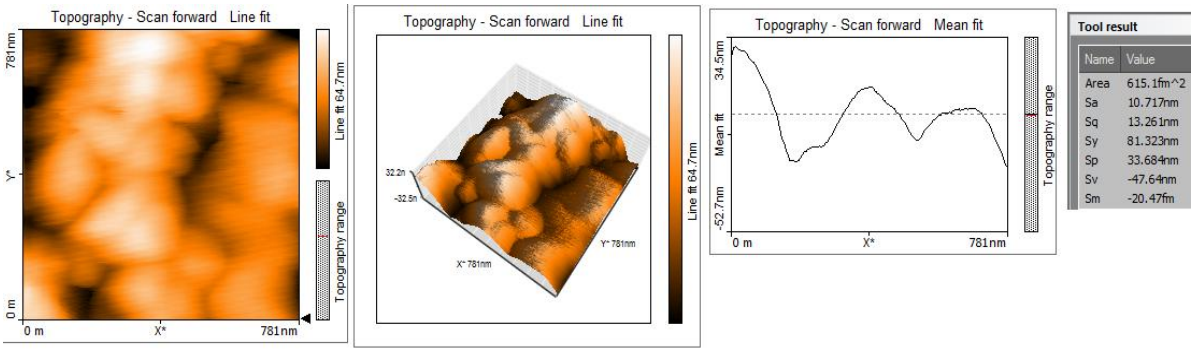

Figure 7: AFM photographs of paracetamol accumulated on electrode surface 2D, 3D, size distribution graph and surface roughness data

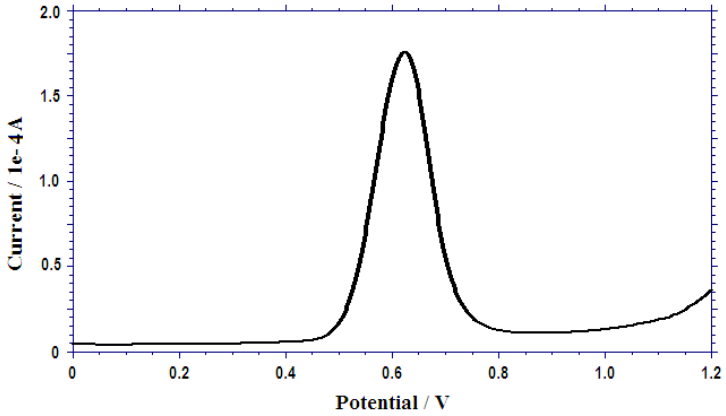

Figure 8: Differential pulse stripping voltammetric behavior of paracetamol on nanostructured PANI/Ag modified GCE under optimum conditions.

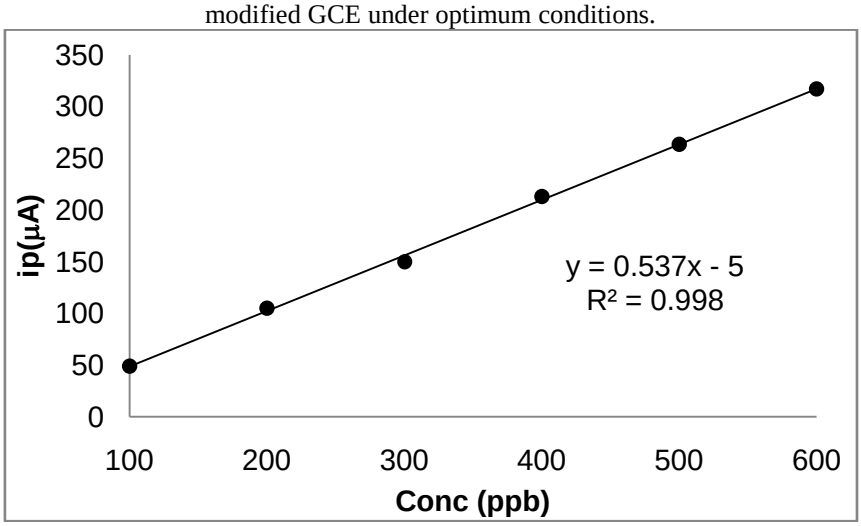

Figure 9: Calibration plot of current vs. concentration of paracetamol